U.S. GEOLOGICAL SURVEY TOXIC SUBSTANCES HYDROLOGY PROGRAM--PROCEEDINGS OF THE TECHNICAL MEETING, PHOENIX, ARIZONA, SEPTEMBER 26-30, 1988

By Gail E. Mallard and Stephen E. Ragone, editors

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MANUEL LUJAN, JR., Secretary

U.S. GEOLOGICAL SURVEY

Dallas L. Peck, Director

For additional information
write to:

Coordinators, Toxic Substances
Hydrology Program
U.S. Geological Survey
412 National Center
Reston, Virginia 22092

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PREFACE

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

Much new information has become available as the result of studies conducted by the Toxic Substances Hydrology Program. In order to facilitate exchange of information among the many scientists working on relevant research, a series of technical meetings have been held in Tucson, Arizona (1984), Cape Cod, Massachusetts (1985), Denver, Colorado (1987), and Pensacola, Florida (1987). These meetings provided an opportunity to present research results and to plan new field efforts. This report documents the results of research presented at a technical meeting held in Phoenix, Ariz., in September 1988. The Phoenix meeting is the first to include both ground- and surface-water contamination studies and to have a major session on nonpoint source contamination.

The report is organized into 10 chapters that focus on field-site investigations, nonpoint source research, or methods research. The 11th chapter contains abstracts and short papers on a variety of subjects presented as posters during the meeting. Chapters A through F and I and J present results of research, still in progress, on the occurrence and movement of hazardous substances within specific hydrologic systems. These intensive interdisciplinary investigations represent a key element of the research approach taken by the Toxic Substances Hydrology Program. The sites, selected to study a variety of contaminants, provide a focus for both process-oriented and methods-development research. Each chapter presents the results of research on specific types of contaminants in specific environments. Ground-water quality problems currently under investigation include contamination by crude oil, creosote, sewage, trace metals, and chlorinated organic solvents. The river systems being studied have been affected by mine wastes containing high concentrations of arsenic, industrial effluent containing a variety of organic chemicals, and water from mine drains and abandoned tailings that contains high concentrations of metals. The first paper in most of these chapters provides an overview of the hydrologic setting and describes the nature and history of the contamination problem. Subsequent papers report the results of a specific research problem.

Chapter G describes results of nonpoint source ground-water contamination research. The focus in these studies is more statistical and less deterministic than the intensive field studies because of the large number of natural and anthropogenic factors being studied and their spatial and temporal variation. Existing data on aquifer characteristics, ground-water flow patterns, ground- water quality, and land use have been assembled and where necessary, pertinent new data have been collected to augment existing data bases. The ultimate goal of the regional studies is to develop procedures that can be used to associate ground-water quality with land-use practices for representative hydrogeologic and climatic settings.

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

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

Gail E. Mallard Stephen E. Ragone
Coordinators, Toxic Substances Hydrology Program

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CHAPTER A – CRUDE OIL IN THE SUBSURFACE ENVIRONMENT AT BEMIDJI, MINNESOTA

(p. 3 follows)

SUBSURFACE CONTAMINATION AT THE BEMIDJI, MINNESOTA, RESEARCH SITE

By Marc F. Hult[1]

ABSTRACT

In August 1979, the subsurface was contaminated near Bemidji, Minnesota, when a pipeline burst, spilling crude oil on a glacial-outwash aquifer. After cleanup efforts were completed, approximately 400,000 liters of crude oil remained in the aquifer. In 1983, the U.S. Geological Survey began research on the mobilization, transport, and fate of petroleum derivatives at the site. In the 9 years since the spill, petroleum has moved about 30 meters downgradient as a separate fluid phase, constituents dissolved in ground water have moved 200 meters, and vapors through the unsaturated zone have moved 100 meters. Each phase continued to advance during June 1987 through July 1988, although the rate of advance of the plume of contaminated water was less than the calculated ground-water velocity. The petroleum source is becoming increasingly viscous, dense, and depleted in volatile compounds. The petroleum derivatives moving with ground water and through the unsaturated zone are being degraded to water, carbon dioxide, and methane. The maximum extent of ground-water contamination eventually may be controlled by the near-equilibrium condition between the rate at which the petroleum is dissolved and transported by ground water and the rate at which it is degraded by microbes. If this hypothesis is confirmed by additional long-term research, it implies that many problems of ground-water contamination by petroleum derivatives might be managed successfully without direct remedial action if the volume of the subsurface affected at the maxium extent of contamination is acceptably small.

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

(p. 5 follows)

SILICA MOBILITY IN A PETROLEUM-CONTAMINATED AQUIFER

By Philip Bennett[1]

ABSTRACT

Sediments and water from a petroleum-contaminated aquifer near Bemidji, Minnesota, were examined to determine the effects of dissolved organic compounds on silica mobility. The results of this study indicate that the dissolution of quartz and aluminosilicate minerals is accelerated in the zone with the highest concentration of dissolved organic carbon, as shown by an increase in dissolved-silica concentration from 18 milligrams per liter to greater than 20 milligrams per liter, indicating an apparent increase in the solubility of quartz. Microscopic evidence of rapid weathering of quartz can be seen where dissolved silica is highest. This interaction occurs at neutral pH and is most apparent where the redox potential is lowest. Downgradient from the zone of dissolution, silica rapidly precipitates from solution as both amorphous silica and authigenic quartz. The zone of precipitation coincides with an increase in ground-water redox potential, and is accompanied by the precipitation of iron.

Laboratory dissolution experiments and spectroscopic investigations suggest that silica is being complexed by multifunctional organic acids. This increases the solubility and rate of dissolution of quartz and aluminosilicates at neutral pH, conditions in which aluminum complexation is insignificant. The interaction of silica and organic acids at the Bemidji site may be analogous to processes associated with organic-rich environments of geologic and economic importance.

INTRODUCTION

When evaluating the consequences of ground-water contamination by oil, research commonly focuses on the distribution and transport of *organic* compounds released or generated from the oil. The geochemical effects of oil contamination, however, are not confined simply to the introduction of dissolved organic compounds to water. Changes also occur in the distribution of dissolved inorganic solutes, in the equilibrium redox chemistry, and in the equilibrium chemistry of rock-water reactions. These reactions, if associated with oil in ground water, may be analogous to processes that occur in other organic-rich environments and, thus, offer the researcher a modern analog to geologic processes.

This paper describes results of a study of the effects of petroleum and its biodegraded byproducts on the equilibrium rock-water chemistry of silicate minerals in ground water at the Bemidji, Minn., research site. The results of this study may offer alternative mechanisms for silica mobility in peat bogs, oil-field formation waters, and organic-rich sediments.

METHODS

For the purpose of this study, four general physiochemical zones at the site are defined (fig. A-1): "background" sample sites, which include uncontaminated wells both upgradient and downgradient from any oil contamination; "spray zone" sample sites, which are in the region upgradient from the floating pool of oil where the major contamination is in the unsaturated zone; "oil-pool zone" sample sites, which are in the aquifer immediately below the floating pool of oil; and "downgradient plume" sample sites, which are in the region affected by the plume of dissolved contaminants that has extended downgradient from the original pool.

Ground-water samples were collected during the summer of 1987 and 1988 from all four zones. Samples were collected by use of a down-hole submersible pump from polyvinyl chloride (PVC) wells screened at the water table and at selected positions below the water table. Samples were passed through a 0.2 μm (micrometer) filter in the field and, where appropriate, acidified with ultrapure hydrochloric acid. All water samples were analyzed for cations and silica by Direct Current Plasma Atomic Emission spectroscopy. The detection limit for silica by this method is 20 μg/L

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[1] Department of Geological Sciences, University of Texas, Austin.

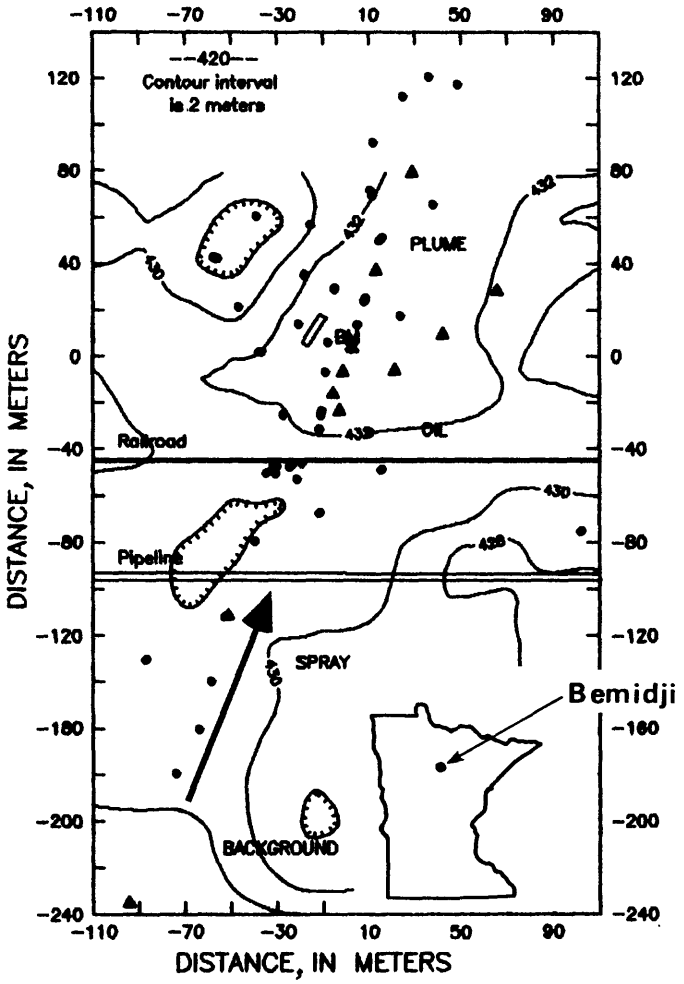

Figure A-1.—Location map, Bemidji research site, Minnesota. Filled circles are piezometers, filled triangles are piezometer nests. Elevations are meters above sea level. Arrow shows approximate direction of ground-water flow.

(micrograms per liter) (as SiO_2). In addition, several samples also were analyzed for dissolved monomeric silicic acid by the molybdate blue method (American Public Health Association, 1975).

Sediment samples were collected from the water table by split-spoon auger. Samples were dry-sieved, and the 75 to 200 μm fraction was cleaned with distilled water, dried, and mounted for examination by scanning-electron microscope (SEM). Cleaning procedures were minimized in order to eliminate the introduction of weathering artifact, such as etch pitting.

RESULTS

Figure A-2 shows the areal distribution of dissolved silica at the Bemidji site. Although the silica concentrations are reported as total SiO_2, supplemental analyses by the molybdate method show that the silica is entirely as monomeric silicic acid (H_4SiO_4).

Dissolved-silica concentrations in background waters are about 18 mg/L (milligrams per liter) SiO_2. Concentrations of silica in the spray-zone water table wells are slightly higher and average about 22 mg/L. Other cations, however, including calcium and magnesium, are present in highest concentrations in the spray zone. In addition, pH is lowest in this zone, decreasing from a background value of 7.6 to as low as 6.6 (Siegel, 1987). Total dissolved iron also is slightly elevated in the spray zone (fig. A-3).

The highest concentration of silica is found in the oil-pool zone, where the concentration of dissolved SiO_2 exceeds 70 mg/L. Concentrations of dissolved organic carbon (DOC) are highest in this zone, where a significant fraction of the DOC consists of complex organic acids (Aiken and others, 1987). Total dissolved iron also is highest in this zone (fig. A-3), reflecting the very low Eh and complete absence of dissolved oxygen (Baedecker and others, 1987). Dissolved-iron concentration increases from 0.1 mg/L in the spray zone to greater than 55 mg/L in the oil-pool zone. The high concentration of dissolved silica and iron remains elevated in the proximal region of the contaminant plume zone where dissolved-oxygen concentration is still very low.

Concentrations of potassium and sodium rise sharply with increasing concentrations of dissolved silica. Concentration of total dissolved aluminum does not increase with the concentration of dissolved silica and does not exceed 10 μg/L at any sampled location. Concentrations of other dissolved inorganic constitutents, such as magnesium and alkalinity, decline between the spray zone and oil-pool zone as pH increases (fig. A-3).

A short distance downgradient from the trailing edge of the oil pool, the concentration of SiO_2 decreases sharply. Concentrations of dissolved iron also decrease at this location, suggesting an increasing redox potential.

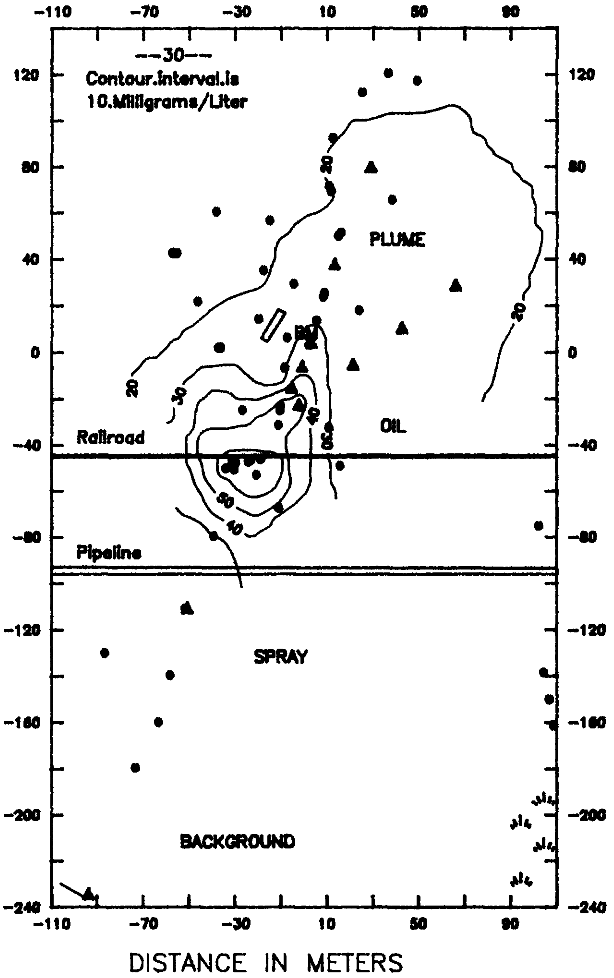

Figure A-2.— Areal distribution of silica. Concentration of dissolved silica as milligrams per liter SiO_2.

Concentrations of alkaline and alkaline earth cations continue to decrease, although more slowly than concentrations of silica and iron (fig. A-3).

Sediments examined from the oil-pool zone show that both quartz and aluminosilicate minerals are being chemically weathered at an accelerated rate (Bennett and Siegel, 1987). Quartz grains have etch pits and solution channels characteristic of chemical etching (fig. A-4A). Feldspar grains have deep solution channels and accretion of secondary minerals (fig. A-4B). Amphiboles have deep, lenticular etch pits resembling amphibole grains found in rapidly weathering soil zones. Where sand grains are physically covered with oil, no dissolution features were present.

Quartz grains from the water table downgradient from the oil-pool edge have silica accretions and quartz overgrowths, but little evidence of etching (fig. A-4C). Evidence of iron precipitation is also suggested. Very minor etch features are present on the calcic feldspar grains. Farther than 50 meters downgradient from the oil-pool edge, no chemical etching is found on any grain surface.

DISCUSSION

Dissolution of quartz and silicate minerals is occurring immediately under the oil at near-neutral pH where the concentration of dissolved silica is about 15 times the equilibrium solubility of quartz at 10 °C (degrees Celsius). The concentration of silica strongly correlates with concentrations of dissolved organic carbon. These findings suggest that silica is complexed by the dissolved organic compounds, increasing the solubility as well as the rate of dissolution of quartz and aluminosilicates (Bennett and Siegel, 1987).

The dissolved organic compounds at the Bemidji site consist primarily of various complex organic acids. Organic acids are strong complexing agents previously shown to accelerate the dissolution of aluminosilicates (Huang and Keller, 1970). However, the mechanisms that cause the enhanced weathering

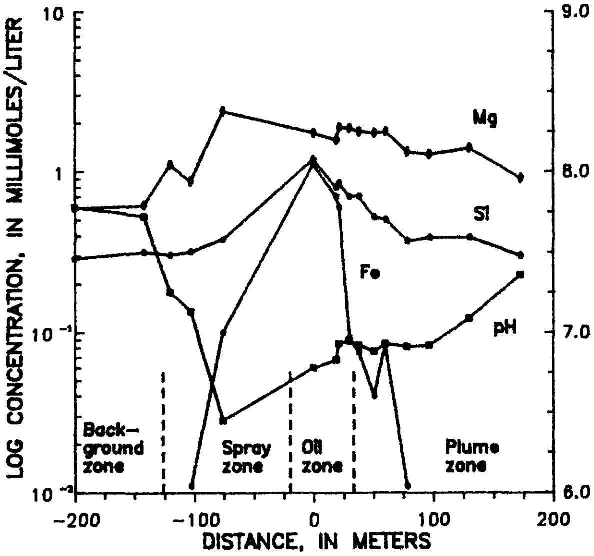

Figure A-3.—Log concentration of dissolved solutes along the contaminant plume axis.

of aluminosilicates by organic acids are the complexation and mobilization of aluminum by the organic acids and/or an increase in the hydrogen-ion activity and acceleration of the normal hydrolysis reaction (Tan, 1980). At the Bemidji site, however, the zone of silicate dissolution is not in the spray zone, where the pH is lowest, but rather in the oil-pool zone, where pH is close to neutral (fig. A-3). This suggests that the interaction is not a direct function of hydrogen-ion activity. The complexation of aluminum by organic acids, also pH dependent, is not significant above a pH of about 5.5 (Smith and Martell, 1976) and, therefore, is not a significant reaction at the Bemidji site, where the pH is about 6.5 at all sampled locations. The

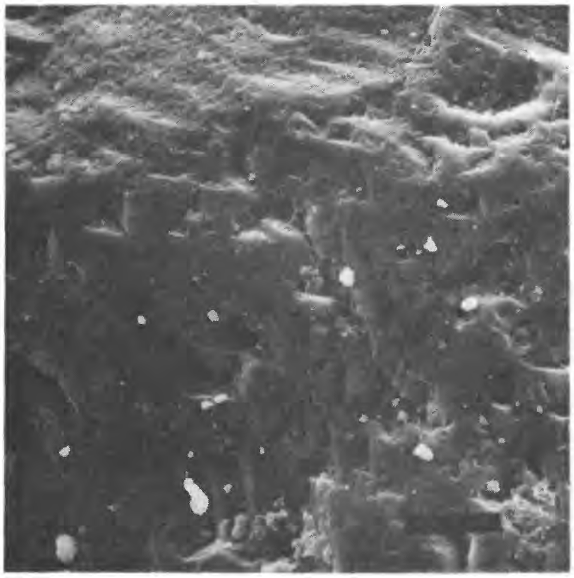

Figure A-4A.— Etched quartz grain.
Bar scale = 10 micrometers.

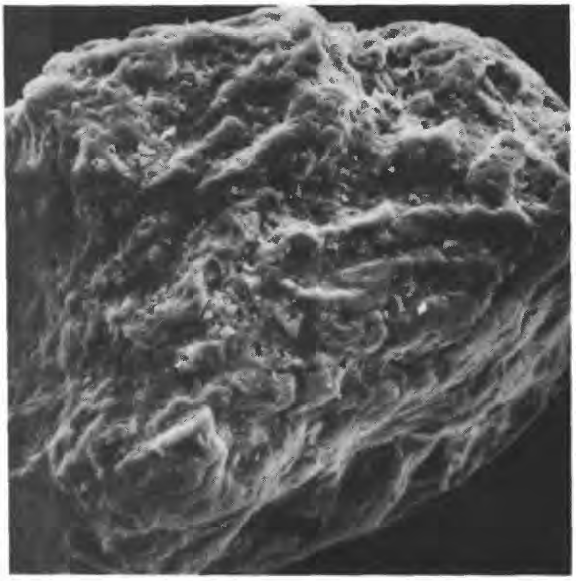

Figure A-4B.—Etched plagioclase grain.
Bar scale = 20 micrometers.

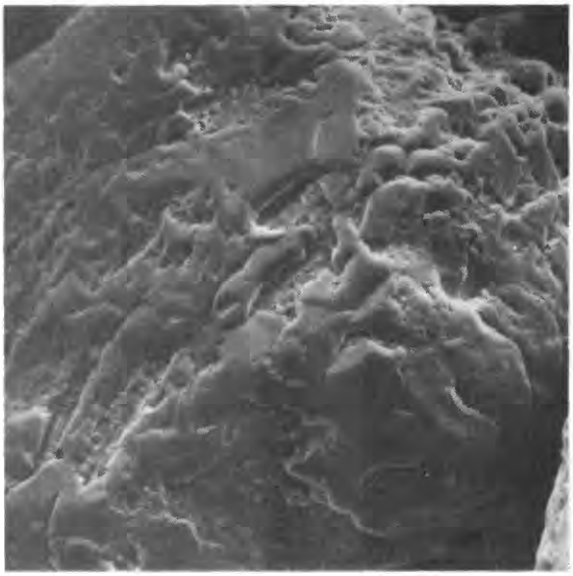

Figure A-4C.—Quartz overgrowth on previously etched quartz grains. Bar scale = 10 micrometers.

absence of significant aluminum complexation is supported by the very low concentrations of dissolved aluminum in the contaminated zones and by the apparent conservation of aluminum in secondary solid phases on weathered silicate grains. In addition, neither of these mechanisms is likely to influence the dissolution of quartz.

In the absence of significant complexation of aluminum, the data support the concept that the organic acids are accelerating the dissolution of both quartz and aluminosilicate minerals by complexation of silica. Laboratory experiments using simple batch reactors have shown that some organic acids, such as citric and oxalic acids, accelerate the dissolution of quartz and increase its solubility (fig. A-5)(Bennett and others, 1988). Additional experiments using UV-VIS, Raman, and FTIR spectroscopy show that some organic acids react with silica in solution at neutral pH and room temperature (Bennett and others, 1988; N.A. Marley, P. Bennett, D.R. Janecky, and J.S. Gaffney, written commun., 1988). These experiments show that only certain multifunctional organic acids will react with silica, initially with a charge-transfer type of reaction. Furthermore, the complexation reaction was shown to be pH dependent; the silica–organic-acid complex was able to form only at a pH above the pK_1 of the organic acid. A possible reaction for silica complexation, therefore, would be:

$$2R(COO^-)_2 + H_4SiO_4 \rightarrow R(COO^-)_2{:}H_4SiO_4{:}R(COO^-)_2;$$

or, for a reaction at the quartz grain surface:

$$2R(COO^-)_2 + 2H_2O + SiO_2\,(s) \rightarrow R(COO^-)_2{:}H_4SiO_4{:}R(COO^-)_2.$$

For the aluminum silicate minerals, if aluminum complexation is eliminated, the reaction might be:

$$2KAlSi_3O_8 + 9H_2O + 2H^+ + 2R(COO^-)_2 \rightarrow Al_2Si_2O_3(OH)_4 + 2K^+ + R(COO^-)_2{:}H_4SiO_4{:}R(COO^-)_2.$$

The rapid loss of both iron and silica immediately downgradient from the oil pool probably is caused by the precipitation of a solid phase. This hypothesis is supported by the observed silica accretions on silicate grains and by the presence of iron coatings. The coincidence of mobility of silica and iron can be interpreted in several ways. One possibility is that iron is reacting with silica and that the mobility of silica is controlled by the concentration of iron. However, iron-silica complexation occurs only with ferric iron, and then only at very low pH (2-3) (Reardon, 1979). Complexation does not apparently occur with ferrous iron at neutral pH. Another possibility might be that the complexation of silica is sensitive to a redox potential similar to that for iron. This hypothesis is not supported by the experimental evidence, however, where complexation clearly occurs in aerobic systems.

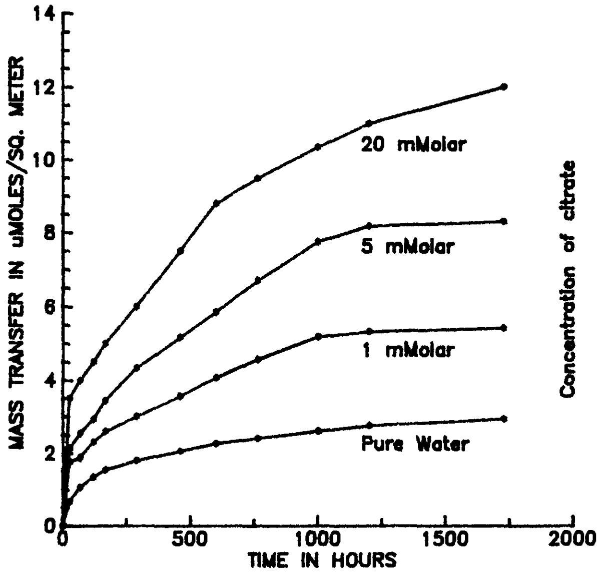

Figure A-5.—Mass transfer of silica as SiO_2 from quartz over time in sodium citrate solutions at pH = 7.

The current hypothesis is that the difference in speciation of organic-carbon compounds between the aerobic and anaerobic zones affects the mobility of silica. The types of compounds that are stable in the anaerobic zone might degrade rapidly in even slightly aerobic environments, disrupting any complexes that might be present. The sensitivity of the organic compounds to the concentration of dissolved oxygen may be similar to that of iron, causing a coincidental correlation of mobility. This hypothesis is supported somewhat by experimental evidence: dilute solutions of freshly prepared pyruvic acid and silica show evidence of silica complexation in spectroscopic experiments, but the complex degrades in a matter of hours to days as the pyruvic acid oxidizes (Bennett and others, 1988).

The identification of the precipitating mineral phases is not yet clear. SEM examination of the mineral grains clearly shows both amorphous silica and authigenic quartz overgrowths on detrital quartz grains. Iron precipitates are not as clearly defined. A ground water with very high concentrations of silica and ferrous iron, under reducing conditions, and low concentrations of aluminum might, for example, precipitate authigenic nontronite (Bodine, 1987).

CONCLUSIONS

The presence of dissolved organic compounds in a shallow sand and gravel aquifer clearly is changing the equilibrium rock-water chemistry of the system. In particular, the solubility and rate of dissolution of quartz and aluminosilicates are greatly increased where concentrations of organic acids are elevated. Aluminum is not mobilized with the silica and apparently is conserved in secondary-mineral phases. Silica is mobilized, not where pH is lowest, but rather where dissolved organic-carbon concentration is highest and the redox potential is lowest. Laboratory experiments support the hypothesis that a silica – organic-acid complex is responsible for the mobilization of silica. Complexes are measurable under aerobic conditions but seem to be most effective in dissolving silicate minerals under the reducing conditions encountered under the floating oil pool. When the ground-water redox potential increases slightly, the silica precipitates, forming authigenic quartz overgrowths on detrital quartz grains.

The mechanisms of silica complexation proposed here might be applicable to other organic-rich aqueous environments. One example might be oil-field brines in sandstones, where concentrations of organic acids are extremely high (Surdam and others, 1984). Sandstones in these environments commonly have high secondary porosity and evidence of chemical etching of the silicate sand grains. Another possibility is that silica – organic-acid complexes are related to the formation of the clays that underlie many coal beds. Commonly, these clays are found to be anomalously quartz-poor in the few centimeters closest to the coal where interstitial organic-carbon content is very high. Several of these ideas are being pursued, and preliminary results are encouraging.

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THE FATE AND EFFECTS OF CRUDE OIL IN A SHALLOW AQUIFER

I. THE DISTRIBUTION OF CHEMICAL SPECIES AND GEOCHEMICAL FACIES

By Mary Jo Baedecker[1], Donald I. Siegel[2], Philip Bennett[3], and Isabelle M. Cozzarelli[1]

ABSTRACT

Crude oil floating at the surface of a shallow aquifer of glacial outwash, near Bemidji, Minnesota, is altered by geochemical processes. Hydrocarbons from the oil are attenuated by several reactions that include aerobic and anaerobic microbial degradation. These degradation reactions result in the development of geochemical facies in the shallow ground-water system. Ground water most affected by the presence of organic compounds is anoxic, and concentrations of methane, dissolved organic carbon, and total inorganic carbon are high--0.76 millimole per liter, 2.9 millimoles per liter, and 12.3 millimoles per liter, respectively. The concentrations of chemical species and $\delta^{13}C$ isotope values indicate that the plume near the oil lens has become progressively more reducing. Over a 4-year period (1984 through 1987), the concentrations of methane and iron have increased by a factor of greater than 25. The data suggest that sequential degradation occurs, as predicted by thermodynamics: manganese is reduced before iron is reduced, which occurs before methanogenesis. These data provide field evidence that reduction of iron and manganese is an important mechanism of decomposition of organic matter in aquifers.

The $\delta^{13}C$ values of inorganic carbon of the native ground water range from -12 parts per thousand to -15 parts per thousand as a result of mixing of soil carbon dioxide with carbon dioxide from the dissolution of carbonates. Nonmethanogenic biodegradation of oil constituents adds isotopically light carbon dioxide to the ground water because the oil has a $\delta^{13}C$ value of -28 parts per thousand. The $\delta^{13}C$ values of inorganic carbon in the reducing zone have become progressively heavier from 1985 through 1987. The maximum change occurs 15 meters downgradient from the oil lens, where the $\delta^{13}C$ values increased from -21.6 parts per thousand to -5.35 parts per thousand. This change indicates that the plume has become more reducing and methanogenic over time.

INTRODUCTION

Geochemical reactions in a shallow aquifer contaminated with crude oil, near Bemidji, Minn., are controlled by the dissolution, degradation and transport of organic compounds. It is well documented that the presence of organic material in aquifers causes changes in the abundance of aqueous species due to oxidation and reduction reactions. Localized regions of shallow aquifers that are affected by human activities have markedly different distributions of chemical species (Golwer and others, 1975; Baedecker and Back, 1979; Nicholson and others, 1983; Siegel and others, 1986; Smith and others, 1987; Baedecker and others, 1988).

At the Bemidji site, a pipeline ruptured in 1979, and crude oil moved vertically to the water table where the oil formed a lens, about 2 to 4 meters thick. A plume containing dissolved constituents from oil and byproducts from biochemical reactions, developed downgradient from the oil lens in the saturated zone, 5 to 7 meters below land surface (fig. A-6). Crude oil from the pipeline break was also sprayed upgradient on the land surface and has slowly moved through the unsaturated zone to the saturated zone, however, no separate oil body has formed in this area. The ground water flow rate is about 0.3 to 1.2 m/d (meters per day). The aquifer, in glacial outwash, is a well-sorted, medium, quartz sand containing about 6 percent carbonate minerals, 30 percent feldspars, less than 5 percent clay minerals, and less than 0.2 percent organic carbon.

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

[2] Department of Geology, Syracuse University, Syracuse, N.Y.

[3] Department of Geological Sciences, University of Texas, Austin.

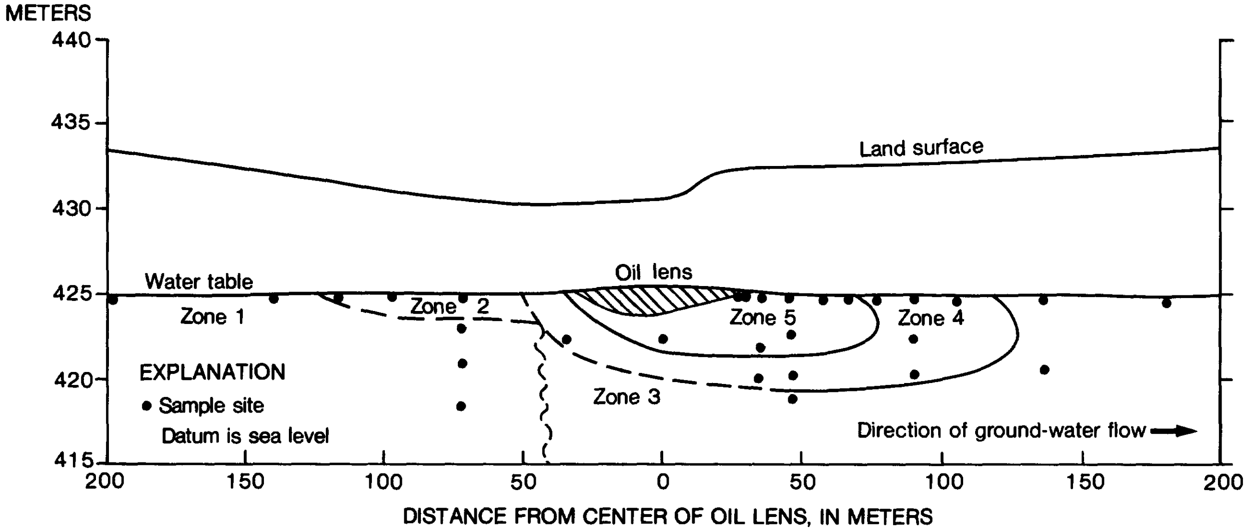

Figure A-6.— Schematic cross section of a shallow aquifer near Bemidji, Minnesota, with an oil lens, showing zones (1 through 5) of differing water chemistry. Sampling points are represented by dots.

The two types of oil contamination, overland spray, and the subsurface oil lens, affect the ground-water chemistry and alter the geochemical processes in a localized part of the aquifer. This paper shows how the distribution of unstable constituents that are reactants in or products of reactions with organic compounds delineate zones in the aquifer where differing geochemical processes occur. The methods used for sampling and analyses are presented in Baedecker and others (1984) and Baedecker and Lindsay (1986).

The authors acknowledge the helpful discussions with Robert Eganhouse, Southern-California Coastal Water Research Authority.

RESULTS AND DISCUSSION

The oil is a light crude and consists predominantly of aliphatic and volatile aromatic hydrocarbons (Baedecker and others, 1984). Aliphatic hydrocarbons are found in ground water near the source but, because of their low solubilities, are not found in ground water farther than 10 meters downgradient from the source. Aliphatic hydrocarbons are found on aquifer solids in low concentrations (100 ng/g (nanograms per gram) dry-weight sediment) 65 meters from the source. This suggests that the oil moves as a film on the water surface or as stringers through the sediment. The aqueous concentrations of the more-soluble, volatile aromatic hydrocarbons are about 4.2 mg/L (milligrams per liter) near the source and 0.0006 mg/L 180 meters downgradient (Eganhouse and others, 1987; Cozzarelli and others, 1989, this Proceedings). This large loss of hydrocarbons, which is far greater than can be accounted for by processes such as sorption or ground-water mixing and dispersion, primarily is the result of degradative processes.

The distributions of pH, oxygen, bicarbonate, or total dissolved inorganic carbon (TIC), total dissolved organic carbon (TDOC), methane, sulfate, hydrogen sulfide, nitrate, ammonia, iron, manganese, and $\delta^{13}C$ values are used to describe zones where ground-water chemistry is controlled by different geochemical processes (table A-1 and fig. A-6). In this study TDOC refers to volatile and nonvolatile dissolved organic carbon (DOC) with the exception of gases such as methane and DOC refers to nonvolatile dissolved organic carbon. The native ground water (zone 1) has a median pH of 7.60 and is oxygenated. The average concentrations of other chemical species are: less than 0.04 mmol/L (millimoles per liter) sulfate, less than 0.02 mmol/L nitrate, near detection limits for iron, manganese, and methane, 0.18 mmol/L TDOC, and 3.8 mmol/L TIC. These levels of TIC result from the dissolution of carbonates in the aquifer and solution of soil gas. The chemical composition of the native ground water is controlled by carbonate equilibrium, and to a lesser extent by dissolution of quartz, feldspar, and clay minerals and the degradation of naturally-occurring organic material.

Table A-1.—*Mean concentration with standard deviation of aqueous species in ground water*[1]

Type of ground water[2]	Zone[2]	Number of sampling points	pH[3]	Millimoles per liter					
				Oxygen	TIC[4]	TDOC[5]	Methane	Iron (+2)	Manganese (+2)
Native ground water	1	4	7.60	0.24±0.03[6]	3.8±0.20	0.18±0.06	<0.0005	<0.0005	<0.0005
Oxygenated spray area-upgradient	2	4	7.12	.20± .06	10.3±3.7	1.5 ± .82	.005±.003	.003±.004	.002±.002
Oxygenated-downgradient	3	4	7.30	.10± .05	6.8±2.1	.46 ± .30	.02 ±.02	.001	.0005
Oxygenated restricted downgradient	4	8	7.03	.03 ± .03	8.4±1.6	.92± .42	.16 ±.13	.002±.002	.06 ±.05
Anoxic	5	9	6.93	<.0005	12.3±1.7	2.9 ± .97	.76 ±.29	.30 ±.37	.12 ±.05

[1] Data from 1987
[2] Refers to fig. A-6
[3] Median pH
[4] Total inorganic carbon
[5] Total dissolved organic carbon (includes volatile organic carbon, except gases)
[6] Standard deviation

In contrast, ground water most affected by the presence of organic compounds has a median pH of 6.93 and is anoxic (zone 5). In this zone, average concentrations of the aqueous species are low or near detection limits for sulfate and nitrate, 0.30 mmol/L iron, 0.12 mmol/L manganese, 0.76 mmol/L methane, 12.3 mmol/L TIC, and 2.9 mmol/L TDOC. Iron and manganese are solubilized and methane is generated downgradient of the oil where dissolved organic compounds are oxidized. Water in the anoxic plume (zone 5) is buffered by the degradation of organic material in addition to carbonate and silicate mineral equilibria reactions.

The concentrations of constituents in the other zones (table A-1 and fig. A-6) are intermediate between those in zones 1 and 5. Ground water from the oxygenated spray area (zone 2), has TDOC and TIC concentrations that are unusually high, but has only trace levels of identifiable hydrocarbons (less than 10 micrograms per liter). Hydrocarbons that were transported in the unsaturated zone were altered and the organic material that reached the water table is different from that found in zone 1. The predominant hydrocarbons are the more refractory high molecular-weight hydrocarbons in the C_{20} to C_{30} range rather than soluble aromatic components. The low molecular-weight hydrocarbons were selectively removed by dissolution, or more likely, lost by oxidative degradation. In oxygenated ground water downgradient from the plume (zone 3), concentrations of most constituents are greater than background concentrations (table A-1), and trace levels of hydrocarbons are present.

The water in zone 4, a transition area with low concentrations of dissolved oxygen (0.03 mmol/L), has manganese concentrations greater than those of iron. Thermodynamics predicts that in an oxygen restricted environment manganese should dissolve before iron. In the presence of oxygen, manganese (+2) will precipitate at a higher Eh than iron (+2). Thus, the dissolved manganese in this zone may originate from dissolution reactions that occurred upgradient and remained in solution after the iron precipitated. Dissolved organic species are rapidly attenuated by aerobic degradative processes in zone 4. As a result the TDOC consists of more refractory, nonidentifiable organic compounds (Aiken, 1989, this Proceedings).

The concentrations of some chemical constituents in ground water at the downgradient edge of the oil lens varied markedly over a 4-year period (fig. A-7). The concentrations of bicarbonate and DOC were nearly constant from 1984 through 1987, whereas concentrations of iron and methane increased by more than 25 times. These results indicate that iron reduction and methanogenesis are important mechanisms of organic degradation. Concentrations of manganese decreased at the oil edge, possibly

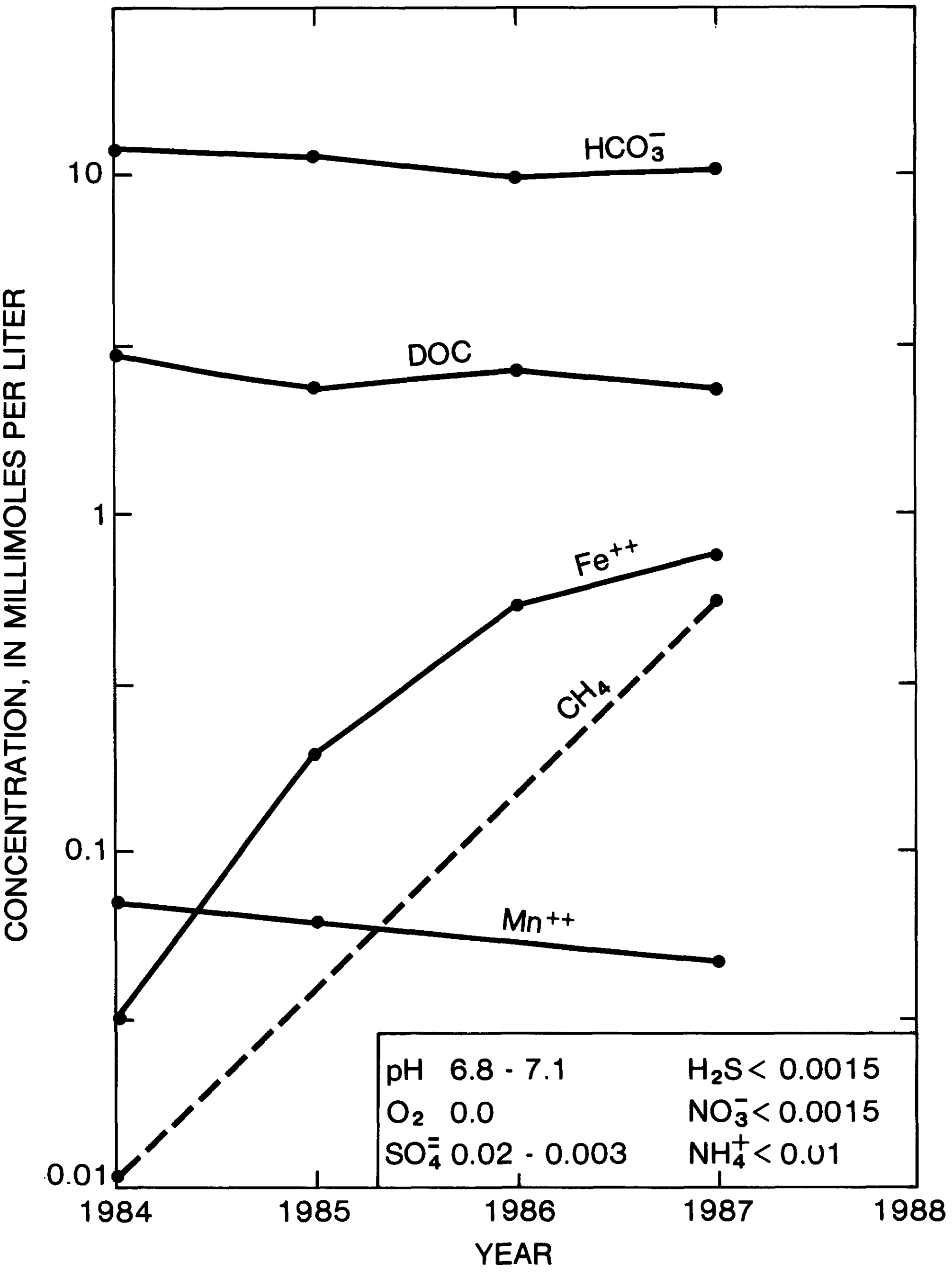

Figure A-7.— Concentrations of bicarbonate (HCO_3^-), dissolved organic carbon (DOC), iron (Fe^{++}), manganese (Mn^{++}) and methane (CH_4) in water near the edge of the oil lens, for 1984 through 1987. CH_4 distribution (dashed line) is defined by two data points, and linearity is not implied.

because leaching of manganese from the aquifer solids occurred after the oil spill but before the beginning of this study (1984). Manganese reduction appears to be an important geochemical process farther downgradient, 30 meters from the edge of the oil lens, where the concentration of manganese increased from 1984 through 1987. The temporal increases in concentrations of reduced species over the 4-year period suggest that the anoxic plume has become increasingly reducing with time.

Downgradient of the oil lens, sulfide and ammonia were absent or present in only trace amounts during the 4-year study. Sulfate and nitrate reduction are not major processes because of the low levels of these species in solution. Some sulfate reduction has occurred because the concentrations of sulfate decreased from 0.02 to 0.003 mmol/L, however, sulfide was found in concentrations of less than 0.0015 mmol/L. Because the concentrations of bicarbonate and iron are high, small amounts of sulfide may have been removed from solution as siderite or pyrite. This has been observed in another shallow aquifer with an anaerobic zone (Cozzarelli and others, 1987). The low concentrations of ammonia found in the water are probably the result of reduction of nitrogen-containing organic compounds present in the crude oil. The amount of nitrogen and sulfide in the crude oil is 0.28 and 0.56 percent, respectively. Similarly, sulfur-containing organic compounds would be expected to yield sulfide in concentrations above background levels. However, it is possible that the organosulfur compounds are not in a degradable form, or as discussed above, the sulfide that formed was removed from solution by precipitation.

Water upgradient from the oil lens (zone 2) contained some nitrate and sulfate after 1987. The source of these ions is fertilizer that was applied during replanting of forest trees. Farther downgradient the aqueous concentrations of reduced and oxidized sulfur-and nitrogen-containing species are near detection limits, and therefore the geochemistry in zones 3, 4, and 5 has not been affected by the fertilizer application.

The distribution of unstable constituents and $\delta^{13}C$ values of inorganic carbon along the axis of the plume indicate that most geochemical reactions occur upgradient in the spray zone and in the first 100 meters downgradient from the oil lens. In the downgradient plume (fig. A-8), the concentrations of bicarbonate gradually decrease along the flow path, whereas the other constituents decrease more rapidly. The distribution of iron reflects its sensitivity to oxygen; in water where oxygen is detected, iron concentrations are near detection limits. The concentrations of manganese and methane remain high in the anoxic zone within 80 meters from the source and decrease rapidly downgradient. Data for 1986 and 1987 are surprisingly similar for bicarbonate and TDOC (fig. A-8). The consistency in the 1986 and 1987 data suggests that reactions occur in microenvironments. For example, the small increase in TDOC, from 46 to 76 meters downgradient from the oil lens, in both 1986 and 1987 may reflect a slight difference in lithology, such as the presence of a silty layer that sorbs more organic material.

The distribution of carbon isotopes in ground water near the water table is controlled by the mixing of inorganic carbon from (1) soil gas, (2) aerobic and anaerobic degradation of compounds from the oil, and (3) dissolution of carbonate minerals (fig. A-8). The $\delta^{13}C$ values of TIC (relative to the PDB standard) of the native water is in the range of -12 parts per thousand to -15 parts per thousand because of the mixing of soil TIC, with a $\delta^{13}C$ value of -21 parts per thousand, and TIC from the dissolution of carbonates, with a $\delta^{13}C$ value assumed to be 0 ± 2 parts per thousand. Nonmethanogenic degradation of oil constituents adds isotopically light TIC to the ground water because the oil has a $\delta^{13}C$ value of -28.5 parts per thousand. Isotopic values of aqueous TIC that are lighter than the native ground water are the result of reactions such as aerobic degradation and iron and manganese reduction that mineralize organic compounds to TIC. The lightest $\delta^{13}C$ value in ground water (-21.9 parts per thousand) was found at the edge of the oil lens in 1985. Thus, in 1985, and to a lesser extent in 1986 (fig. A-8), processes that oxidize organic material were dominant in the plume. This does not mean that the plume near the oil was aerobic, but that molecular oxygen and other electron acceptors, such as iron and manganese were available in recharge and upgradient water to oxidize organic material to TIC. The $\delta^{13}C$ values of TIC have become progressively heavier from 1985 through 1987. Methanogenesis fractionates carbon isotopes and results in isotopically light methane and heavy carbon dioxide. The isotope results

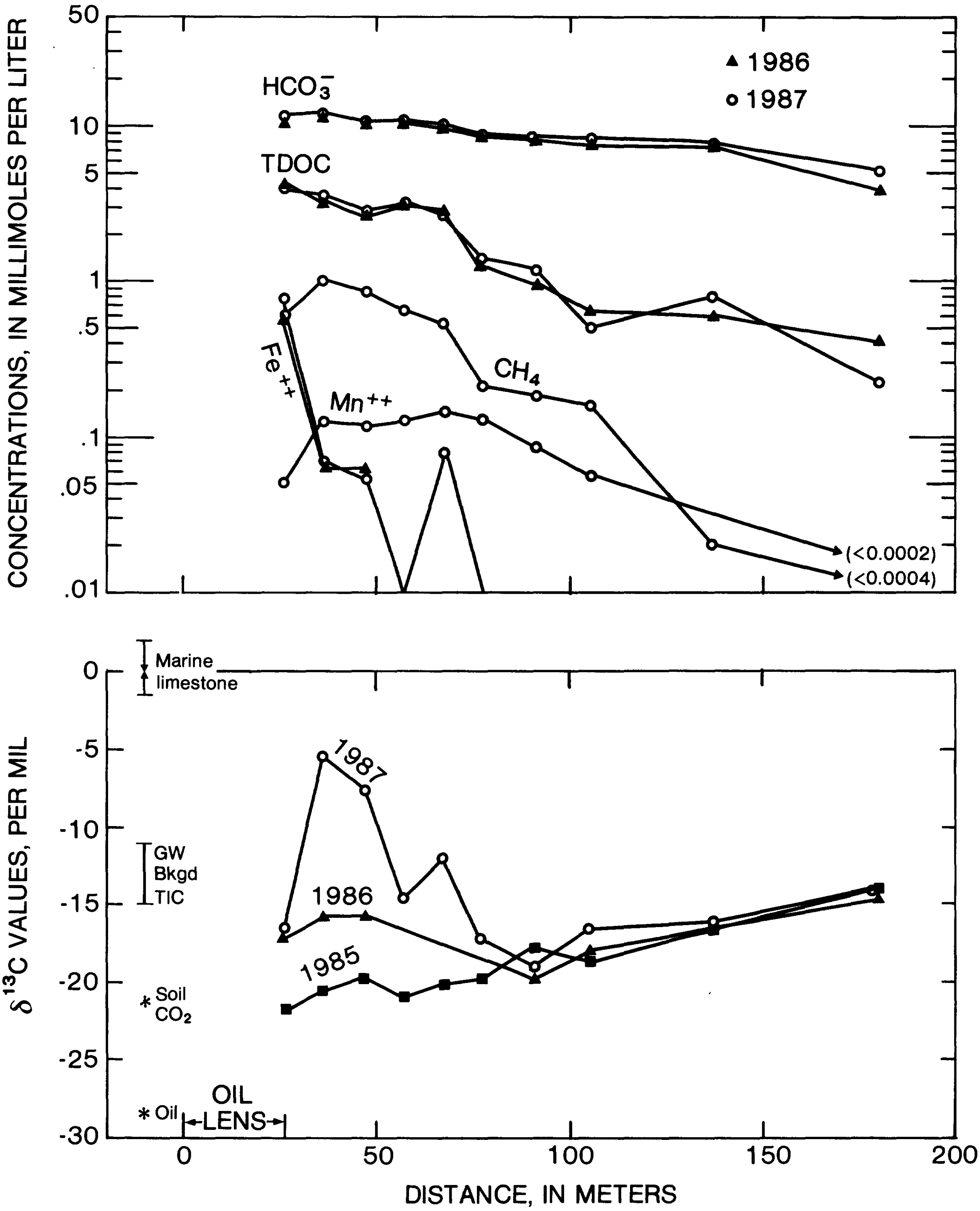

Figure A-8.— Concentrations of bicarbonate (HCO_3^-), total dissolved organic carbon (TDOC), methane (CH_4), iron (Fe^{++}), manganese (Mn^{++}) and δ^{13} C values of inorganic carbon, in water downgradient of the oil lens.

indicate that the plume has become more reducing and methanogenic. Further evidence for this is that the field Eh measurements near the edge of the oil lens decreased from +20 mV (millivolts) in 1984 to -145 mV in 1987. The heaviest $\delta^{13}C$ value of -5.35 parts per thousand is 15 meters downgradient from the edge of the oil lens, which also is where the highest concentration of methane is found. Thus, the zone of highest methanogenic activity is not at the oil-lens/water interface but a few meters downgradient. The high concentrations of dissolved hydrocarbons may inhibit bacterial activity at the edge of the oil lens. More than 100 meters downgradient of the oil lens, the $\delta^{13}C$ values for the 3-year period gradually become heavier and reach background levels 180 meters downgradient from the lens. The $\delta^{13}C$ values appear to be conservative in this region and may provide information on the amount of vertical recharge and mixing that occurs.

CONCLUSIONS

Crude oil in contact with ground water is altered by several processes that have resulted in small zones of differing water chemistry. These geochemical facies are the result of aerobic degradation of organic compounds followed by the depletion of oxygen and the formation of an anaerobic environment. The distributions of chemical species and carbon isotopes indicate that competing oxidation-reduction reactions occur within a zone 80 meters downgradient from the oil lens. The major reactions are methanogenesis and reduction of iron and manganese. These data suggest that reduction of iron and manganese are important mechanisms of decomposition of organic material in aquifers. In the anaerobic zone, the identifiable organic compounds are a major part of the DOC. Farther downgradient, aerobic processes are dominant, the concentrations of constituents decrease rapidly, and the DOC is composed of more refractory, nonidentifiable organic compounds.

Although the concentrations of major chemical parameters such as TIC and TDOC are relatively constant over a 3- to 4-year period, the concentrations of some constituents have varied significantly. The distributions of iron, manganese, and methane and the carbon-isotopic data indicate that part of the plume has become increasingly reducing over time. In the anaerobic zone, the $\delta^{13}C$ values of TIC are lighter by as much as 15 parts per thousand and methane concentrations have increased by a factor of 100. The data indicate that the processes attenuating organic material in the aquifer are dynamic and the system is not at equilibrium.

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THE FATE AND EFFECTS OF CRUDE OIL IN A SHALLOW AQUIFER II. EVIDENCE OF ANAEROBIC DEGRADATION OF MONOAROMATIC HYDROCARBONS

By Isabelle M. Cozzarelli[1], Robert P. Eganhouse[2], and Mary Jo Baedecker[1]

ABSTRACT

The presence and fate of dissolved monoaromatic hydrocarbons and low-molecular weight organic acids were investigated in ground water downgradient from a subsurface crude-oil spill in Bemidji, Minnesota. Degradation of soluble crude-oil components has resulted in the formation of a reducing geochemical environment characterized by increased concentrations of dissolved organic carbon, carbon dioxide, and methane, and the absence of oxygen. Benzene, C_1- to C_4- alkylbenzenes, and aliphatic, aromatic, and alicyclic organic acids were identified in anaerobic ground water downgradient from the oil. Concentrations of the monoaromatic hydrocarbons and organic acids decrease rapidly, relative to the bulk of the dissolved organic carbon, with distance downgradient. Benzene and alkylbenzenes decrease from 8.5 percent to 4 percent of the dissolved organic carbon in 30 meters from the edge of the oil lens, whereas low molecular weight organic acids decrease from 6.5 percent to less than 1 percent. Concentrations of some alkylbenzenes approach detection limits within the anaerobic plume. Individual monoaromatic hydrocarbons differ in the rates at which they are removed from the aquifer. The preferential removal of specific alkylbenzenes may reflect structure-dependent degradation rates. The highest concentrations of organic acids, CH_4, and CO_2 are in the anaerobic zone. The organic acids represent microbial intermediates that can be related to proposed methanogenic-degradation pathyways. The presence of organic acids and phenols, and the generation of gases in the anaerobic ground water support the conclusion that anaerobic degradation of aromatic hydrocarbons is an important geochemical process.

INTRODUCTION

Crude oil is a complex mixture of hydrocarbons that have a wide range of physical characteristics and considerable diversity in their geochemical behavior in the environment. The aqueous solubilities of the different types of hydrocarbons differ significantly. When crude oil comes in contact with ground water, the more soluble components are preferentially leached into the water. Benzene, with a solubility in pure water of 1,780 mg/L (milligrams per liter), is one of the most soluble hydrocarbons. In addition, mononuclear aromatic hydrocarbons do not significantly sorb onto aquifer solids with low organic content and therefore they can be rapidly transported (Schwarzenbach and Westall, 1981). There has been considerable interest in understanding the behavior of benzene and alkylbenzenes in the subsurface because of their high mobility and toxicity. The ultimate fate of these hydrocarbons is, in large part, a function of their biodegradability in the geochemical environment.

In ground water, anaerobic conditions may develop when the amount of molecular oxygen available for aerobic degradation is limited. Under these conditions, anaerobic degradation of dissolved organics may become important. The anaerobic degradation of substituted aromatics such as benzoic acid, phenols, and catechols (Ferry and Wolfe, 1976; Evans, 1977; Shlomi and others, 1978; Healy and Young, 1979) is well established. However, anaerobic degradation of nonoxygenated aromatic hydrocarbons, such as benzene, toluene, and xylenes, has traditionally been regarded as insignificant.

Results of recent laboratory and field studies indicate that the importance of anaerobic microbial degradation of monoaromatic hydrocarbons has been underestimated (Reinhard and others, 1984; Kuhn and others, 1985; Wilson and others, 1986; Grbić-Galić and

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

[2] Southern California Coastal Water Research Project, Long Beach, Calif.

Vogel, 1987; Major and others, 1988). The degradation of benzene, ethylbenzene, and *ortho*xylene in microcosms constructed of methanogenic aquifer material (Wilson and others, 1986) and the preferential removal of xylenes in methanogenic landfill leachate (Reinhard and others, 1984), are evidence that anaerobic degradation of benzene and alkylbenzenes may be important biogeochemical processes in methanogenic environments. Grbić-Galić and Vogel (1987) suggested that anaerobic microbial pathways result in the complete mineralization of aromatic hydrocarbons, such as toluene, under methanogenic conditions. In laboratory microcosm and column experiments, Kuhn and others (1985), and Major and others (1988), showed that benzene, toluene, and xylenes were degraded under denitrifying conditions.

The purpose of this study is to gain an improved understanding of the anaerobic transformation of aromatic hydrocarbons that is necessary to predict their ultimate fate in the subsurface environment. In this paper, the distribution of aromatic hydrocarbons and low-molecular weight organic acids and their fate in ground water downgradient from an underground oil spill in Bemidji, Minn., are described. The apparent disappearance of monoaromatic hydrocarbons in ground water downgradient of the oil was previously reported (Eganhouse and others, 1987). In this paper, the discovery of several types of oxygenated compounds, including aromatic, aliphatic and alicyclic organic acids, that were identified in reducing ground water, are presented. The presence of these organic acids to proposed anaerobic degradation pathways are related. The preferential disappearance of specific alkylbenzenes, coupled with the occurrence of structurally related microbial intermediates and end products, represents the most conclusive field evidence of anaerobic degradation of monoaromatic hydrocarbons offered to date.

METHODS

The research site is located near Bemidji, Minn., where an accidental spill of crude oil occurred in 1979 when an underground pipeline broke. The spill has resulted in the formation of a lens of crude oil at the water table (fig. A-9). A series of wells were installed at and below the water table along a transect downgradient from the oil lens in the direction of ground-water flow. Wells were 2 inches in diameter, constructed of polyvinylchloride (PVC), and screened over a 0.5- to 5-foot interval. The 5-foot screens used for water-table wells were centered approximately at the water table. Ground-water samples were collected annually between 1984 and 1987. Water samples were collected using a Keck [3] pump for measurement of temperature, pH, dissolved oxygen (O_2), ammonia (NH_3), hydrogen sulfide (H_2S), methane (CH_4), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and inorganic cations and anions. Determination of these constituents is described in Baedecker and Lindsay (1986).

Water samples for analysis of hydrocarbons and organic acids were obtained with a Teflon bailer. Samples were poisoned with mercuric chloride and transported, on ice, to the laboratory. Benzene and C_1 to C_4 alkylbenzenes (C_n refers to the number of alkyl carbons on the benzene ring) were determined by purge-and-trap gas chromatography with flame-ionization detection. Structural confirmation of peak identities was achieved on selected samples by coinjection and gas chromatography/mass spectrometry. Water samples for low molecular weight organic acid analysis were made basic ($pH = 10$) by addition of potassium hydroxide (KOH), freeze dried, and then acidifed with phosphoric acid (H_3PO_4). Organic acids were extracted from the acidic solution with diethyl ether and determined by gas chromatography with flame-ionization detection. Positive identification of acid structures was made on selected samples by coinjection of samples and authentic standards combined with gas chromatography/mass spectrometry.

RESULTS AND DISCUSSION

The degradation of dissolved crude oil constituents has resulted in the formation of a reducing geochemical environment downgradient from the oil. Results of unstable constituent (O_2, CH_4, iron (Fe^{2+})) analyses indicate that anoxic conditions prevail downgradient of the oil (fig. A-9). Close to the oil, in zone 1,

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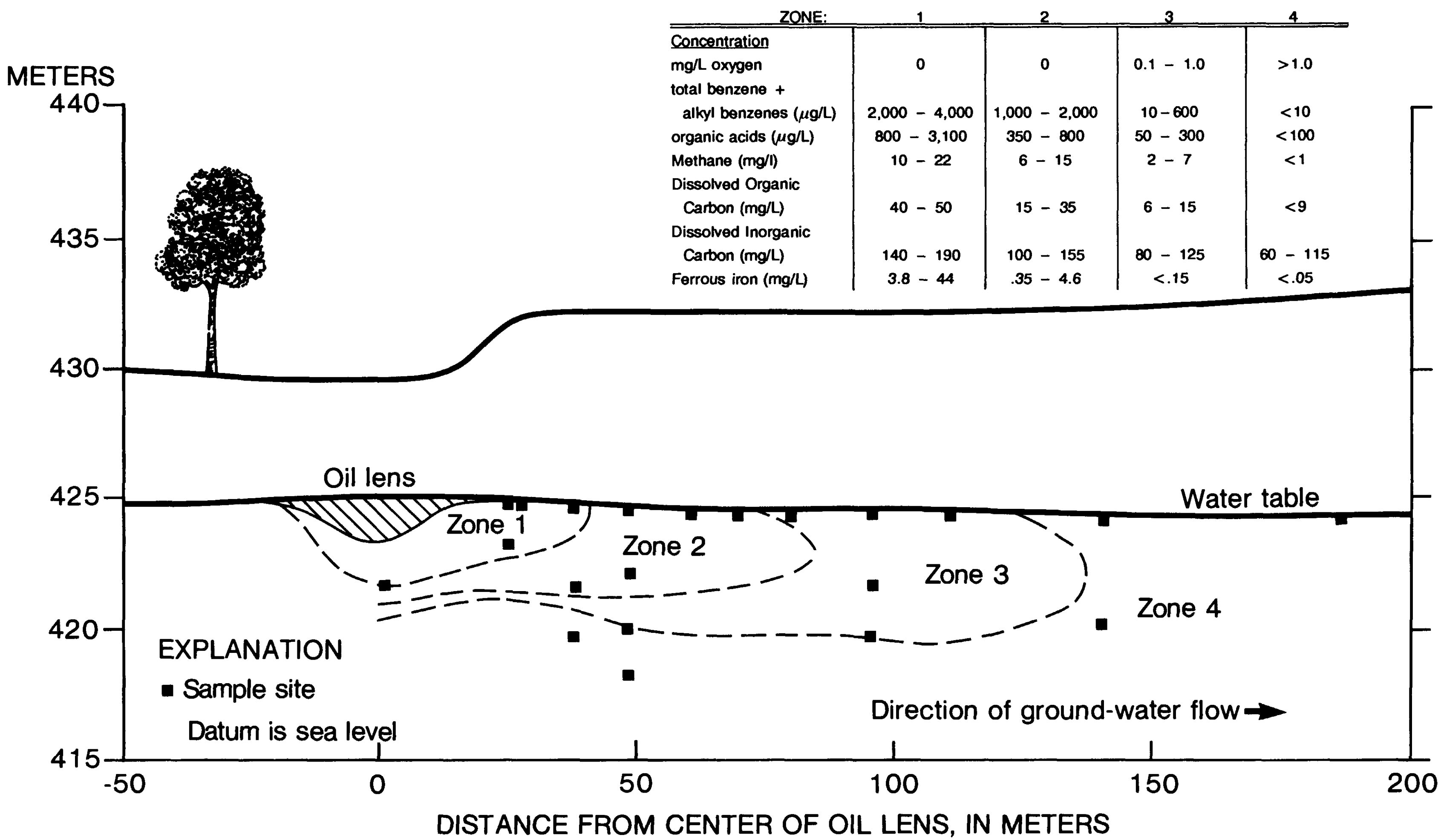
[3] Use of brand or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.



ZONE:	1	2	3	4
Concentration				
mg/L oxygen	0	0	0.1 - 1.0	>1.0
total benzene + alkyl benzenes (μg/L)	2,000 - 4,000	1,000 - 2,000	10 - 600	<10
organic acids (μg/L)	800 - 3,100	350 - 800	50 - 300	<100
Methane (mg/l)	10 - 22	6 - 15	2 - 7	<1
Dissolved Organic Carbon (mg/L)	40 - 50	15 - 35	6 - 15	<9
Dissolved Inorganic Carbon (mg/L)	140 - 190	100 - 155	80 - 125	60 - 115
Ferrous iron (mg/L)	3.8 - 44	.35 - 4.6	<.15	<.05

Figure A-9.—Schematic cross section of the shallow aquifer near Bemidji, Minnesota, showing location of oil lens and zones of differing ground-water chemistry based on 1987 data. Concentration ranges of oxygen, benzene, and alkylbenzenes, low-molecular weight organic acids, methane, dissolved organic carbon, dissolved inorganic carbon, and ferrous iron are shown for zones 1 through 4.

dissolved organic carbon (DOC) concentrations are as high as 50 mg/L where the crude oil contacts the ground water. The relatively soluble aromatic hydrocarbons (benzene and C_1 through C_4 alkylbenzenes) reach concentrations of 4,000 μg/L (micrograms per liter). Concentrations of low-molecular weight (molecular weight less than 180) organic acids are as high as 3,100 μg/L. In this zone, the monoaromatic hydrocarbons and organic acids represent a significant fraction of the DOC. Ground water is anoxic (less than 0.1 mg/L O_2) from the water table to a maximum depth of 4 meters. Dissolved inorganic carbon (DIC) and methane concentrations reach 190 mg/L and 22 mg/L, respectively, due to the production of gases during anaerobic degradation of hydrocarbons. In addition, iron and manganese are mobilized in the anoxic ground water (Siegel, 1987).

The anoxic plume extends through zone 2, 80 meters downgradient from the center of the oil body. Trace amounts of oxygen are present in zone 3, which can be considered a transition zone between a reducing and oxidizing environment. Concentrations of most of the reduced chemical species such as Fe^{2+} and DIC decrease with distance from the oil but are still above background levels in zone 4. The evolution of the reducing geochemical environment and the important redox reactions are described in detail by Baedecker and others (1989, this Proceedings).

There is a rapid attenuation of the monoaromatic hydrocarbons and organic acids, relative to the bulk of the DOC, with distance downgradient from the oil. Concentrations of benzene and C_1 to C_4-alkylbenzenes decrease from 8.5 percent to 4 percent of the DOC within zone 1, whereas low molecular weight organic acids decrease from 6.5 percent to less than 1 percent. This decrease occurs in the anoxic ground water as the alkylbenzenes and organic acids are degraded. At 30 meters from the oil, in zone 2, a larger part of the remaining DOC consists of unidentified, recalcitrant compounds. This refractory organic material has been characterized by Aiken and Thorn (1989, this Proceedings) as a complex, heterogeneous mixture of nonvolatile organic acids. These nonvolatile organic acids may be composed of complex metabolic products from the degradation of oil components and, perhaps, microbial cellular material.

The individual aromatic hydrocarbons found in ground water at the downgradient edge of the

Table A-2.—*Monoaromatic hydrocarbons identified in anaerobic ground water*

Benzene
Toluene

C_2-benzenes
o-xylene
m and *p*-xylene
Ethyl benzene

C_3-benzenes
1,3,5-trimethylbenzene
1,2,4-trimethylbenzene
1,2,3-trimethylbenzene
1-methylethylbenzene
n-propylbenzene
1-ethyl-3-methylbenzene
1-ethyl-4-methylbenzene
1-ethyl-2-methylbenzene

C_4-benzenes
1,2,3,5-tetramethylbenzene
1,2,3,4-tetramethylbenzene
1,2-diethylbenzene
1,3-diethylbenzene
1,4-diethylbenzene
2-methylpropylbenzene
1-methylpropylbenzene
1-methyl-2-propylbenzene
1-methyl-3-propylbenzene
1-methyl-4-propylbenzene
1-methyl-2-(1-methylethyl)benzene
1-methyl-3-(1-methylethyl)benzene
1-methyl-4-(1-methylethyl)benzene
n-butylbenzene
1-ethyl-3,5-dimethylbenzene
1-ethyl-2,4-dimethylbenzene
1-ethyl-2,3-dimethylbenzene
2-ethyl-1,3-diemthylbenzene
2-ethyl-1,4-dimethylbenzene
4-ethyl-1,2-diemthylbenzene

floating oil lens are shown in table A-2. Benzene and all the C_2-, C_3-, and C_4-benzene isomers (except *t*-butyl benzene) were identified. The composition of monoaromatic hydrocarbons changes dramatically with distance from the oil body. Examination of changes in concentrations of five major alkylbenzenes over a 10-meter distance reveals that their rate of loss in anaerobic ground water decreases in the following order: toluene > *o*-xylene > *m*-, *p*-xylene > ethylbenzene (fig. A-10). If the composition of aromatics in ground water contacting the oil body has been constant through time, changes in hydrocarbon concentration downgradient from the oil can be regarded as apparent disappearance rates. It is clear, then, that individual monoaromatics differ in the rates at which they are removed from the aquifer. This difference extends to alkylbenzene isomers whose physicochemical properties are very similar. Moreover, examination of the homology (a series of compounds in which each member differs from the next member by a CH_2 group): benzene, toluene, ethylbenzene, and *n*-propylbenzene indicates that apparent disappearance rates are not systematically related to chain length. Together, these observations suggest that biological, not physical, processes are mainly responsible for changes in alkylbenzene composition downgradient from the oil lens (Eganhouse and others, 1987).

Examination of the alkylbenzene data reveals that some of the alkylbenzenes are lost in the anaerobic part of the plume while others are not. One of the C_4-alkylbenzenes, 1,2,3,4-tetramethylbenzene (1,2,3,4 TMB), appears to be the most persistent of all the aromatic hydrocarbons identified (fig. A-10). This compound becomes the most dominant hydrocarbon 90 meters downgradient from the oil (data not shown). The nearly conservative behavior of 1,2,3,4 TMB persists in ground-water zones with low oxygen concentrations, which suggests that this compound can be used as a molecular marker in the anoxic plume. Figure A-11 shows the concentrations of several alkylbenzenes relative to 1,2,3,4 TMB as a function of distance downgradient from the oil lens. Toluene and *ortho*xylene are completely degraded within the anoxic plume. Benzene and ethylbenzene concentrations decrease by about 30 and 35 percent, respectively, relative to 1,2,3,4 TMB, in the anaerobic zones. The rates of disappearance of these compounds increase significantly with distance downgradient, in zones where the ground water contains detectable amounts of oxygen. The distributions of *n*-propylbenzene and 1-methylethyl benzene, shown in fig. A-11, suggest conservative behavior within the anaerobic plume. The concentrations of these two alkylbenzenes decline dramatically in zone 3 after exposure to oxygenated water and an aerobic microbial ecosystem.

Greater persistence of ethylbenzene relative to the xylenes has also been observed in studies of methanogenic landfill leachate (Reinhard and others, 1984). The more rapid disappearance of *ortho*xylene over the *meta* and *para* isomers observed in the current study agrees with the observations of Barker and others (1986) who studied methanogenic ground water downgradient of a landfill in North Bay, Ontario. These results contrast with the laboratory studies under nitrate reducing conditions (Kuhn and others, 1985; and Major and others, 1988). These workers found that *o*-xylene degraded at a significantly slower rate than *m*- and *p*-xylenes. Similar behavior for the xylenes has been observed in laboratory studies of the oxidation of dissolved hydrocarbons under aerobic conditions (van der Linden, 1978). The rapid apparent degradation of *o*-xylene at Bemidji indicates that the traditional belief, that adjacent methyl groups on an aromatic ring increase the stability of a compound, may not hold under the methanogenic and iron-reducing conditions encountered in the current study.

Organic acids found in ground water at the downgradient edge of the oil lens are shown in table A-3. A large number of aromatic, alicyclic, and aliphatic organic acids were identified. Although phenolic compounds were not quantified, phenol was detected in the anaerobic ground-water zone. The oxidized compounds identified in ground water downgradient from the oil were not detected in ground water from background wells outside the plume. Furthermore, analysis of water equilibrated with oil from the site, revealed that these acids are not original components of the oil. It appears, therefore, that the organic acids are produced within the plume during degradation of dissolved oil constituents. Organic acids are well known metabolic intermediates representing different pathways in the microbial degradation of aromatic and alicyclic hydrocarbons. The organic acids identified in this study appear in the same ground-water zone

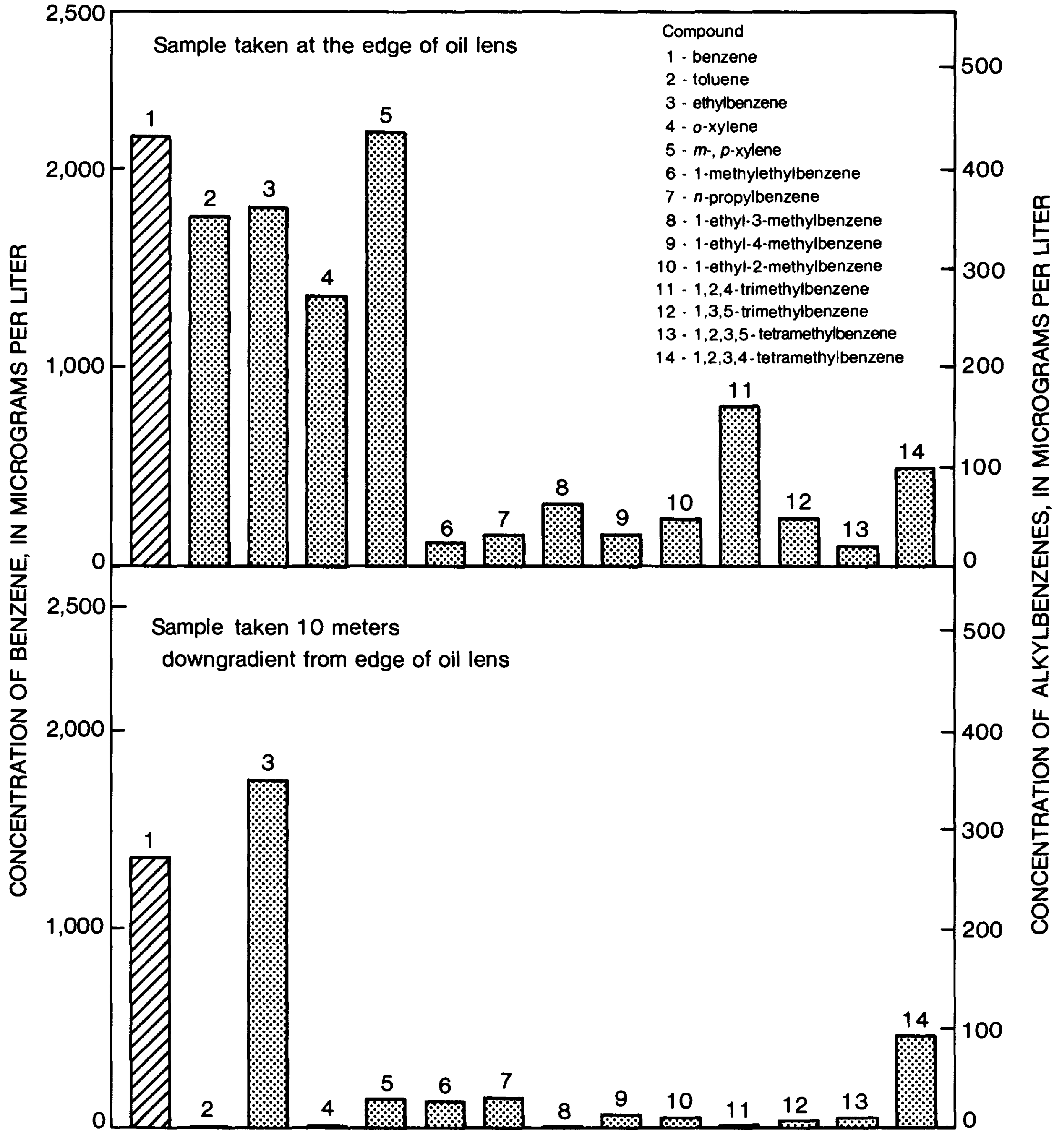


Figure A-10.—Concentrations of benzene and alkylbenzenes in ground water at the edge of the oil lens and 10 meters downgradient from the edge of the oil (1987 data).

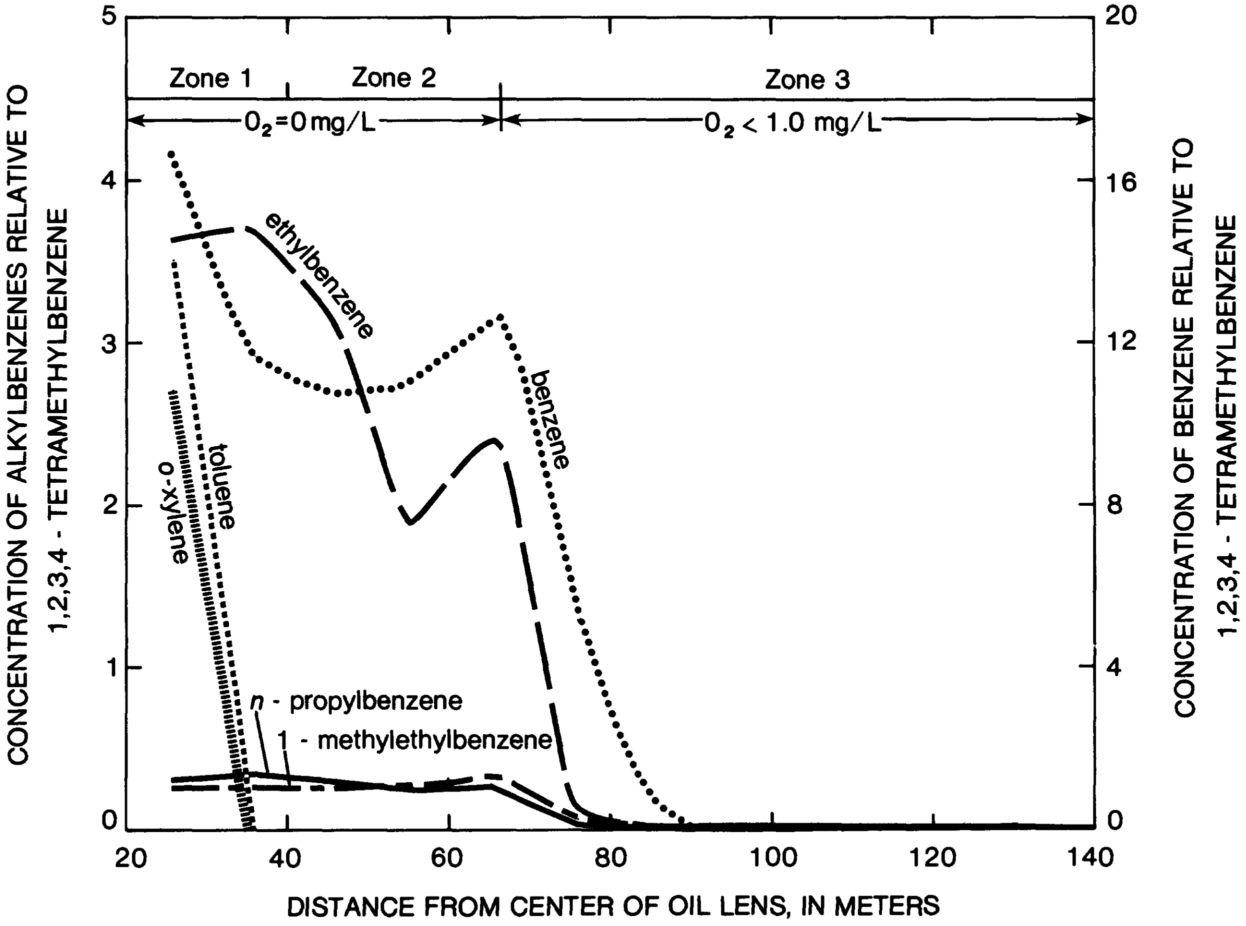


Figure A-11.—Concentrations of benzene, ethylbenzene, toluene, *ortho*xylene, *n*-propylbenzene, and 1-methylethylbenzene relative to 1,2,3,4-tetramethylbenzene as a function of distance from the center of the oil lens (1987 data).

Table A-3.—*Metabolites identified in anaerobic ground water at edge of oil lens*

Aliphatics	*Aromatics*
Formic acid	Phenol
Acetic acid	Benzoic acid
Propanoic acid	*O*-toluic acid
Methyl-butanoic acid	*m* and/or *p*-toluic acid
C_2-butanoic acid	Phenylacetic acid
Methyl-pentanoic acid	2, 4 and/or 2/5 dimethylbenzoic acid
Heptanoic acid	2,6 dimethylbenzoic acid
	3,4 diemthylbenzoic acid
Alicyclics	*m*-methylphenylacetic acid
Cyclohexanecarboxylic acid	*p*-methylphenylacetic acid
C_2-cyclohexanecarboxylic acid	2,4,6,trimethylbenzoic acid

where large amounts of aromatic hydrocarbons apparently are being degraded.

Acetic acid is the major aliphatic acid observed in ground water near the edge of the oil (fig. A-12). Its low concentration 10 meters downgradient from the oil lens likely results from its conversion to methane and carbon dioxide by methanogenic bacteria. The organic acids produced during anaerobic degradation of the aromatic hydrocarbons have different degrees of persistence in the ground water. For example, concentrations of the toluic acids decrease by a factor of 8 within 10 meters, whereas the concentration of a C_2- cyclohexanoic acid (specific structure not determined) decreases only by a factor of 1.3 (fig. A-12). However, interpretation of these data as a function of distance downgradient is complicated by these metabolites being both produced and consumed in the ground water. In general, the cyclohexanoic acids appear to persist farther downgradient than the benzoic acids. The aliphatic acids are in greater abundance close to the oil edge and then disappear rapidly within the anaerobic zones. No significant increase in any of the acids is observed at the anoxic-oxic boundary (between zones 2 and 3; fig. A-9) where many of the more persistent alkylbenzenes rapidly degrade. It is likely that the metabolic intermediates produced during aerobic degradation are subsequently metabolized so quickly in the oxygenated water that they cannot be detected.

The alkylbenzenes can be divided into two groups depending on their behavior within the 80 meter anaerobic plume; those that significantly decrease in concentration relative to 1,2,3,4 TMB and those that appear to be persistent and do not decrease relative to 1,2,3,4 TMB. For those alkylbenzenes that disappear within the anaerobic zones, a corresponding organic acid that is a primary oxidation product was identified (fig. A-13). Although confirmation that these hydrocarbons are the precursors to these specific acids is lacking, each of these hydrocarbons (with one exception: 1-ethyl-2-methylbenzene), has a corresponding oxidized analog (fig. A-13). Other oxidation products may be formed as well. In contrast, no oxidized analogues of compounds that showed relatively greater persistence in the anaerobic ground water (for example: ethyldimethyl-, n-butyl-, methylpropyl-, and diethyl-benzenes) were identified. These compounds either were not oxidized or their oxidation products were below the detection limit. Concentrations of the alkylbenzenes in the latter group were generally less than 10 μg/L, and therefore, the concentrations of intermediates produced as oxidation products would be low. The results indicate that the presence of phenol and aromatic organic acids is related to the biodegradation of benzene and alkylbenzenes. These oxidized intermediates may be useful indicators of biodegradability of parent alkylbenzenes.

Many of the same organic acids reported in the current field study have been identified by others in laboratory experiments under controlled conditions. In methanogenic cultures grown on toluene and benzene, Grbić-Galić and Vogel (1987), described several pathways of

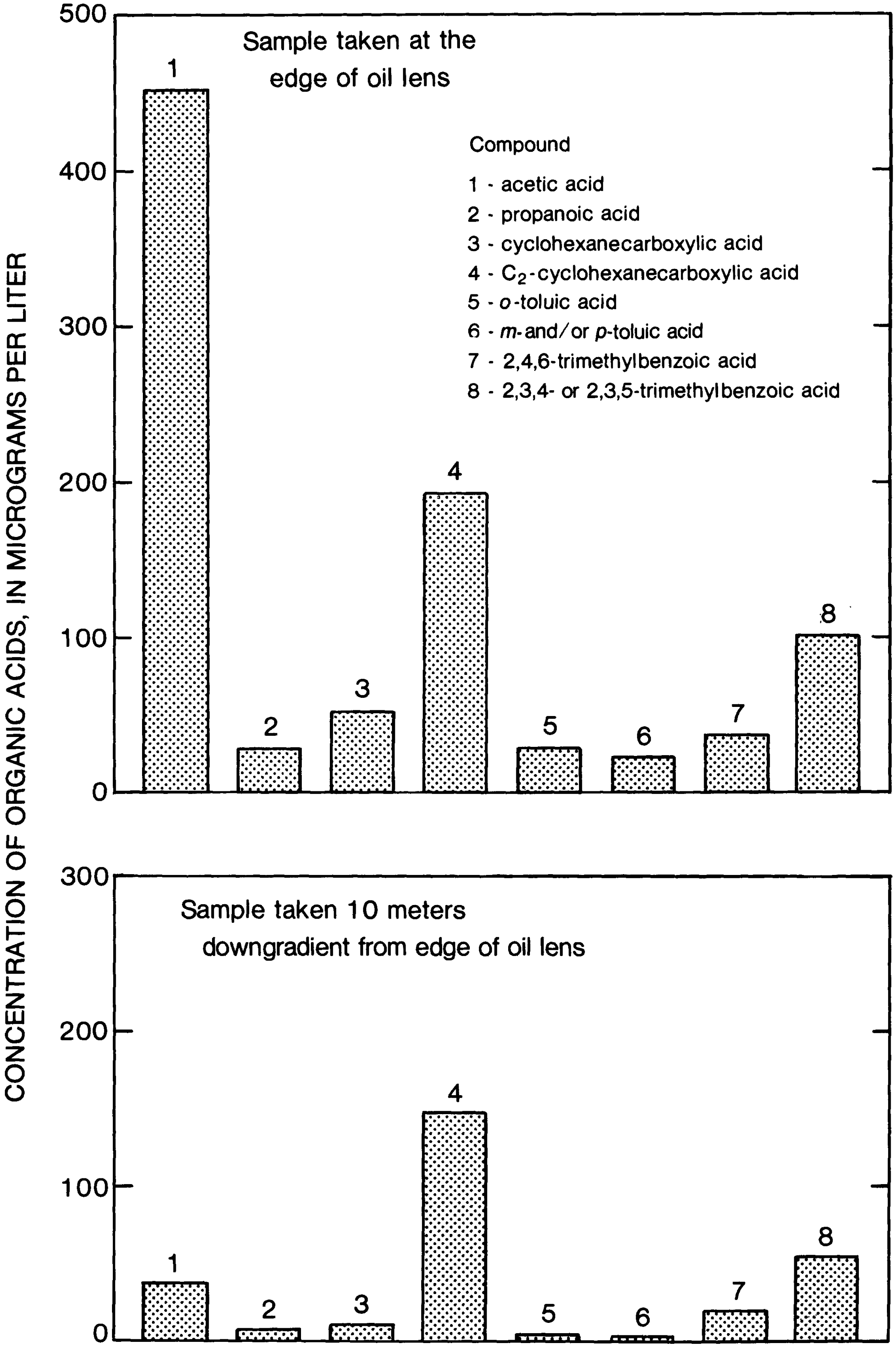


Figure A-12.—Concentrations of low-molecular weight organic acids in ground water at the edge of the oil lens and 10 meters downgradient from the edge of the oil lens (1987 data).

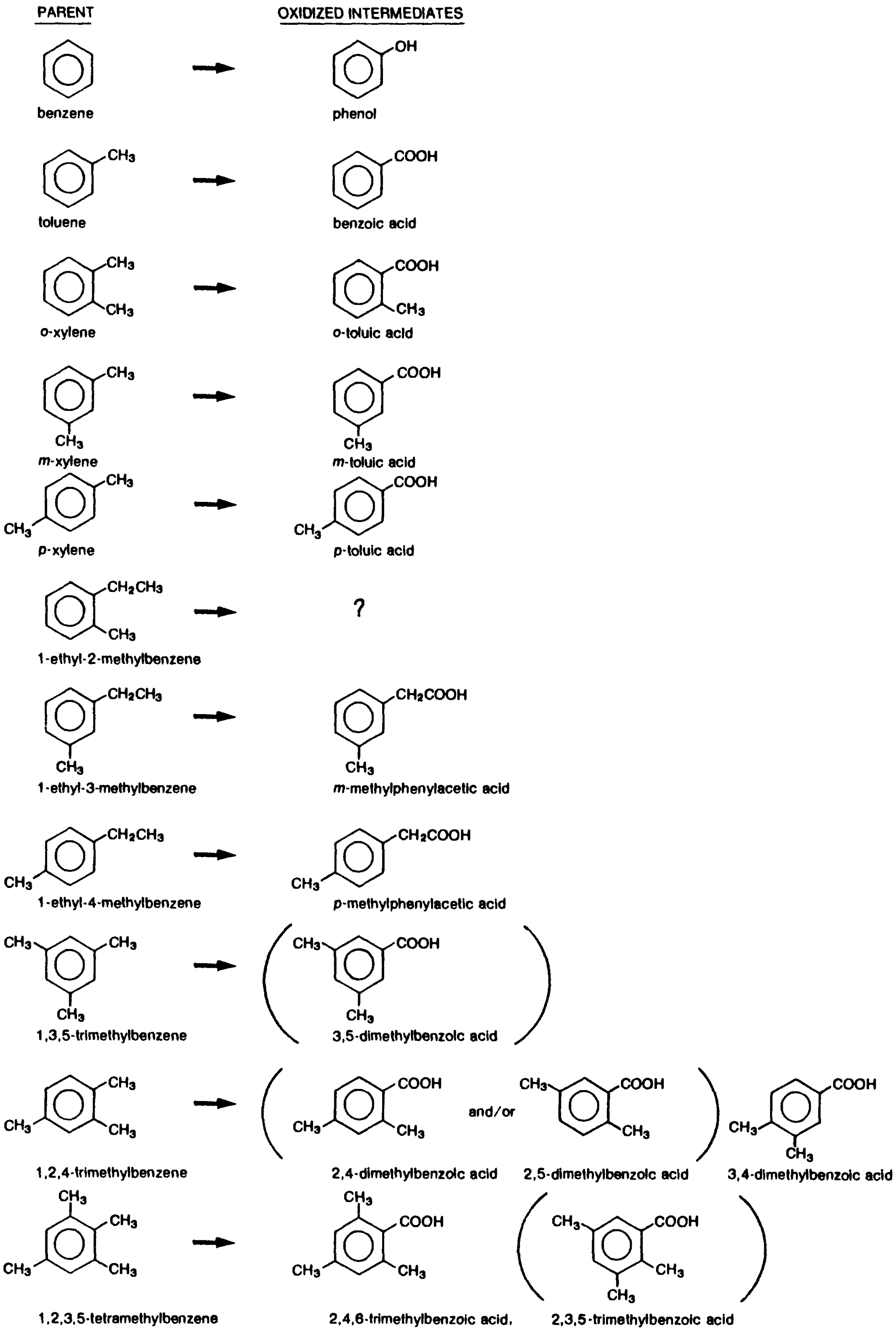


Figure A-13 – Schematic showing volatile aromatic hydrocarbons that are partially degraded within the anaerobic plume and some of their possible oxidation products that have been identified (1986 and 1987 data).

toluene degradation, including oxidation of the aromatic ring leading to cresol (methylphenol) formation, oxidation of the methyl side chain leading to benzoic acid formation, and reduction of the aromatic ring resulting in formation of alicyclic acids. Cresol, produced through the above pathway, may subsequently be degraded to benzoic acid (Smolenski and Suflita, 1987). In contrast, toluene degradation under aerobic conditions proceeds through the dihydroxylated intermediate, catechol (Cerniglia, 1984).

Reactions similar to those described for toluene might be expected for the degradation of higher alkylbenzenes, leading to the formation of the alkylbenzoic acids identified in the anaerobic plume (table A-3). The C_2-cyclohexanoic acid may be produced from the degradation of alkylbenzenes through a pathway analogous to the documented anaerobic degradation pathway of benzoic acid through alicyclic intermediates (Evans, 1977). The straight-chain aliphatic acids likely result from several reaction pathways including ring cleavage of cyclohexanoic acids while the branched-chain aliphatic acids may result from ring cleavage of alkylated rings. Several workers have demonstrated the production of short-chain aliphatic acids during the methanogenic fermentation of benzoic acid through the ring reduction pathway (Fina and others, 1978; Keith and others, 1978; Shlomi and others, 1978). In addition to being intermediates in the degradation of aromatic hydrocarbons, these alicyclic and aliphatic acids could be produced from methyl oxidation of alkylated cyclohexanes and C_1- to C_9- alkanes that have been detected in ground water close to the oil lens.

The organic acids detected in the oil-contaminated water can clearly be related to anaerobic pathways of degradation proposed by other workers and they indicate that once the system becomes anoxic, anaerobic degradation is a significant hydrocarbon degradation process. The considerable amount of ferrous iron detected in ground water at the edge of the oil lens indicates that iron reduction is also an important biogeochemical process. Microorganisms capable of reducing iron during the metabolism of organic matter are numerous. Complete mineralization of organic matter with ferric iron reduction is possible in anaerobic environments (Lovley, 1987). Iron-reducing bacteria capable of using aromatic hydrocarbons, such as benzoic acid, as a sole energy source, have been isolated, and the pathways of hydrocarbon oxidation coupled to iron reduction are being investigated (D.R. Lovley, U.S. Geological Survey, oral commun., 1988). Current work utilizing laboratory microcosm experiments may help to determine the relative importance of the many different pathways discussed above.

SUMMARY AND CONCLUSIONS

The degradation of dissolved crude-oil constituents from a subsurface oil spill has resulted in the formation of a reducing geochemical environment downgradient from the oil lens. At the downgradient edge of the oil, concentrations of dissolved alkylbenzenes and low-molecular weight organic acids reach concentrations of 4,000 $\mu g/L$ and 3,100 $\mu g/L$ respectively. Selected alkylbenzenes and aromatic organic acids are rapidly attenuated within the anaerobic plume. The aromatic, alicyclic and aliphatic organic-acid intermediates can be related to the methanogenic degradation pathways proposed by Grbić-Galić and Vogel (1987). The organic acids identified in the anaerobic ground water along with high concentrations of CH_4 and CO_2, are evidence that anaerobic degradation pathways are operative.

Some compounds, such as toluene and xylene, decrease to detection limits within 10 meters of the source, whereas others, such as *n*-propyl benzene, were significantly degraded only after ground water was reoxygenated downgradient. Among the more abundant alkylbenzenes, relative apparent loss rates were as follows: toluene > *o*-xylene > *m,p*-xylene > ethylbenzene. The 1,2,3,4- tetramethylbenzene appears to be more persistent in both anoxic and oxygen-restricted water.

Organic acids, representing oxidized analogues of most of the alkylbenzenes that degrade anaerobically, were identified. The organic acids apparently are produced during anaerobic degradation of the alkylbenzenes. No oxidized intermediates were identified in the oxygenated water farther downgradient from the oil. Presumably, the acids were rapidly mineralized under aerobic conditions.

The structural dependence of anaerobic degradation and behavior of persistent alkylbenzenes is currently being investigated in laboratory microcosm experiments. Rates of anaerobic conversion of some of the more abundant hydrocarbons to CO_2 and CH_4 also will be addressed in C^{14}-labeled microcosm experiments. In addition, the importance of iron reduction as a degradation pathway will be investigated. These experiments also may clarify the origin of specific metabolic intermediates and the relative importance of ring reduction or ring or methyl oxidation degradation pathways. Understanding the degradation of aromatic hydrocarbons is important, considering the mobility of these compounds and the frequent occurrence of hydrocarbon contamination in subsurface environments.

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VARIABILITY IN THE CHEMISTRY OF NONVOLATILE ORGANIC ACIDS DOWNGRADIENT FROM THE OIL BODY AT BEMIDJI, MINNESOTA

By George R. Aiken[1] and Kevin A. Thorn[1]

ABSTRACT

The distribution and chemistry of nonvolatile organic acids were studied in an aquifer contaminated with crude oil near Bemidji, Minnesota. For the six wells sampled during the summer of 1987, dissolved organic carbon concentrations ranged from a high value of 42 milligrams carbon per liter for the well closest to the oil body, to a low value of 2.9 milligrams carbon per liter for the uncontaminated ground water. Dissolved organic carbon fractionation analyses indicated that the majority of the dissolved organic carbon in each sample was comprised of nonvolatile organic acids resulting from the microbiological degradation of the crude oil. A two-column array consisting of XAD-8 resin and XAD-4 resin was used to isolate and fractionate the nonvolatile organic acids into a hydrophobic-acid fraction and a hydrophilic-acid fraction. Results of elemental analyses and molecular-weight determinations indicate that the hydrophobic acids from the contaminated wells have higher carbon and hydrogen contents and lower oxygen and nitrogen contents, and much lower molecular weights (250 daltons) than the hydrophobic acids from the background well, reflecting differences in composition of original source materials for these samples. Analyses of the structural composition of the molecules comprising the hydrophobic-acid fractions by carbon-13 nuclear-magnetic resonance spectroscopy and infrared spectroscopy have demonstrated that the hydrophobic acid fractions isolated from the contaminated wells have lesser amounts of carboxyl carbon and hetero-aliphatic carbon and greater amounts of aromatic carbon and aliphatic carbon than the sample from the background well. Therefore, our results indicate that differences between the sample obtained from the uncontaminated well and those obtained from the contaminated wells are significant. In addition, the solid state carbon-13 nuclear-magnetic resonance spectra suggest that there is little variation in the composition of the hydrophobic acids downgradient from the oil body and that aromatic and isoparaffinic components of the crude oil have been preserved in the form of carboxylic acids.

INTRODUCTION

The microbiological degradation of crude oil at the water table of a shallow aquifer near Bemidji, Minn. (fig. A-14) has resulted in an extensive plume of dissolved organic carbon (DOC) that is migrating from the oil body. This DOC is composed of a heterogeneous mixture of organic compounds, the majority of which are yellow-colored organic acids that can be chromatographically fractionated into a hydrophobic-acid fraction and a hydrophilic-acid fraction. The nonvolatile organic acids that comprise these fractions of the DOC at the Bemidji site are intermediates in the microbiological degradation of the crude oil. Knowledge of the composition and distribution of these acids is important in understanding the microbiological processes at the site. In addition, both of these organic-acid fractions are geochemically and biologically reactive, influencing, for example, the chemistry and transport of trace metals and organic compounds of low aqueous solubility. Therefore, to model the transport and fate of organic compounds in the plume, and to improve the understanding of the geochemical processes at work at the Bemidji site, it is important to define the composition and properties of these organic-acid fractions.

During the summer of 1987, samples were collected from a variety of wells to determine differences in the chemical composition of the DOC downgradient of the oil body. In this paper, the results of DOC and DOC fractionation analyses of these samples, and the results of characterization analyses on the hydrophobic organic-acids isolated from each well sampled are presented.

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

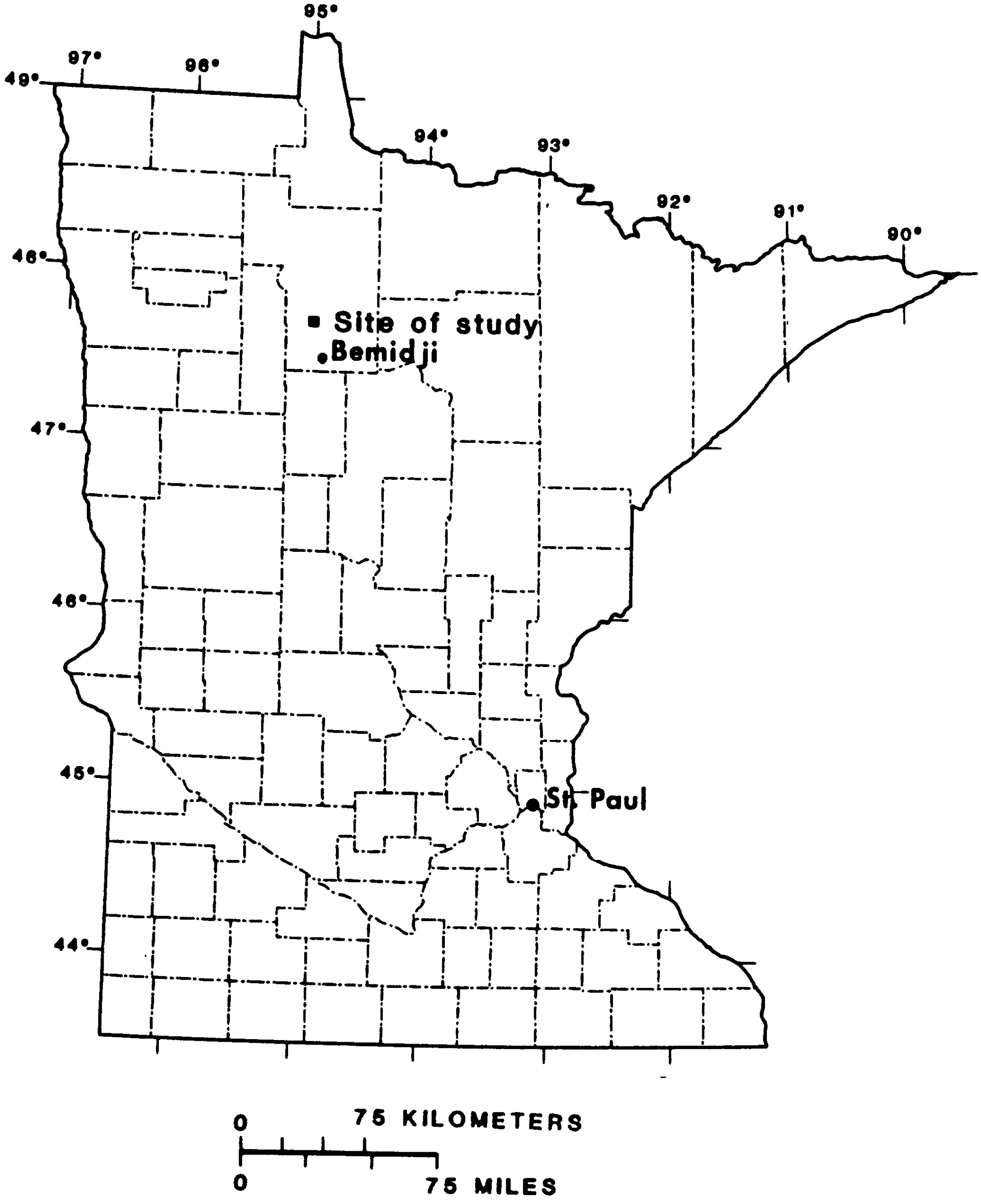

Figure A-14.—Location of research site near Bemidji, Minnesota (from Hult, 1987).

METHODS

Samples were collected from six wells at the Bemidji site. Water was pumped from the wells by means of a Keck[2] pump and the necessary volumes collected in 10-gallon stainless-steel milk cans. The methods used for DOC fractionation analysis have been presented by Leenheer (1981).

For the isolation of the hydrophobic and hydrophilic acid fractions, samples were transferred to glass containers and the pH adjusted to 2 with concentrated hydrochloric acid. Details of the extraction procedure using XAD resins are given by Thurman and Malcolm (1981) and Aiken and others (1987). Elemental analyses were performed according to the methods published by Huffman and Stuber (1985), and molecular weights were determined by vapor-pressure osmometry according to Aiken and Malcolm (1987). Details for the carbon-13 (^{13}C) nuclear magnetic resonance (NMR) analyses are given by Thorn and Aiken (1989, this Proceedings).

RESULTS AND DISCUSSION

DOC values of the samples collected along the axis of the plume (fig. A-15) range from a high value of 42 mgC/L (milligrams carbon per liter) for well 522, the well closest to the oil body, to a low value of 2.9 mgC/L for the uncontaminated ground water from well 310 upgradient from the oil body (table A-4). As expected, the amount of DOC in the contaminated plume decreases downgradient from the oil body; well 515 has the lowest DOC concentration of the contaminated wells (8.1 mgC/L). Although the background DOC concentration of 2.9 mgC/L at well 310 is higher than the mean value of 1.25 mgC/L, as reported by Leenheer and others (1974) for other shallow sand and gravel aquifers, it is within the range of values reported by those authors.

The components of the DOC can be divided chromatographically into six fractions: hydrophobic acids, bases, and neutrals; and hydrophilic acids, bases and neutrals (Leenheer, 1981). Each of the fractions generated in the DOC-fractionation analysis is operationally

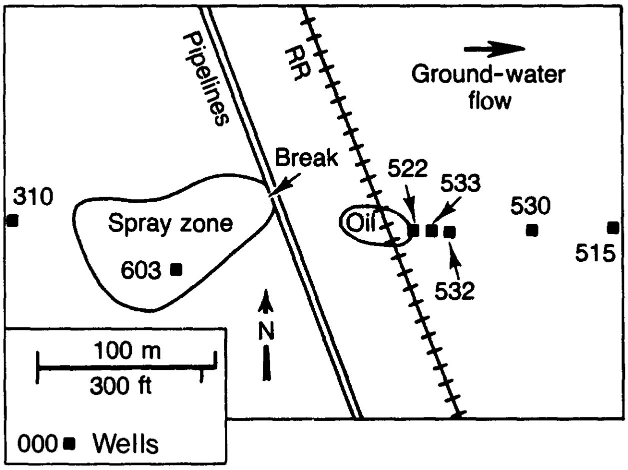

Figure A-15.—Schematic diagram showing approximate location of wells at the Bemidji site sampled for nonvolatile organic acids.

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

Table A-4.—*Dissolved organic carbon fractionation data for selected wells sampled at Bemidji, Minnesota*

[Values are in milligrams of carbon per liter, DOC; numbers in parentheses are the percentage of the total dissolved organic carbon of that fraction]

		Hydrophobics			Hydrophilics		
Sample	DOC	Acids	Bases	Neutrals	Acids	Bases	Neutrals
Well 310	2.9	1.3(45)	0.1(3)	0.1 (3)	0.2 (7)	0.4(14)	0.7(24)
Well 603	15	7.0(47)	0.0(0)	1.0(34)	1.5(11)	0.0 (0)	1.0 (7)
Well 522	42	26 (62)	1.0(2)	1.0 (2)	8.5(20)	0.5 (1)	5.0(12)
Well 532	31.5	17.5(55)	0.0(0)	0.5 (2)	10.5(33)	0.5 (2)	3.0(10)
Well 530	21	11.7(56)	0.6(3)	0.9 (4)	4.5(22)	0.3 (1)	3.3(16)
Well 515	8.1	4.4(55)	0.3(4)	0.8(10)	1.6(20)	0.3 (4)	0.6 (7)

defined on the basis of the affinities of organic compounds for the resins employed in the fractionation scheme. Long-chain fatty acids with fewer than one carboxylic acid functional group per 10 carbon atoms, for example, are classified as hydrophobic neutrals according to the DOC fractionation scheme. DOC-fractionation analyses of the samples collected during the summer of 1987 (table A-4) provide some insights into the composition of the DOC at each of the wells sampled. In each case, nonvolatile organic acids were found to be the major components of the DOC. The composition of the DOC at each of the contaminated wells differed from that of well 310, the background well, where the hydrophobic-acid fraction was the major fraction of DOC (45 percent), and the hydrophilic-acid fraction was only 7 percent of the DOC. Well 603, which is in the spray zone upgradient from the oil body, showed a similar pattern to well 310 with respect to the concentrations of hydrophobic and hydrophilic acids; however, water from well 603 had the highest concentrations of hydrophobic neutrals of any of the wells sampled, perhaps reflecting slower degradation of the oil sprayed in this area relative to the contaminated wells near the oil body itself. Starting at well 522, which samples the anoxic waters immediately under the oil body, and moving downgradient to well 515, the hydrophobic- and the hydrophilic-acid fractions account for more than 75 percent of the DOC. The hydrophobic-acid fraction is highest for well 522 (62 percent), and is relatively constant for the other wells sampled. The hydrophilic-acid fraction, on the other hand, increases to a high value at well 532 (33 percent), and then gradually decreases to a value of 20 percent at well 515. These trends may indicate that the hydrophobic-acid fraction is more refractory than the hydrophilic-acid fraction and consequently more resistant to biodegradation in the aerobic part of the DOC plume.

In order to characterize these two fractions of organic acids further, the hydrophobic and hydrophilic acids from the sampled wells were isolated by adsorption chromatography on Amberlite XAD 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 is an acrylic ester resin routinely used to isolate aquatic humic substances and retains the more hydrophobic organic acids in the sample. XAD-4 is a styrene-divinyl benzene resin with a greater surface area, and, in general, a greater capacity for retaining low molecular weight solutes than XAD-8. In the isolation scheme employed for the samples from Bemidji, the more hydrophobic acids were first removed from the sample on the XAD-8 resin; then, the hydrophilic acids were subsequently removed on the XAD-4 resin. Currently (1988), the hydrophobic-acid fractions have been characterized by ^{13}C-NMR spectroscopy, infrared (IR) spectroscopy, elemental analysis and molecular-weight determination.

The results of the elemental analyses for the hydrophobic-acid fractions show a large difference between the background material at well 310 and the contaminated wells. The hydrophobic-acid fraction from well 310 is composed primarily of the naturally occurring fulvic acid; this fraction has lower carbon (C), and hydrogen (H) contents and higher oxygen (O), and nitrogen (N) contents than do samples from the contaminated wells. With a molecular weight of 782 daltons, this sample appears to be fairly similar to other aquatic fulvic acids isolated from ground waters (Thurman, 1985) and surface waters (Steelink, 1985). This result is consistent with the fact that the aquifer is a relatively shallow (20 meters deep) sand and gravel aquifer underlain by low-permeability till (Hult, 1987). In addition to comparatively high C and H contents and low O and H contents, the hydrophobic acids from the contaminated wells have much lower molecular weights (250 daltons) than does the background fulvic acid. The differences in molecular weight and elemental compositions between the background well and the contaminated wells reflect differences in the original source materials. When the H:C atomic ratios are plotted against the O:C ratios (van Krevelen diagram) the hydrophobic acids from the contaminated wells plot near fulvic acids from deep aquifers, and trend away from fulvic acids from shallow aquifers and surface waters. In addition, the hydrophobic acid fractions from the contaminated wells have O:C atomic ratios that are similar to those obtained for coal and leonardite humic substances.

^{13}C-NMR spectroscopy is a powerful tool for studying complex samples of environmental significance, providing important information concerning the structural composition of the molecules in the mixture (Thorn, 1987). Solution state ^{13}C-NMR analyses, including the acquisition of quantitative spectra and attached-proton test spectra, have been obtained for selected samples from the Bemidji site (see Thorn and Aiken, 1989, this Proceedings). Quantitative spectra for the hydrophobic organic acids from the contaminated wells downgradient from the oil body show that the samples contain almost identical C distributions: 17 percent carboxyl and ketone C (160-220 ppm (parts per million)); 19 percent aromatic C (90-160 ppm); 7 percent hetero-aliphatic C (60-90 ppm); and 57 percent aliphatic C (0-60 ppm). These results indicate that there is little difference in the composition of the hydrophobic acids from the contaminated wells downgradient from the oil body, and this is consistent with the elemental data for these samples. APT spectra for these samples also suggest that aromatic and isoparaffinic components of the crude oil have been selectively preserved in the form of carboxylic acids. The quantitative spectrum of the background fulvic-acid sample indicates that this sample contains greater amounts of carboxyl C and hetero-aliphatic C, and less aromatic C and aliphatic C than do the hydrophobic acids from the contaminated wells. In general, the ^{13}C-NMR results have been confirmed by IR spectroscopy, which also provides structural information on organic molecules.

SUMMARY

DOC-fractionation analyses of selected samples from the Bemidji site indicate that nonvolatile organic acids are the major component of the DOC in the plume downgradient from the oil body. These organic acids were isolated and fractionated using XAD resins into a hydrophobic-acid fraction and a hydrophilic-acid fraction. To date (1988), the results of the characterization analyses of the hydrophobic-acid fractions in samples from wells at the Bemidji site indicate that, as expected, differences between the samples obtained from the contaminated wells and the uncontaminated ground water are significant. Surprisingly, differences in the chemical nature of the hydrophobic-acid fraction among the contaminated wells are relatively few. This fraction of the DOC results from the microbiological degradation of the crude oil; the highest concentration of this material was found at well 522 in the anoxic waters under the oil itself. It is a possibility that this fraction is sufficiently refractory to resist further degradation as it is transported downgradient from the oil body.

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CHARACTERIZATION OF NONVOLATILE ORGANIC ACIDS RESULTING FROM THE BIODEGRADATION OF CRUDE OIL BY NUCLEAR MAGNETIC RESONANCE SPECTROMETRY

By Kevin A. Thorn[1] and George R. Aiken[1]

ABSTRACT

Three fractions of nonvolatile organic acids resulting from the biodegradation of crude oil have been isolated from wells downgradient from the oil body at the Bemidji, Minnesota, site. The organic acids and the undegraded whole crude oil have been characterized by using carbon-13 nuclear magnetic resonance spectroscopy. Hydrophilic acids, hydrophobic acids, and the hydrophobic neutral fraction of organic acids were analyzed using quantitative and attached proton-test carbon-13 nuclear magnetic resonance. The crude oil was analyzed by quantitative and distortionless enhancement by polarization transfer carbon-13 nuclear magnetic resonance. The hydrophobic acids and hydrophobic neutral fraction were found to be enriched in aromatic carbons compared to the whole crude oil. All three fractions of organic acids appear to have been derived from the aromatic, branched chain, and cyclic components of the original crude oil.

INTRODUCTION

Biodegradation is one of the important processes by which petroleum is altered in the shallow subsurface. This project was undertaken to learn something of the chemical structure of the nonvolatile organic acids resulting from the microbial degradation of crude oil at the Bemidji, Minn., site. Hydrophilic acids (HPI), hydrophobic acids (HPO), and the "hydrophobic neutral" (HPO-N) fraction of organic acids were isolated on XAD resins from wells 515A, 522, 530B, and 532B, all downgradient from the oil pool, and well 603, in the spray zone, in May 1987, as described by Aiken and Thorn (1989, this Proceedings). These corresponding three fractions of the naturally occurring dissolved organic carbon (DOC) also were isolated from an uncontaminated well upgradient from the oil pool, well 310. Hydrophilic and hydrophobic acids also had previously been isolated from wells 530B, 532B, and 533B in July 1986 (Aiken and others, 1987). Hydrophobic and hydrophilic acids were isolated on XAD-8 and XAD-4 resins, respectively. The hydrophobic neutral fraction is that fraction of organic acids that adsorbs on XAD-8 resin at pH2, and elutes with acetonitrile, but not with dilute base. The organic acid fractions from both the contaminated and uncontaminated wells have been analyzed using solution state carbon-13 (^{13}C) nuclear-magnetic-resonance spectrometry (NMR). The undegraded whole crude oil, and the saturate, aromatic, asphaltene, and resin fractions of the undegraded crude oil, are also being characterized by ^{13}C NMR to provide complementary information to the gas chromatography-mass spectrometry (GC-MS) analyses reported by Baedecker and others (1984). In this paper, spectra of the whole crude oil and the acid fractions from contaminated wells are described. Elemental analysis and molecular weight data for the acid fractions are reported by Aiken and Thorn (1989, this Proceedings).

METHODS OF STUDY

Isolation and Preparation of Samples for NMR Spectroscopy

The isolation of the HPI, HPO, and HPO-N fractions from contaminated wells using XAD resins has been described by Aiken and Thorn (1989, this Proceedings). The samples were prepared for NMR analyses at the following concentrations: 289 mg (milligrams) of the potassium-salt of freeze dried HPI (well 530, 1986) was dissolved in 1.5 mL (milliliters) H_2O and 0.5 mL D_2O in a 10 mm (millimeter) NMR tube; 367 mg of the potassium-salt of freeze dried HPO (well 530, 1986) was dissolved in 1.5 mL H_2O and 0.5 mL D_2O in a 10 mm NMR tube; 75 mg of the H-saturated, freeze dried HPO-N fraction was dissolved in 0.5 grams of dimethylsulfoxide-d_6, ^{13}C-depleted (99.9 atom % ^{12}C), in a 5 mm NMR tube.

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

The whole crude oil was prepared by dissolving 2 mL of the oil in 1 mL of chloroform-d. For the quantitative carbon-13 NMR spectrum, 42 mg of the paramagnetic relaxation reagent chromium (III) acetylacetonate was added to the sample to shorten relaxation times.

Nuclear Magnetic Resonance Spectroscopy

Organic Acid Fractions

All ^{13}C NMR spectra were recorded on a VARIAN XL-300[2] NMR spectrometer at a carbon resonant frequency of 75.4 MHz (megahertz). The acquisition parameters for the quantitative spectra included a 50,000 Hertz (Hz) spectral window, 45° pulse angle, 0.2 second acquisition time, 10.0 to 12.0 second pulse delay, and inverse gated decoupling. Line broadenings of 100.0, 100.0, and 50.0 Hz were applied to the free induction decays of the HPI, HPO, and HPO-N spectra, respectively. Acquisition parameters for attached proton test (APT) spectra included a 30,000 Hz spectral window, 45° pulse angle, and 0.2 second acquisition time. Pulse delays of 1.0, 0.0, and 0.0 seconds, and tau delays of 7.0, 7.0, and 8.0 ms (milliseconds), were employed for the HPI, HPO, and HPO-N spectra, respectively.

Crude Oil

The acquisition parameters for the quantitative spectrum included an 18,867.9 Hz spectral window, 45° pulse angle, 0.5 second acquisition time, 5.0 second pulse delay, inverse gated decoupling and 1.0 Hz line broadening.

The distortionless enhancement by polarization transfer (DEPT) spectra were acquired using the standard Varian software. The value of J, the carbon-proton, one-bond coupling constant, was set equal to 140 Hz.

RESULTS

The crude oil contaminating the aquifer at Bemidji has been described as a light aliphatic crude oil (Baedecker and others, 1984). The quantitative ^{13}C NMR spectrum of the whole crude oil is shown in figure A-16. In quantitative ^{13}C NMR spectra, which are acquired using inverse gated decoupling to eliminate nuclear Overhauser enhancement, and pulse delays long enough to allow complete relaxation of nuclei between pulses, peak areas accurately represent the number of carbon nuclei present. The spectrum indicates that the aliphatic carbons in the region from approximately 10 to 55 ppm (parts per million) comprise 83 percent of the carbons present in the sample, and the aromatic carbons in the region from approximately 110 to 150 ppm comprise 17 percent of the carbons present. Vertical and horizontal scale expansions of the aliphatic and aromatic regions of the spectrum also are shown in figure A-16. The DEPT spectra of the aliphatic region of the crude oil are shown in figure A-17. The DEPT experiment (Doddrell and others, 1982) generates subspectra of methyl only, methylene only, methine only, and all protonated carbons. Although, in theory, polarization transfer experiments do not necessarily produce quantitative results, practical results with fossil fuels suggest that DEPT can be used to quantitate aliphatic functions (Dennis and Pabst, 1987; Netzel, 1987). The DEPT spectra indicate, as expected, that methylenes are the most abundant types of carbons present within the aliphatic structures. Methine carbons are less abundant, but not insignificant; they are an indication of the number of branching points and ring junctures within the aliphatic structures of the hydrocarbon molecules.

Quantitative and APT (Patt and Shoolery, 1982) ^{13}C NMR spectra of the HPI and HPO fractions from well 530B (1986), and the HPO-N fraction from well 515A (1987), are presented in figure A-18. The quantitative spectra all exhibit five major bands from approximately 0 to 60 ppm, representing primarily sp^3 hybridized carbons bonded to other carbons (aliphatic I peak); 60 to 90 ppm, representing primarily sp^3 hybridized carbons bonded to oxygens, that is, alcohol and ether carbons (aliphatic II peak, or hetero-aliphatic peak); 90 to 160 ppm, representing primarily aromatic carbons; 160 to 190 ppm, representing carboxyl carbons, with possible overlap of lactone, ester, and amide carbonyl carbons; and 190 to 220 ppm, representing ketone carbons. The distribution of carbons determined by integration of peak areas is presented in table A-5. The HPO and the HPO-N fraction are enriched in aromatic carbons relative to the original crude oil. The HPI acids have the highest concentration of carboxyl and hetero-aliphatic carbons, and, therefore, are the most oxidized fraction of the nonvolatile organic acids, followed, in turn, by the HPO and HPO-N fraction.

The APT spectra were acquired using a tau delay of 7.0 ms so that methylene and quaternary

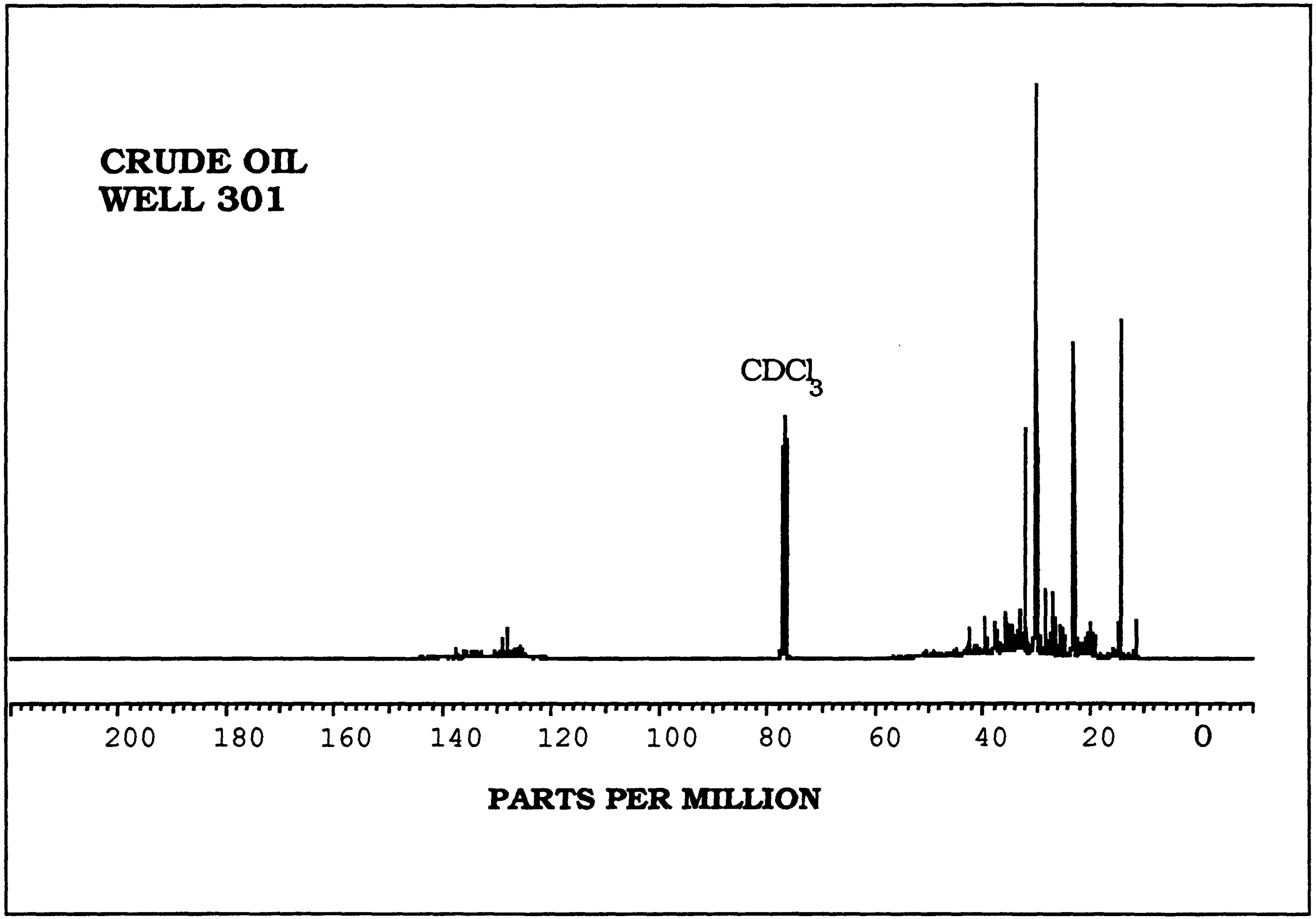

Figure A-16a.—Quantitative carbon-13 nuclear magnetic resonance spectrum of crude oil from well 301.

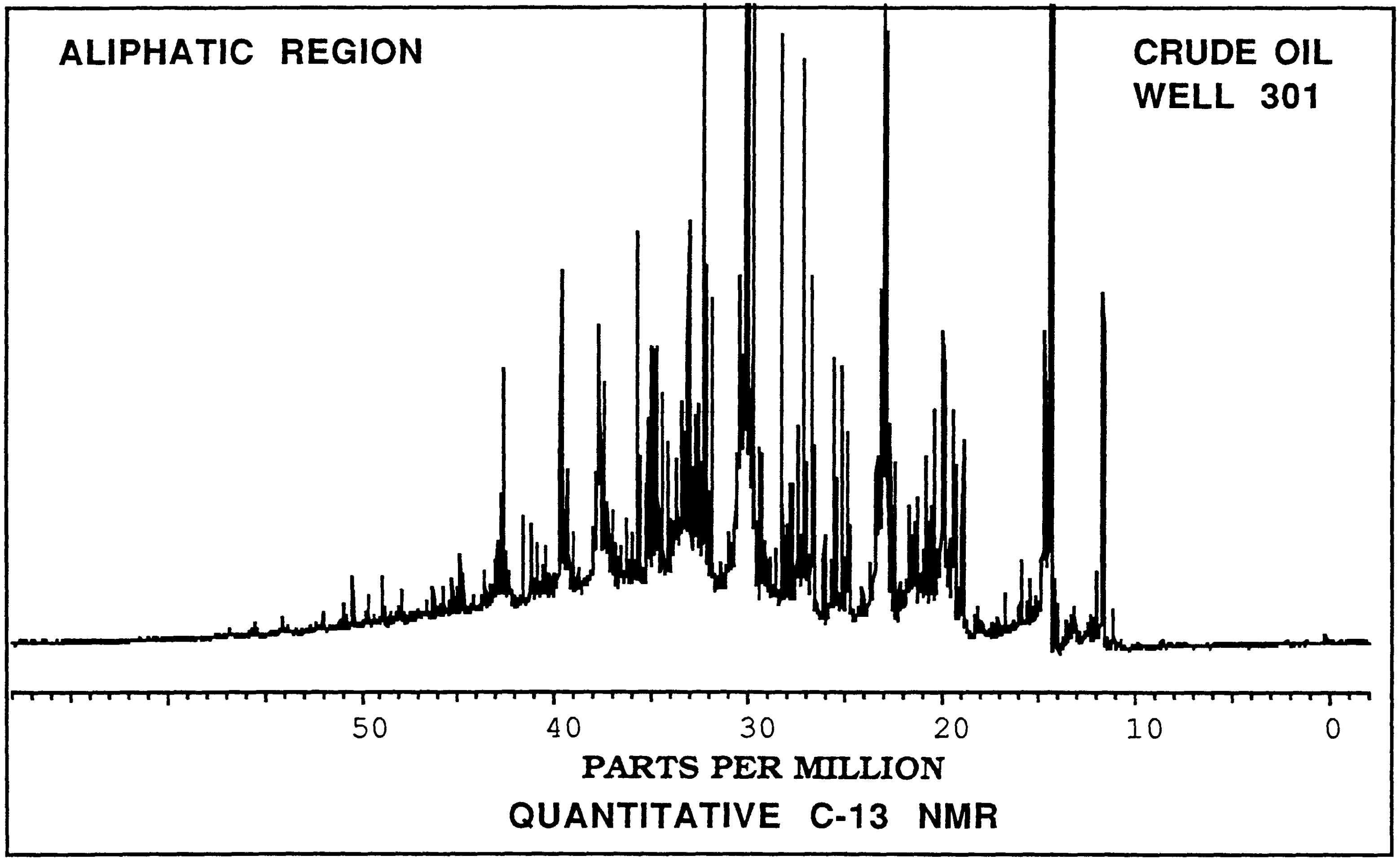

Figure A-16b.—Aliphatic region of quantitative carbon-13 nuclear magnetic resonance spectrum of crude oil from well 301.

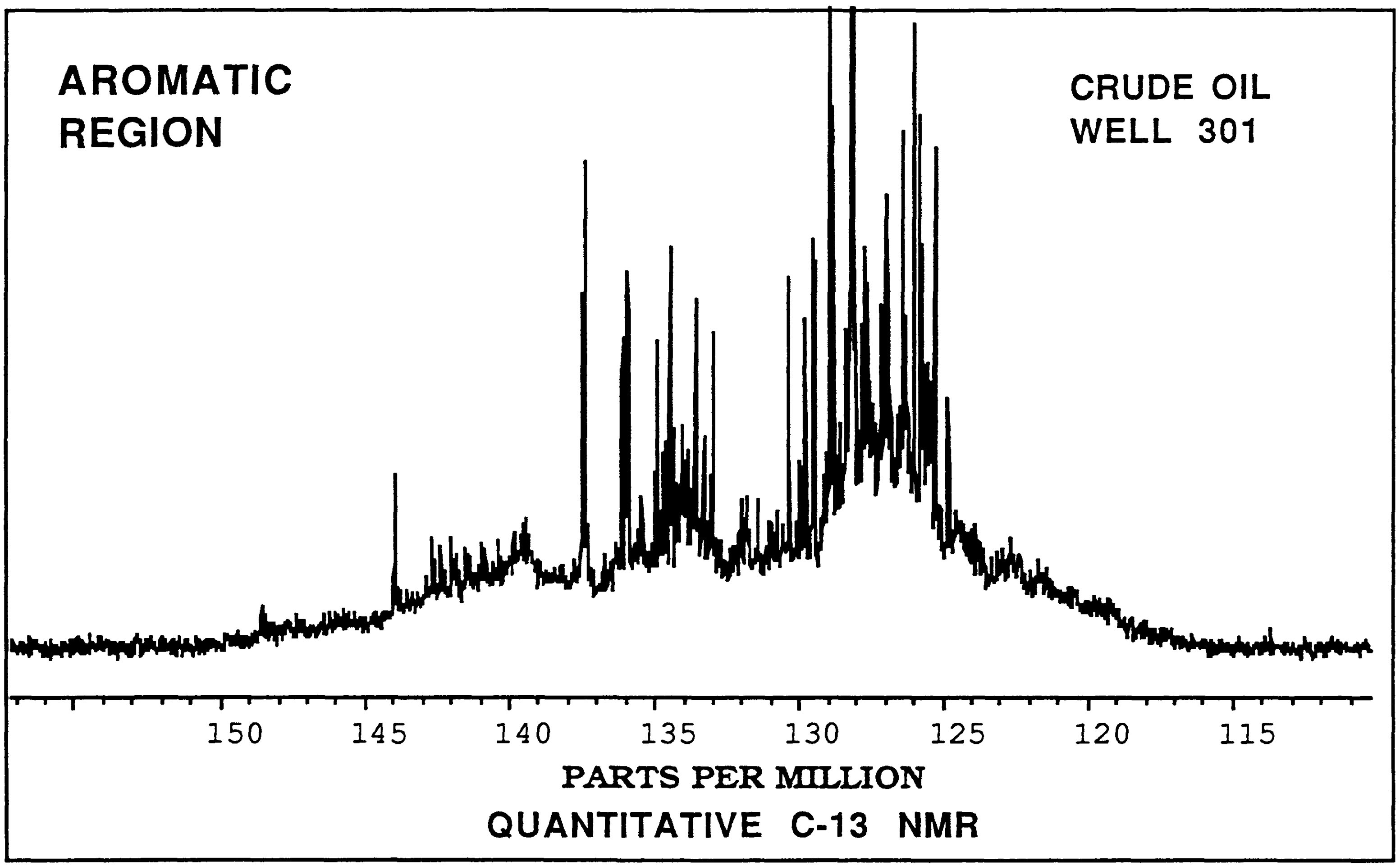

Figure A-16c.—Aromatic region of quantitative carbon-13 nuclear magnetic resonance spectrum of crude oil from well 301.

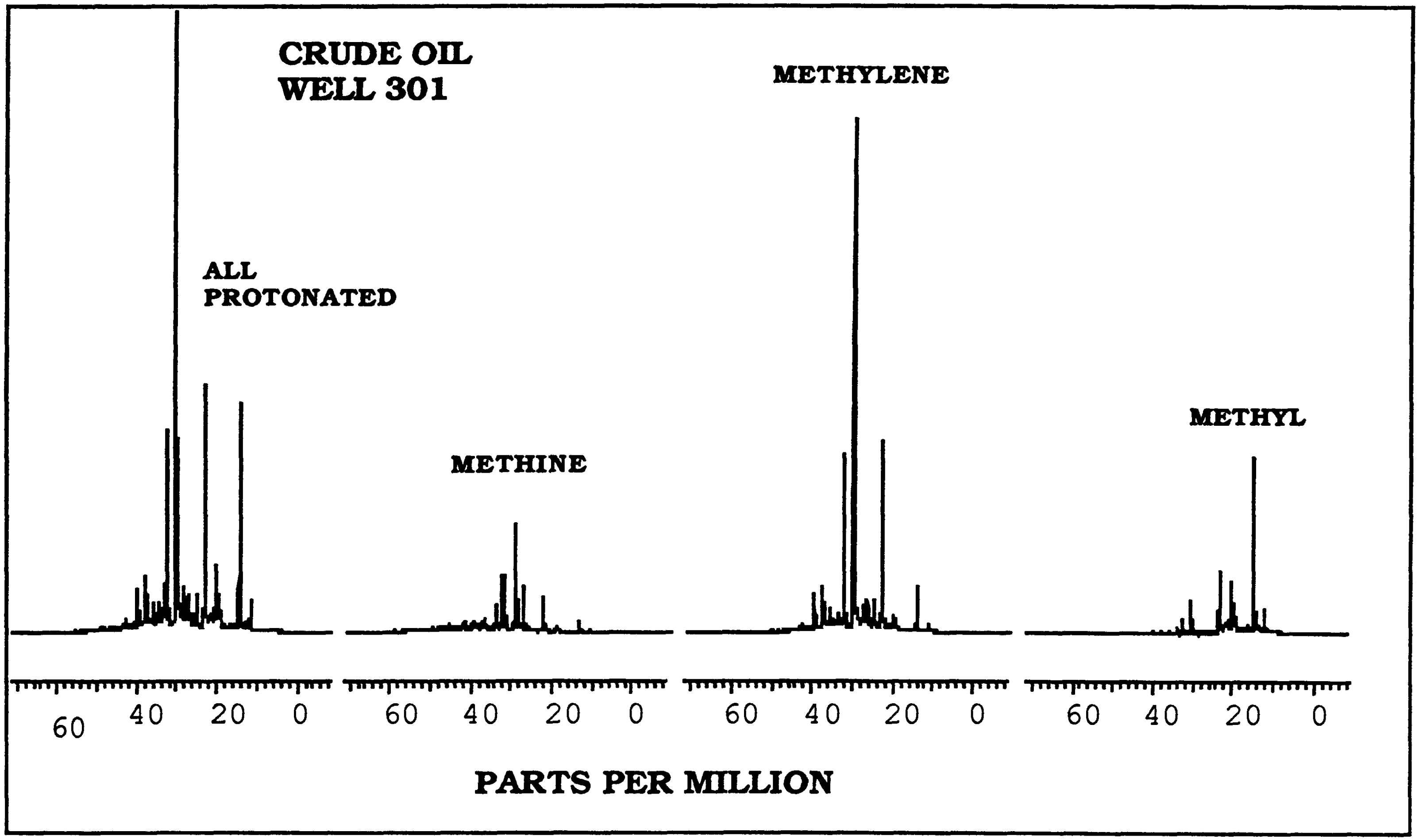

Figure A-17.—Distortion enhancement by polarization transfer carbon-13 nuclear magnetic resonance spectra of crude oil from well 301.

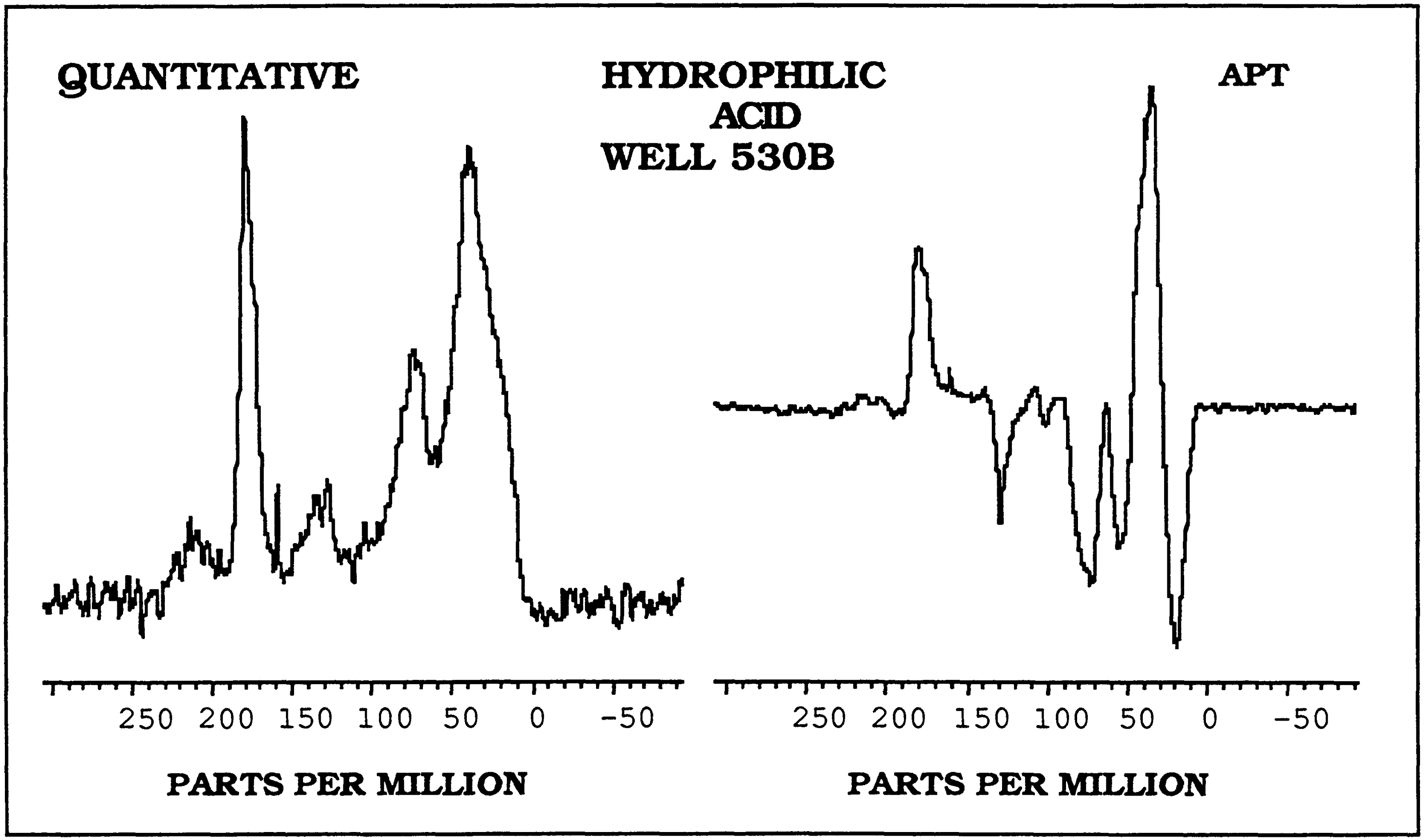

Figure A-18a.—Quantitative and attached proton test carbon-13 nuclear magnetic resonance spectra of well 530B hydrophilic acid.

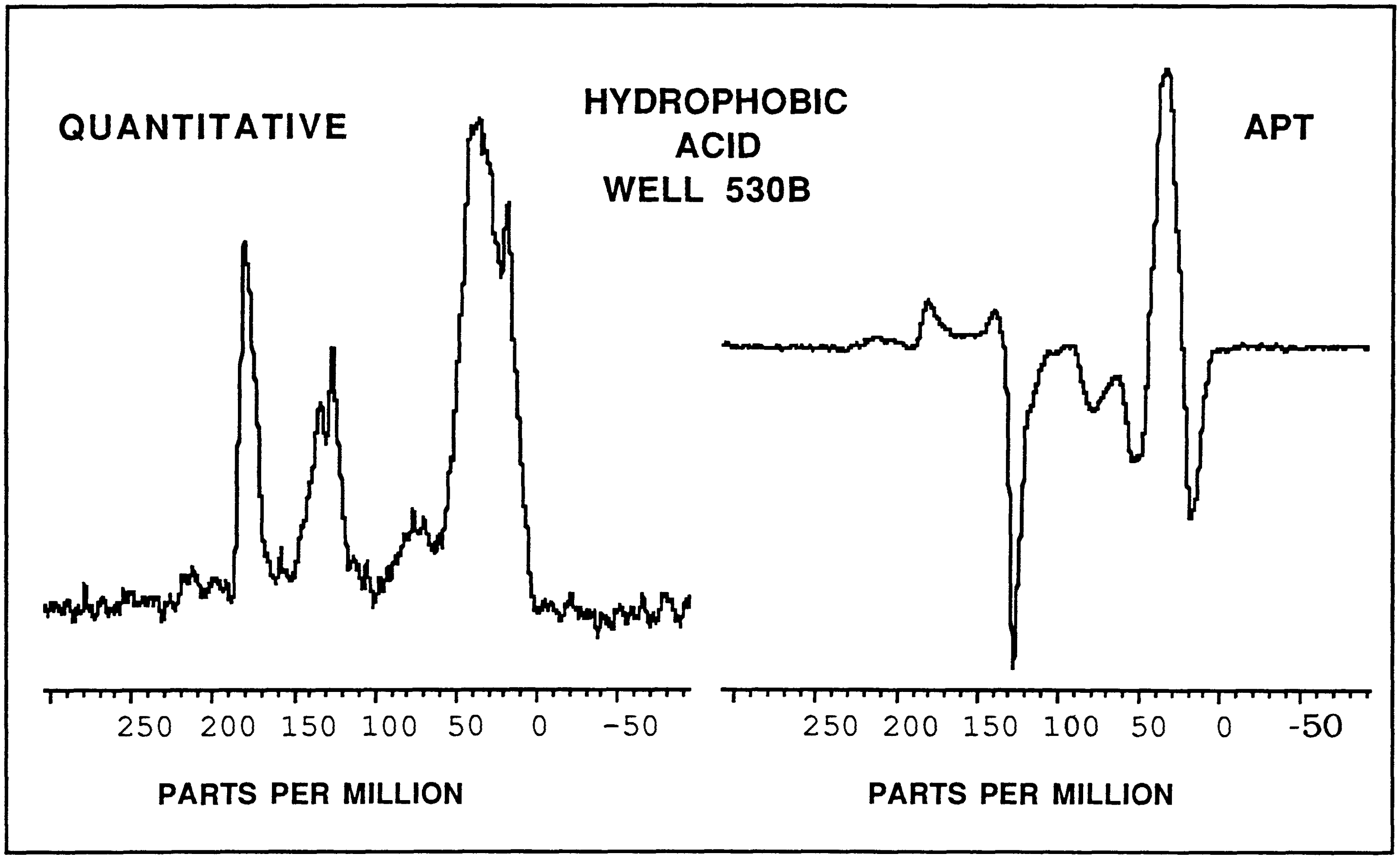

Figure A-18b.—Quantitative and attached proton test carbon-13 nuclear magnetic resonance spectra of well 530B hydrophobic acid.

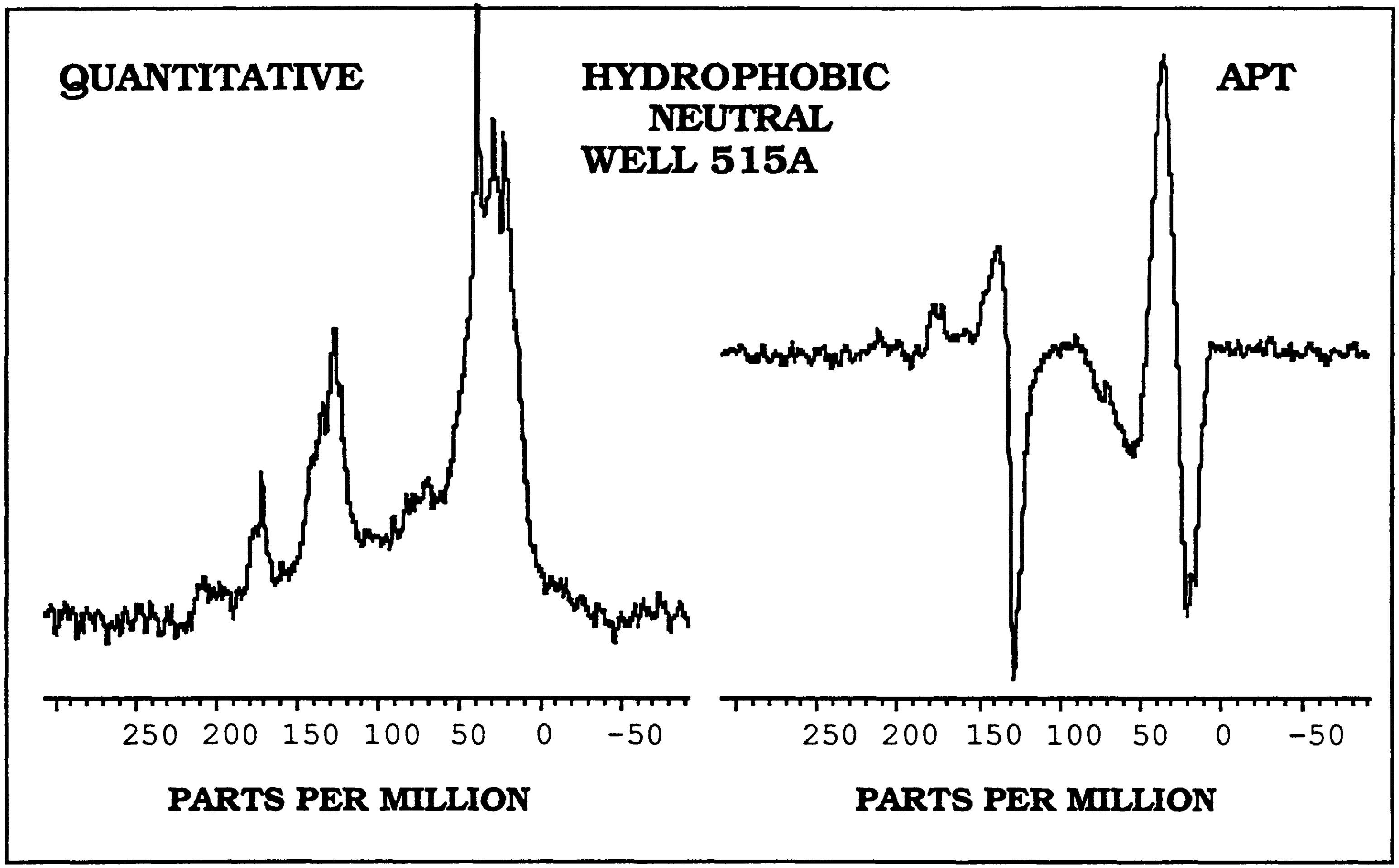

Figure A-18c.—Quantitative and attached proton test carbon-13 nuclear magnetic resonance spectra of well 515 hydrophobic neutral fraction.

Table A-5.—*Peak areas as pecentage of total spectrum area for quantitative carbon-13 nuclear magnetic resonance spectra of hydrophilic acid, hydrophobic acid, and hydrophobic neutral fraction*

[ppm, parts per million]

	Ketone 220-190 ppm	Carboxyl 190-160 ppm	Aromatic 160-90 ppm	Aliphatic II 90-60 ppm	Aliphatic I 60-0 ppm
Hydrophilic (Well 530)	6	19	13	19	43
Hydrophobic (Well 530)	3	15	19	7	55
Hydrophobic Neutral (Well 515)	1	6	27	12	54

carbons are positive, and methyl and methine carbons negative. Spectra also were recorded, but not shown here, using different tau delays to further differentiate methyl from methine carbons, and methylene from quaternary carbons. The assignments made on the APT spectra in figure A-18 are based on three individual experiments. The aliphatic I peaks are resolved into three separate resonances from approximately 0 to 23, 23 to 45, and 45 to 60 ppm, corresponding to methyl, methylene, and methine carbons, respectively. The aliphatic II peaks all are negative, indicating methine carbons, or more precisely, secondary alcohol or secondary ether carbons. The resonances from approximately 90 to 133 ppm are negative, indicating that these aromatic carbons are protonated, whereas the aromatic carbons from approximately 133 to 160 ppm are nonprotonated. The carboxyl and ketone carbons from 160 to 180 ppm and 190 to 220 ppm, respectively, are quaternary carbons, and, therefore, are positive. Because of the conditions under which they were acquired, the APT spectra can only be interpreted semiquantitatively. Nevertheless, it is clear that, in these fractions of organic acids, the amounts of methyl and methine carbons have increased relative to methylene carbons within the aliphatic structures, compared to the original crude oil. The simplest explanation is that the straight-chain aliphatic constitutents of the original crude oil have been selectively degraded away. Thus far, ^{13}C NMR analyses indicate that the HPO acids do not differ from one contaminated well to another; the same conclusion can be made of the HPI and the HPO-N acids.

SUMMARY AND CONCLUSIONS

The HPI, HPO, and HPO-N fractions appear to be the degradation products of the branched chain, cyclic, and aromatic components of the original crude oil. This is consistent with what is understood about the microbial degradation of crude oil. The susceptibility to break down is generally assumed to be, in order: straight-chain aliphatic compounds, branched-chain aliphatic compounds, aromatic and aromatic-heterocyclic compounds, and polycyclic compounds. The enrichment of aromatic components in the HPO and HPO-N fractions also may be explained in part by the fact that at the water table, aromatic compounds preferentially dissolve in the ground water, whereas alkanes of comparable molecular weight partition to the soil gas (Hult, 1987). These observations must be tempered by the fact that the extent, if any, to which the partial degradation products of the original crude oil components may combine with the biochemical constituents from the expired microbial biomass to form new molecules, is not known.

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(p.53 follows)

MOBILIZATION, TRANSPORT, AND FATE OF HYDROCARBON VAPORS IN THE UNSATURATED ZONE

By Marc F. Hult[1]

ABSTRACT

A general conceptual model of the mobilization, transport, and fate of volatile petroleum hydrocarbons in the unsaturated zone is presented on the basis of field data collected at the Bemidji, Minnesota, research site. The primary objective in formulating the model was to provide a practical approach to numerical simulation. The major features of the contaminant plume in the unsaturated zone can be explained by assigning each chemical constituent to one of three groups: (1) light alkanes comprising more than 85 percent of the contaminant mass and, because of their low solubility in water, not readily transported by ground-water flow; (2) aromatic compounds present in minor amounts but which are of major environmental concern even at trace concentrations and are transported in significant amounts both through the unsaturated zone and with ground water; (3) methane that is present as a product of the degradation of petroleum derivatives under anaerobic conditions and is produced in, and transported through, the saturated and unsaturated zones.

All of the compounds are readily oxidized to carbon dioxide and water by microbes. This oxidation causes a change in gas volume that depends on the ratio of carbon to hydrogen in the hydrocarbon being degraded. Consequently, it is necessary to know the concentration of individual compounds in order to quantify the convective transport that results from the volume change. To a significant degree, the transport of reactants and products is driven by pressure and concentration gradients created by microbial activity.

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

(p.55 follows)

DETERMINATION OF THE AIR-PHASE PERMEABILITY TENSOR OF AN UNSATURATED ZONE AT THE BEMIDJI, MINNESOTA, RESEARCH SITE

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

ABSTRACT

A pneumatic test of an uncontaminated part of the unsaturated zone overlying a glacial outwash aquifer was conducted at the research site in Bemidji, Minnesota, to evaluate vertical and horizontal air-phase permeability simultaneously. A Hantush-type, partially penetrating well solution was adapted from well hydraulics to analyze the pressure data collected during withdrawal of air from a test well. A thin but pneumatically significant lens of silt and fine-grained sand was found to be approximately two orders of magnitude less permeable to air than the medium-grained sand beneath it. The medium-grained sand has a ratio of horizontal to vertical permeability of about 2.5 to 1. Low permeabililty lenses could affect the distribution of gases in the contaminated region of the unsaturated zone because of vertical heterogenieties in air-phase diffusion constants. This complicates the field testing of hypotheses concerning biodegradation and transport of vapors by use of mathematical models.

INTRODUCTION

At the Bemidji research site in Minnesota, where crude oil was spilled from a pipeline break, it has been determined that significant amounts of volatile petroleum hydrocarbons are transported through the unsaturated zone as vapors and subsequently dissipate to the atmosphere or biodegrade (Hult and Grabbe, 1986; Hult, 1987). The rates at which these processes occur need to be quantified to understand the time dependence of the subsurface distribution of the contaminants resulting from the crude oil spill.

Mathematical models of vapor movement in the unsaturated zone require estimates of the air-filled porosity, diffusion coefficients, and air-phase permeability. These transport parameters can be determined by laboratory analysis of soil samples. Although the outwash sands, at the site generally are very uniform (Hult, 1984), heterogenieties in the above parameters are anticipated over the scale of the vapor plume (about 150 meters horizontally and 8 meters vertically). Thus, *in situ* determinations that yield values averaged over the volume of soil affected by the field experiment should provide useful information for computing mass fluxes.

The purpose of this paper is to report the results of a pneumatic test of the unsaturated zone conducted at Bemidji in August 1987. This field experiment was designed to evaluate the *in situ* air-filled porosity and air-phase permeability tensor (horizontal and vertical components). The design of the experiment and the analysis of the data collected are based on existing well hydraulics theory. This experiment was the first of a series of experiments that are planned to measure parameters needed for an unsaturated-zone transport model of hydrocarbons at the Bemidji site.

Mathematical models of air movement in unsaturated porous media have been calibrated with air-pressure data in previous investigations to determine *in situ* air permeability. Muskat and Botset (1931) developed a one-dimensional (radial) air-flow model to evaluate the horizontal permeability of gas reservoirs. Boardman and Skrove (1966) injected air into isolated sections of test holes and measured pressure distributions at radial distances to obtain the horizontal permeability of fractured granitic rock. Stallman and Weeks (1969) and Weeks (1977) described the use of depth-dependent air pressure to calculate vertical air permeability in the unsaturated zone. Rosza and others (1975) documented an application of this technique to determine vertical air permeability of debris from nuclear explosions at the Nevada Test Site. None of the investigations cited measured both vertical and horizontal permeability.

In order to provide data for unsaturated zone vapor transport models, it is desirable to assess anisotropy by evaluating the air-phase permeability tensor because both the horizontal and vertical components are required to model vapor advection. In addition, a directionally-dependent

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

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

evaluation of air-phase permeability will improve the determination of *in situ* air-filled porosity and provide insight into the directional dependence of diffusion constants. The methods to evaluate the air-phase permeability tensor reported here also will be used to design air-venting systems for recovering volatile contaminants from the subsurface (Baehr and others, 1989.

AIR-PUMPING TEST DESIGN AT THE BEMIDJI RESEARCH SITE

Figure A-19 is a schematic diagram of the test site instrumentation. The test site is located approximately 100 meters from the contaminated part of the unsaturated zone. Air is withdrawn during the test from a borehole cased and screened in the unsaturated zone. The hole was drilled using a 23-cm (centimeter) diameter hollow-stem auger. Split-spoon samples were collected at approximately 1-meter intervals. The stainless-steel casing had an inside diameter of 10.2 cm and a wall thickness of 0.64 cm. The 60-cm long screened interval (slot width, 0.127 cm), was placed in the middle of the 840-cm thick unsaturated zone. The annulus between the casing and borehole wall was filled with pea gravel adjacent to the screened interval. To prevent air flow between the atmosphere and screen through the annulus, a cement and bentonite grout was pumped into the annulus at a point just above the screened interval up to land surface by use of a tremie line. Pressure probes and thermistors also were installed adjacent to the well screen. Pressure probes were constructed of flexible copper tubing that had a 0.159-cm inside diameter and a 0.159-cm wall thickness. The copper tubing was slotted over a length of 10 cm at the lower end, and the slotted interval was covered by a slotted stainless-steel sheath. The copper tubing extended to land surface and was attached to a ±5 psi (pounds per square inch) pressure transducer. The probes were nested, as illustrated by figure A-19, in holes drilled with a 10-cm diameter auger at radial distances of 100, 300, and 1,000 cm from the center of the withdrawing well. The holes were filled with native, medium-grained sand. Granulated bentonite was used to provide a 10-cm thick low-permeability layer equidistant between nested probes to prevent air flow between probes in the annulus.

Each test consisted of pumping air from the well and measuring the pressure response in the monitor network and the mass flux through the screen. A temperature-compensated flow meter, thermistor, and pressure probe were installed in the piping system to enable the calculation of mass flux using the ideal gas assumption. A digital recording system was used to facilitate the collection of transient data; however, in this paper, only steady-state pressure and mass flux data are presented and analyzed. For the purpose of obtaining steady-state pressure distributions, water manometers were found to be satisfactory.

When designing the system, it was anticipated that a decline in pressure would be observed in the probes nearest the ground surface. However, only probes at and below the screen demonstrated measurable responses to the pumping. This suggested the presence of a low-permeability layer, which had not been detected during the original split-spoon sampling, that separated the well screen from the probes in the upper part of the unsaturated zone. Additional test holes using a continuous sampling technique revealed a layer approximately 20 cm thick consisting of very fine sand and silt approximately 60 cm above the top of the screened interval. This situation is quite analogous to a confined aquifer overlain by a leaky confining unit; thus, the data were analyzed using Hantush-type solutions for partially penetrating wells. The presence of the fine-grained layer, although unexpected, was fortuitous, because direct connection of the entire sand unit to the atmosphere would have precluded the application of the Hantush-type analytical solution. A numerical solution has been developed (Baehr and others, 1989) to analyze more general cases and will be used to measure the air-phase permeability tensor in future pumping tests of the upper unsaturated zone.

ANALYSIS OF STEADY-STATE PRESSURES WITH A HANTUSH-TYPE ANALYTICAL SOLUTION

The basic air flow equation in porous media can be derived from applying the conservation of mass principal and is as follows:

$$\frac{\partial}{\partial t}(\rho\theta) + \nabla\cdot(\rho\underset{\sim}{q}) = 0, \qquad (1)$$

where ρ is the density of air, in grams per cubic centimeter, θ is air filled porosity (dimensionless), and $\underset{\sim}{q}$ is the specific discharge vector for air in centimeters per second.

It is assumed that air flow is Darcian and that, in the induced flow field, the gravity component

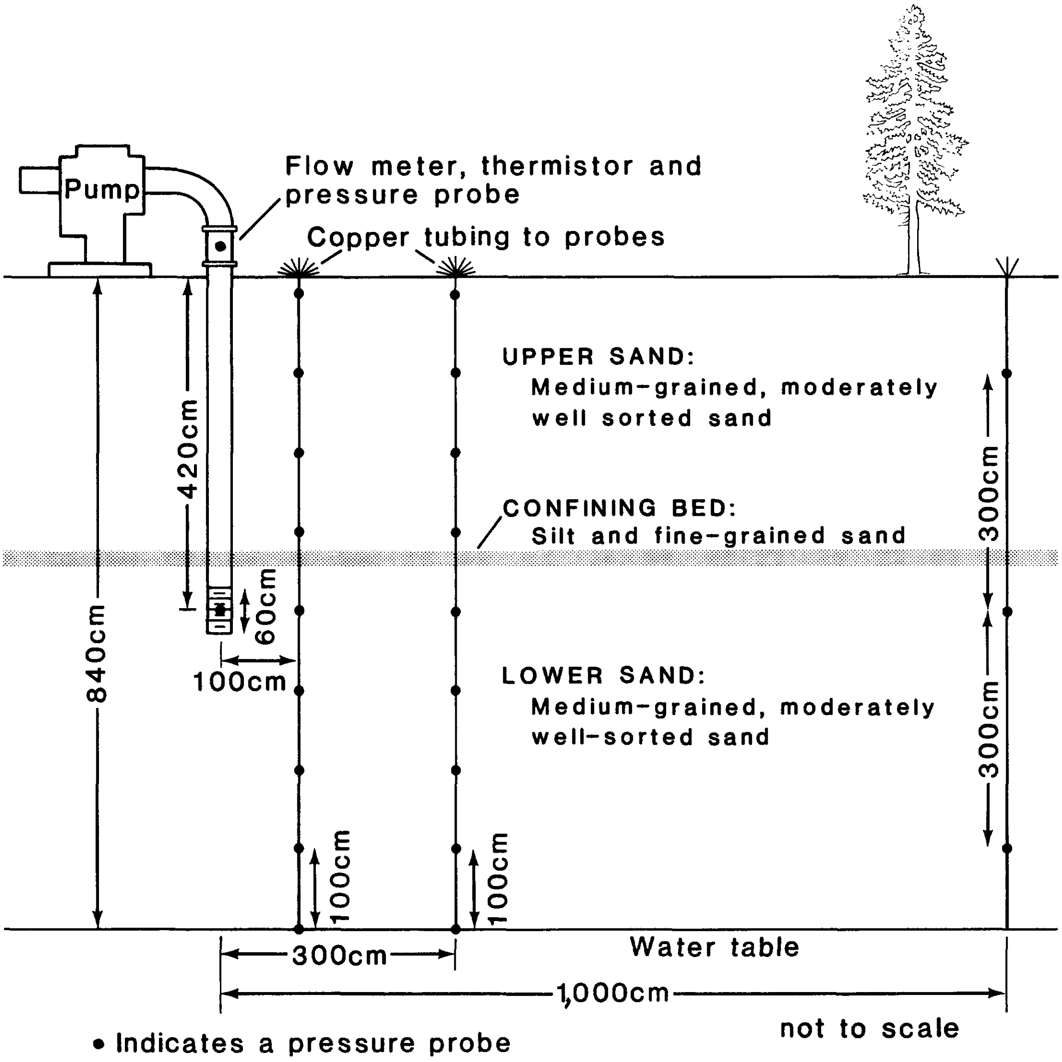


Figure A-19.— Schematic of site instrumentation for conducting pneumatic tests of the unsaturated zone.

of head can be neglected. Under these assumptions for a radially symmetric flow field, $\underset{\sim}{q}$ has the following components

$$q_r = \frac{-k_r}{\mu} \frac{\partial P}{\partial r}, \qquad (2a)$$

$$q_z = \frac{-k_z}{\mu} \frac{\partial P}{\partial z}, \qquad (2b)$$

where r and z are the radial and vertical coordinates respectively, q_r and q_z are the radial (horizontal) and vertical components of specific discharge, in centimeters per second, respectively, k_r and k_z are the radial (horizontal) and vertical components of the air-phase permeability tensor, in square centimeters, respectively, μ is the dynamic viscosity of air, in grams per centimeter per second and P is air pressure, in grams per centimeter per second per second

Pressure is related to density via the ideal gas law:

$$\rho = \frac{\omega P}{RT}, \qquad (3)$$

where ω is the average molecular weight of air, in grams per mole, T is temperature (in degrees Kelvin) and R is the gas constant (8.314×10^7 grams per square centimeter per second per second in mole per degrees Kelvin).

Upon substituting equations (2a), (2b), and (3) into equation (1), employing the change of dependent variable $\phi = P^2$ (Muskat and Botset, 1931) and further assuming that $\frac{\partial k_r}{\partial r}$ and $\frac{\partial k_z}{\partial z} = 0$, one obtains the following equation for a radially symmetric geometry:

$$\frac{\mu\theta}{\sqrt{\phi}} \frac{\partial \phi}{\partial t} - \left(k_r \frac{\partial^2 \phi}{\partial r^2} + k_z \frac{\partial^2 \phi}{\partial z^2} + \frac{1}{r} k_r \frac{\partial \phi}{\partial r}\right) = 0 \qquad (4)$$

Emulating Hantush's leaky aquifer theory (Hantush, 1964) the leakage from the upper unsaturated zone through the confining unit (in the study case the 20 cm fine silt and sand lens) is assumed to be distributed across the aquifer (in this case, the lower unsaturated zone) and is accounted for by adding the term:

$$\frac{-k'}{bb'} \left(\phi - P^2{}_{atm}\right)$$

to the left side of equation (4). In the above expression, k′ and b′ are the permeability and thickness of the confining unit, respectively; b is the thickness of the lower unsaturated zone, and P_{atm} is the prevailing atmospheric pressure.

The mathematical statement of the problem is as follows:

Partial differential equation (PDE), (5a)

$$\frac{\mu\theta}{\sqrt{\phi}} \frac{\partial \phi}{\partial t} = k_r \frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} k_r \frac{\partial \phi}{\partial r} - \frac{k'}{bb'} (\phi - P^2_{atm}) + k_z \frac{\partial^2 \phi}{\partial z^2}$$

Initial condition, (5b)

$$\phi\left(r, z, 0\right) = P^2_{atm},$$

Boundary conditions (5c)

$$\frac{\partial \phi}{\partial z}(r,0,t) = \frac{\partial \phi}{\partial z}(r,b,t) = 0$$

$$\phi(\infty,z,t) = P^2_{atm} \qquad (5d)$$

$$\lim_{r \to 0} \left[\left(l - d\right)\left(r \frac{\partial \phi}{\partial r}\right)\right] = \begin{cases} \dfrac{-Q\mu RT}{\pi k_r \omega} & d<z<l \\ 0 & 0<z<d \\ & l<z<b \end{cases}$$

where *l* and d are the distances from the bottom of the confining unit to the bottom and top of the well screen respectively (fig. A-20) and Q is the mass withdrawal rate, in grams per second, from the well with negative Q implying withdrawal and positive Q implying injection.

Preliminary one-dimensional (radial) simulations indicated that the coefficient of the time derivative in equation (5a) can be approximated by $\frac{\mu\theta}{P_{atm}}$ (a suggestion adapted from gas reservoir engineering). Further, if

$\mu, \theta, k_r, k_z, k', T, \omega$ and Q

are assumed constant, then the problem (5a) (5e) has the following analytical solution (Hantush, 1964):

$$\phi = P^2_{atm} + \left(Q^*/4\pi k_r b\right)\left\{W(u_r, \frac{r}{B_r}) + f\right\} \qquad (6)$$

$$u_r = \frac{r^2}{4V_r t} \qquad V_r = \frac{P_{atm} k_r}{\mu\theta}$$

$$B_r^2 = \frac{bb'k_r}{k'} \qquad Q^* = \left(\frac{2\mu RT}{\omega}\right) Q$$

$$W(u,\beta) = \int_u^\infty \frac{1}{y} e^{(-y-\beta^2/4y)}\, dy$$

and

$$f = \left[\frac{2b}{\pi(l-d)}\right] \sum_{n=1}^{\infty} \left\{\frac{1}{n}\left[\sin\left(\frac{n\pi l}{b}\right) - \sin\left(\frac{n\pi d}{b}\right)\right]\right.$$

$$\cos\left(\frac{n\pi z}{b}\right) W\left(u_r, \sqrt{\left(\frac{n}{B_r}\right)^2 + \frac{k_z}{k_r}\left(\frac{n\pi r}{b}\right)^2}\right)$$

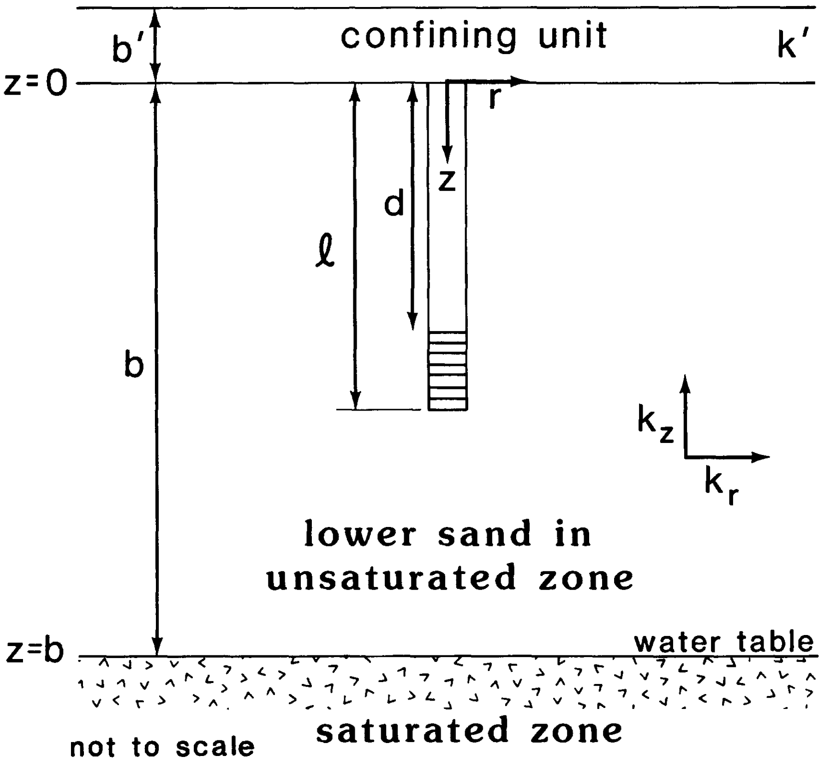


Figure A-20.—Diagram for application of Hantush-type analytical solution for air flow.

The steady-state solution is obtained by making the following substitution:

$$W(u,\beta) = 2\,K_0(\beta) \qquad (7)$$

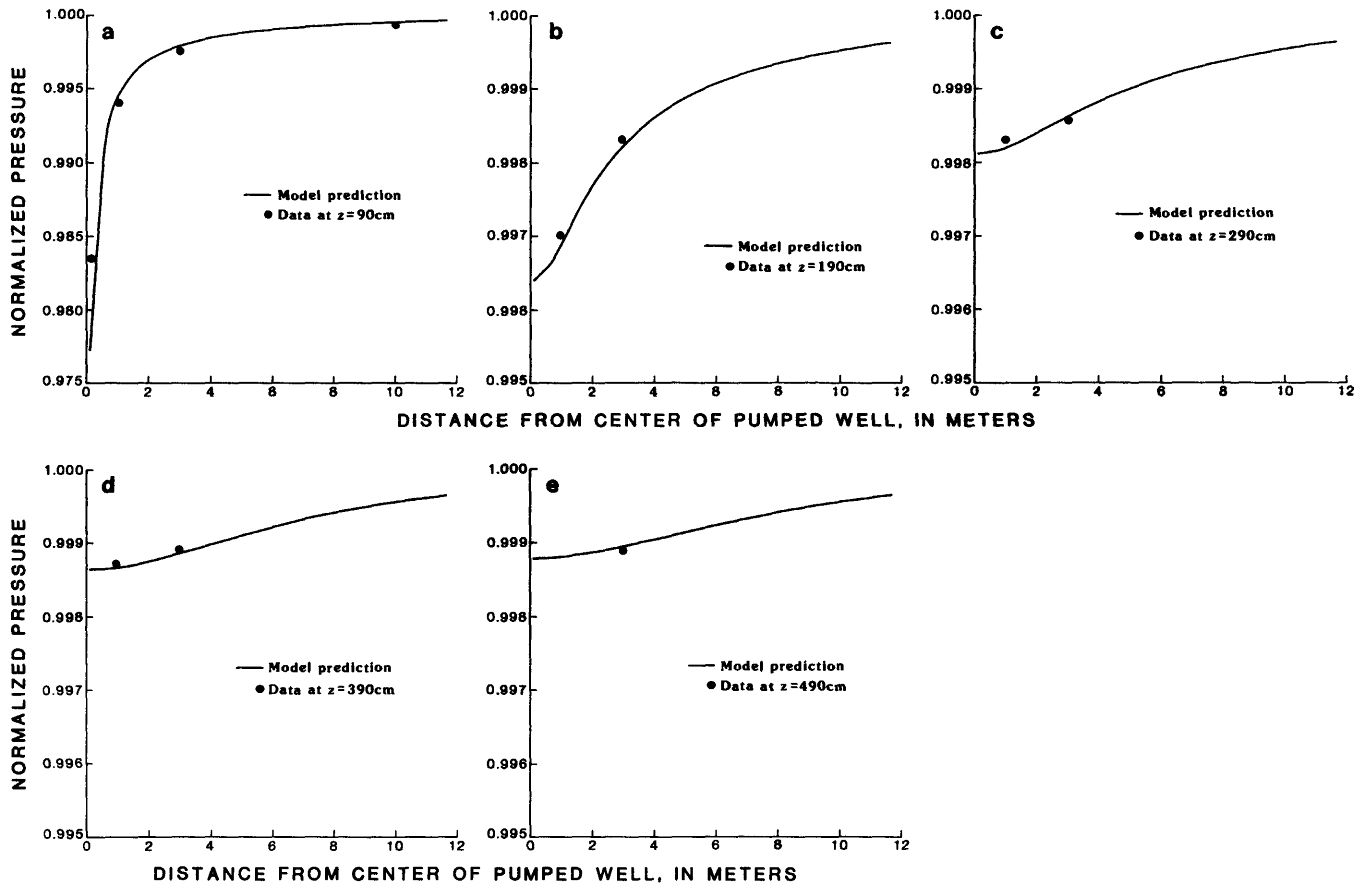
wherever the well function W appears. Here, K_0 is the zero order modified Bessel function of the second kind.

For the purpose of evaluating k_r and k_z only the steady-state solution is required. It is interesting to note, however, that a transient data set can be used to calibrate the solution given by equation (6) to obtain an *in situ* estimate of θ, the air-filled porosity. During the pumping test, however, it was observed that Q varied with time and thus a transient analysis utilizing the analytical solution given by equation (6) was inappropriate. A numerical solution is being developed to analyze our transient data sets for the purpose of obtaining estimates of θ *in situ* in addition to those for k', k_r and k_z.

RESULTS OF A STEADY STATE PNEUMATIC TEST

Table A-6 shows the values of the measured and assumed constants and calculated values of permeability. The results of this steady state pneumatic test are presented on figures A-21a through A-21e. The figures show normalized pressure as a function of radial distance from the center of the well at depths z = 90, 190, 290, 390, 490 cm, respectively. Dots are the observed normalized pressures (P/P_{atm}) and the curves are generated utilizing the steady-state version of the solution given by equation (6) and the best fit values of the air-phase permeabilities. These values were determined to be

$$k' = 4.1 \times 10^{-9}\,\text{cm}^2$$
$$k_r = 3.7 \times 10^{-7}\,\text{cm}^2$$
$$k_z = 1.5 \times 10^{-7}\,\text{cm}^2$$



Figures 21a-21e. — Normalized pressure as a function of radial distance from center of pumped well.

Table A-6.—*Steady state pneumatic test data*

Measured	
Mass withdraw rate (grams per second)	$Q = -9$
Vertical distances (centimeter)	$d = 60$ $l = 120$ $b = 500$ $b' = 20$
Atmospheric pressure (grams per centimeter per second per second)	$P_{atm} = 961609$
Assumed	
Average air molecular weight (grams per mole)	$\omega = 28.8$
Dynamic viscosity (grams per centimeter per second)	$\mu = 1.76 \times 10^{-4}$
Temperature (degrees Kelvin)	$T = 283.0$
Calculated	
Air-phase permeabilities (square centimeters)	$k' = 4.1 \times 10^{-9}$ $kr = 3.7 \times 10^{-7}$ $k_z = 1.5 \times 10^{-7}$

The good fit of the observed pressure suggests that the Hantush-type analytical solution was an appropriate analytical tool.

Of significance, is the two orders of magnitude difference in the vertical permeability between the lower sand zone and confining silt lens. The best fit was obtained for the lower sand zone with an anisotropy of $\frac{k_r}{k_z} \sim 2.5$

SUMMARY AND IMPLICATIONS

A Hantush-type solution for partially penetrating wells was adapted to air-flow in the unsaturated zone. This solution was applied successfully to analyze air-phase pressures obtained during a pneumatic test to obtain the air-phase permeability tensor (vertical and horizontal components) over a 20-meter section of the lower unsaturated zone at the Bemidji research site. Previous investigations using air-flow principles were such that only one component of air-phase permeability could be determined.

The pumping test revealed a thin, but very significant, lens of fine silt and sand with relatively low air permeability. It is reasonable to anticipate that such lenses would affect the distribution of gases in the contaminated region of the unsaturated zone because of vertical heterogenieties in air-phase diffusion constants. Vertical heterogenieties are expected to complicate the testing of hypothesis concerning biodegradation and transport of vapors in the unsaturated zone with mathematical models. The methods employed here to evaluate the air-phase permeability tensor also will be useful in designing air-venting systems for recovering volatile contaminants from the subsurface.

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CHAPTER B—METALS IN THE HEADWATERS OF THE ARKANSAS RIVER, COLORADO

(p. 65 follows)

RESEARCH ON METALS IN ACID MINE DRAINAGE IN THE LEADVILLE, COLORADO, AREA

By Briant A. Kimball[1], Ken E. Bencala[2], and Diane M. McKnight[1]

ABSTRACT

Past mining of ore deposits in the Leadville, Colorado, area has yielded large quantities of valuable metals. Water flowing through abandoned tailings and from adits in this area currently (1988) contributes large quantities of cadmium, copper, iron, lead, manganese, nickel, and zinc to the Arkansas River. Reactive solute-transport processes that occur within the channel are not well quantified. An interdisciplinary study of controls on the transition metal concentrations in streams of the Leadville area is providing an improved understanding of the transport and removal mechanisms that control transition metal concentrations in streams in general. The objectives of the study are to (1) characterize the within-stream chemical processes that control the transport and distribution of transition metals in streams of the Leadville, Colorado, area; (2) characterize the chemistry of sediment and sediment coatings that are active in controlling the dissolved concentrations of trace metals; (3) quantify the time and length scales for chemical and hydrologic processes that affect the metals and the function of chemical equilibrium and kinetics; and (4) quantify the effect of metals on biota and the function of biota in controlling metal concentration. To accomplish these objectives, the project is defining the chemical reactions in the zone where natural conditions change to conditions affected by acid mine drainage. Sediment studies are seeking to determine the concentration, mineralogy, and chemistry of suspended and bed sediment including colloids. Hypotheses about controlling mechanisms will be tested with instream transport experiments.

INTRODUCTION

Many streams in the Rocky Mountains are affected by the inflow of acid water that drains from mines and mine tailings (fig. B–1). Mining of sulfide-ore deposits near Leadville, Colo., has yielded economic quantities of gold (Au), silver (Ag), copper (Cu), lead (Pb), zinc (Zn), iron (Fe), and bismuth (Bi) (Tweto, 1968). Water that flows through abandoned mines and tailings contributes large concentrations of cadmium (Cd), Cu, Fe, manganese (Mn), and Zn to the Arkansas River (Moran and Wentz, 1974; Wentz, 1974). These conditions provide an opportunity to study metal-sediment interactions in a natural setting. The various metals have different behaviors as they move from the acid mine drainages to the neutral pH Arkansas River. Some metal concentrations, notably Mn concentrations, remain large downstream from the primary drainage sources; most other trace metals are removed from solution in the Arkansas River or are transported by colloids and suspended sediment. The metal sources in the Leadville area are well documented (Moran and Wentz, 1974); however, the reactive solute-transport processes that occur in stream channels are not well quantified.

The chemistry of acid mine drainage needs to be studied through an interdisciplinary approach that integrates research on the hydrology, geology, biology, and chemistry of the streams. The Upper Arkansas Surface-Water Toxics Project of the U.S. Geological Survey was begun in 1986 to improve understanding of the reactive mechanisms that affect metal concentrations during transport in mountain streams affected by mine drainage. Investigation of the natural processes in streams is necessary to develop effective treatment of acid mine drainage. The objectives of the Upper Arkansas Surface-Water Toxics Project are to:

1. Characterize the chemical processes that control the transport and distribution of metals in streams in the Leadville, Colo., area.
2. Characterize the chemistry of sediment in contact with dissolved metals.
3. Quantify the time and length scales for chemical and hydrologic processes that affect the metals, and determine the function of chemical equilibrium and kinetics in those processes.

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

4. Quantify the effects of metals on biota and the function of biota in controlling metal concentrations.

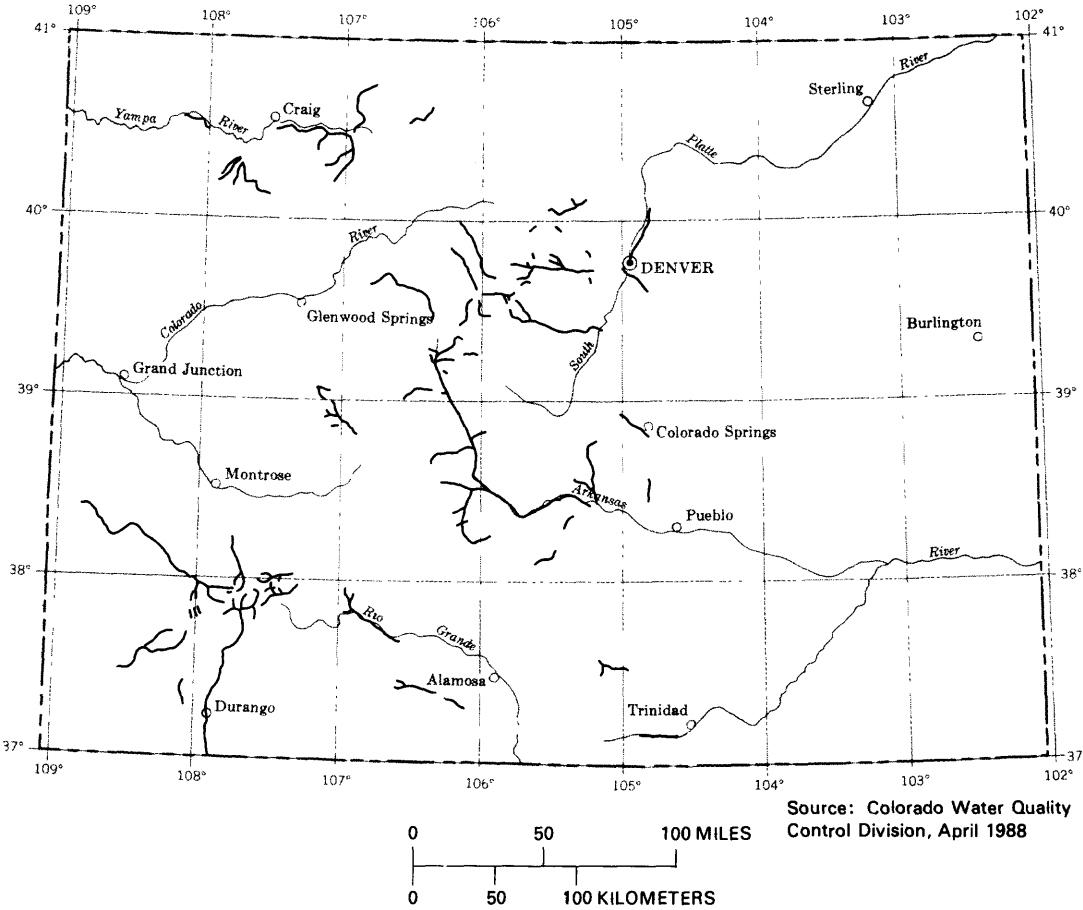
The purpose of this paper is to provide background information about the processes that may affect the transport and fate of metals in acid mine drainage that enters the headwaters of the Arkansas River and to provide an overview of the research currently (1988) being done in this study.

DESCRIPTION OF STUDY AREA

The headwaters of the Arkansas River, which comprise the study area (fig. B–2), drain approximately 590 km^2 (square kilometers). Altitudes range from about 2,700 to 4,200 meters above sea level. Streamflow in the Arkansas River is sustained principally by snowmelt, and flows range from about 3 to 57 m^3/s (cubic meters per second). Streamflow in the Arkansas River approximately triples in the reach of the Arkansas River shown in figure B–2. Ten to forty years of streamflow data are available for two mainstem and two tributary gaging stations. Stream-channel slopes generally are steep to moderate. Bed material consists of cobbles and gravel. Suspended-sediment concentrations are small, generally less than 10 mg/L (milligrams per liter) even during periods of high runoff. Few sediment data are available.

WATER QUALITY

Unaffected streamwater in the area generally is dilute and concentrations of dissolved solids are less than 150 mg/L: however, conditions in



Source: Colorado Water Quality Control Division, April 1988

Figure B-1.—Streams affected by acid mine drainage in Colorado.

areas affected by acid mine drainage are characterized by large concentrations of metals such as Cd, Cu, Fe, Mn, and Zn. Specific conductance generally is less than 100 μS/cm (microsiemens per centimeter) at 25 °C (degrees Celsius) except in mine-affected areas where values may exceed 1,500 μS/cm at 25 °C. Values of pH are slightly basic in most streams but can be less than 3.0 in mine-affected areas. There are three main sources of acid water to streams in the area: the Yak Tunnel, which discharges to California Gulch and then the Arkansas River; the Leadville Drain, which discharges to the East Fork of the Arkansas River; and St. Kevin Gulch, which receives acid water from tailings piles in the drainage basin (fig. B-2). Almost all of the

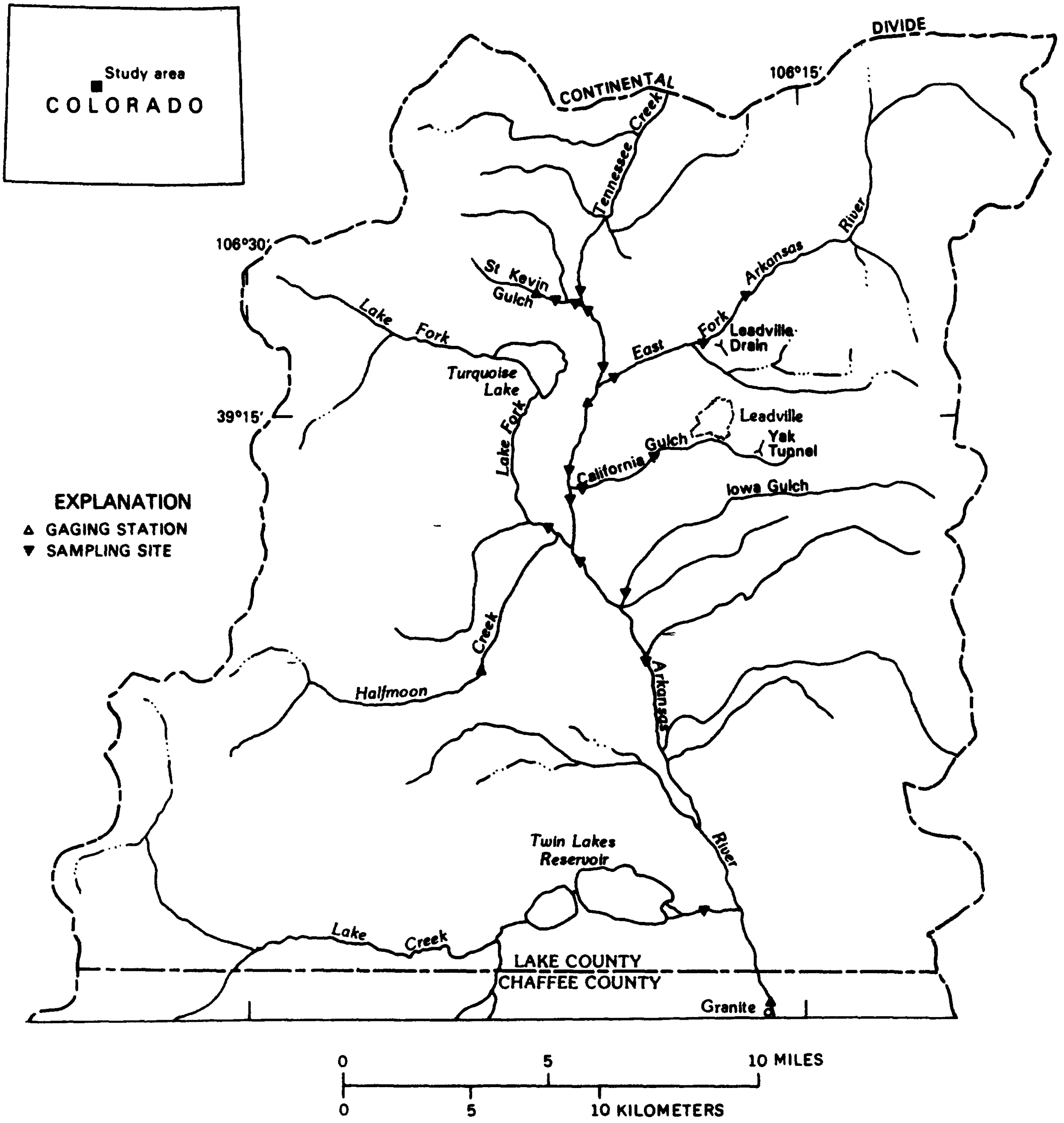


Figure B-2. — Location of study area, gaging stations, and sampling sites.

metals are removed from St. Kevin Gulch in a natural wetland before the stream flows into Tennessee Creek.

DATA COLLECTION

Data-collection sites have been chosen to define the transition from water that is naturally mineralized to water that is affected by acid mine drainage (fig. B–2). Continuous streamflow data are obtained at three gaging stations. At each of the three main inflows of acid mine drainage, and at several of the major confluences, a cluster of three sampling sites provides data about the loading of metals into the Arkansas River (fig. B–2). Data collection at each site includes streamflow measurements and water-quality and sediment samples. In order to document changes with time, the network includes some sites that were previously sampled by Moran and Wentz (1974).

Samples of suspended sediment and bed material are being collected for determinations of suspended-sediment concentration, mineralogy, and particle-size distribution. The small suspended-sediment concentrations have necessitated a technique for dewatering large volumes of streamwater to obtain a sufficient weight of sediment for chemical and mineralogical characterization. X-ray diffraction and scanning electron microscopy will be used to identify mineral and organic phases that might control transition-metal concentrations.

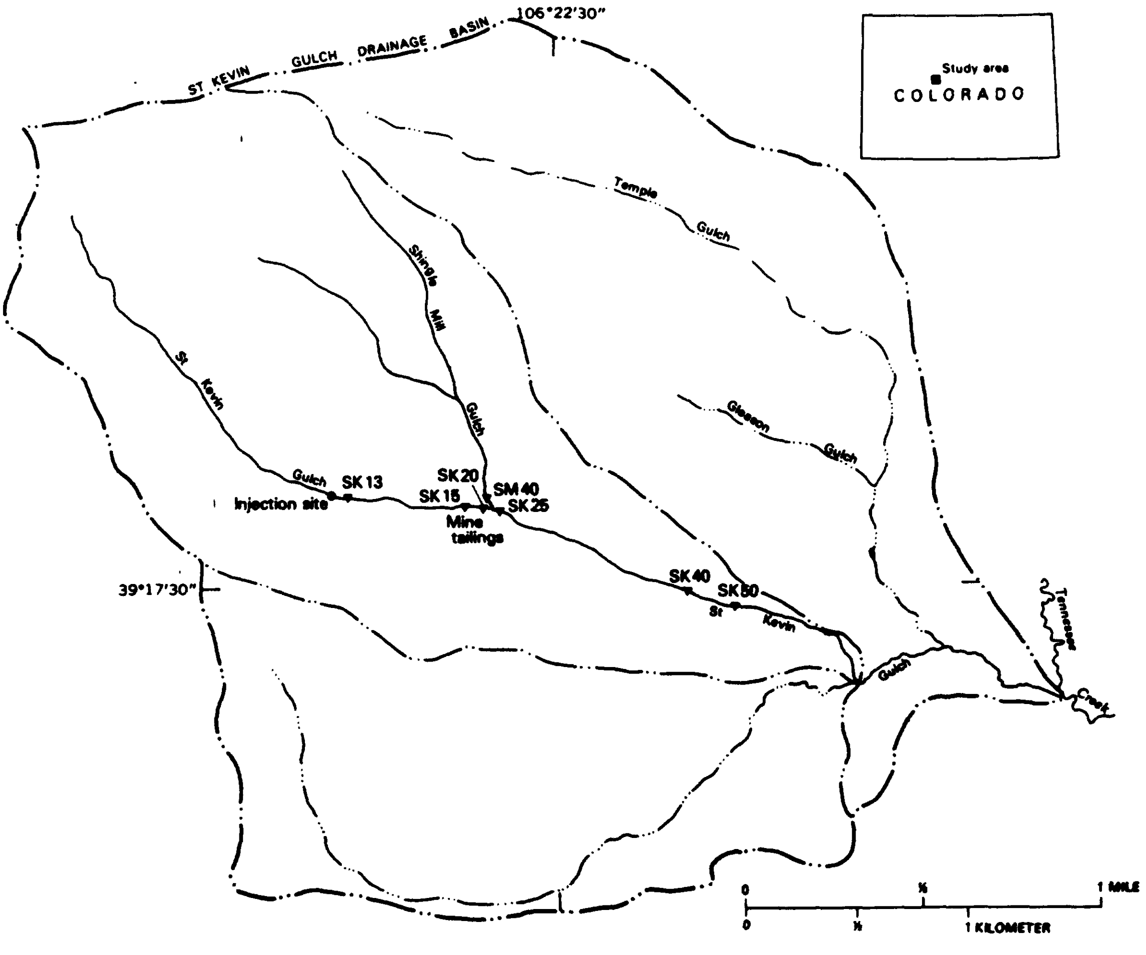
METHODS OF STUDY

The major chemical processes in these streams probably are (1) acid-base reactions, which control pH and, therefore, affect the solubility of transition metals; (2) precipitation/dissolution reactions; and (3) oxidation/reduction reactions, which include photoreduction of iron (McKnight and others, 1984; McKnight and others, 1988). These chemical processes can cause various Fe oxyhydroxides to be formed on stream sediments. Other processes that may affect metal transport occur when these coatings are formed. These processes, which include adsorption on oxide surfaces and ion-exchange reactions, are being studied in detail through onsite experimentation.

In St. Kevin Gulch (fig. B–3), an acid headwater stream, an instream experiment was done in August 1986. Lithium chloride and sodium bromide were injected into the stream as conservative tracers to characterize baseline solute-transport properties such as traveltime, discharge, and dispersion. Diurnal and synoptic sampling was done during this period of known baseline conditions. An open reach of stream was used to study the photoreduction of Fe (McKnight and others, 1988). During daylight hours, ferrous Fe mass flow increased throughout the reach. At night, the pattern reversed and ferric iron increased throughout the reach. During the synoptic sampling, aluminum, Cd, Cu, Mn, and Zn generally were transported conservatively, that is, there was no loss of metal mass during transport. Iron transport was nonconservative, and there was an exponential loss of Fe mass downstream from the tailings inflows (Kimball and others, 1988).

Changes in the mineral form of coatings on bed material and suspended sediment may affect partitioning of metals between water and suspended sediment and the resultant transport rates of metals. Especially important are changes in amorphous Fe phases that occur where acid mine drainage discharges to the Arkansas River and its tributaries. At these confluences, a rapid change in physical and chemical conditions causes changes in the surface chemistry of the sediment. A second instream experiment in St. Kevin Gulch will use reactive and nonreactive solutes to analyze response of the stream system to such transient perturbations in chemistry. Laboratory studies to characterize the amorphous Fe hydroxides in the stream will precede this second instream experiment to develop an appropriate experimental design. Results of this instream experiment will test chemical and hydrologic interactions, particularly with respect to the adsorption of metals on the Fe hydroxide colloids.

During the third year of the project, several areas of research have been included to expand the scope of the original project. The mechanism of Fe photoreduction is being studied in more detail (Kimball and McKnight, 1988; Sigleo and others, 1988). The wetland at the mouth of St. Kevin Gulch (fig. B–3) has been instrumented to study its hydrology and the flux of metals through the wetland (Walton-Day and Briggs, 1989, this Proceedings). The uptake of metals by plants in the area also is being studied. The surface chemistry and mineralogy of colloids in St. Kevin Gulch are being determined, as is the



EXPLANATION

—··— Drainage basin boundary

—··— Intermittent stream

▼SK25 Sample site with identifying number

Figure B-3.—Location of St. Kevin Gulch drainage basin.

function of bacteria and protozoa in the uptake and transport of metals (Fitzpatrick, 1989, this Proceedings; Ranville and others, 1989, this Proceedings; Smith and others, 1989, this Proceedings). The effects of metals from the Leadville area on sediments that accumulate in Pueblo Reservoir, about 160 km (kilometers) downstream from the study area on the Arkansas River, are being studied in cores collected from the reservoir (Callender and others, 1989, this Proceedings). All these studies will provide an improved understanding of the interaction of various components of the stream system.

PLANS FOR FUTURE STUDY

Future work, in addition to the second instream experiment in St. Kevin Gulch, will include monthly synoptic sampling of the Arkansas River and tributaries near Leadville, downstream synoptic sampling of the Arkansas River from Leadville to Pueblo Reservoir (not shown in fig. B-2), additional coring in

Pueblo Reservoir, synoptic sampling of California Gulch (fig. B–2), and studies on the effects of metals on biota. Results of this research will provide information to scientists and water-resource managers about the fate of transition metals in streams.

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INSTREAM CHEMICAL REACTIONS OF ACID MINE WATER ENTERING A NEUTRAL STREAM NEAR LEADVILLE, COLORADO

By Briant A. Kimball[1] and Gregory A. Wetherbee[1]

ABSTRACT

Mixing of acid drainage from mines and mine tailings with neutral-pH streamwater affects the transport of metals in surface waters. In the Leadville, Colorado, area, California Gulch, a stream that contains drainage from many mines, enters the upper Arkansas River and flows into water with a higher pH. The effect of the higher pH on the partitioning of metals between the dissolved phase (less than 0.1-micrometer filtrate) and the suspended-sediment phase (greater than 0.1-micrometer particle size) was studied in two transects downstream from the inflow of California Gulch to the Arkansas River. Iron is totally partitioned to the suspended-sediment phase, whereas manganese remains totally in the dissolved phase. Iron is nonconservative or reactive, and manganese, cadmium, and zinc are conservative. Copper concentrations are near the detection limit, and it is difficult to distinguish between conservative and nonconservative transport because of the small variation in concentration. The quantity of each metal that is partitioned to the suspended-sediment phase can still be transported downstream, because the very small particle size of the suspended-sediment enables it to remain in suspension.

INTRODUCTION

Much work has been devoted to the study of chemical reactions in acid waters (Chapman and others, 1983; Nordstrom and Ball, 1986; Filipek and others, 1987; McKnight and others, 1988). Most acid drainage eventually mixes with streamwater with neutral to alkaline pH. As acid water enters neutral streams, reactions occur that affect the transport of metals, commonly by partitioning the metals among the aqueous phase, colloidal particles, suspended sediment, and bed material.

Transects across the confluence of acid and near-neutral streams previously have been studied by Theobold and others (1963) to identify metals in precipitates removed from streamwater and by Bencala and others (1987) to quantify the percentage of metal removal. This paper gives a preliminary indication of the physical and chemical processes that are most important as acid water enters the Arkansas River, near Leadville, Colo. (fig. B–4). The scope is limited to samples from two transects, downstream from the mouth of California Gulch, where samples were collected during conditions of low flow in the Arkansas River.

METHODS

The first transect (TI) was directly downstream from the mouth of California Gulch (fig. B–5). Samples from this transect are designated as TR11 through TR16, from east to west across the transect. The second transect (T2) was about 50 meters downstream from the first, at site AR20. Samples from this transect are designated as TR21 through TR25. Samples for dissolved metals and anions were filtered in the field using a 0.1-μm (micrometer) membrane filter, and the sample for dissolved-metal analysis was acidified with concentrated nitric acid. Metal determinations were made by inductively coupled argon-plasma spectrophotometry and anion determinations by ion chromatography (Fishman and Friedman, 1985).

An unfiltered sample also was acidified to dissolve colloidal iron phases that were present. There is little or no clay- or silt-size suspended sediment at this site, particularly in August when streams in the upper Arkansas drainage basin contain relatively small concentrations of suspended sediment. Suspended-sediment concentrations at site AR20 (fig. B–4) range from less than the detection limit at the time of the August 1987 sampling (using a 0.45-μm filter for retention of suspended sediment) to 18 mg/L (milligrams per liter) during runoff in May 1987. Despite suspended-sediment concentrations being below detection limits, a plume is visible as water from California Gulch enters the Arkansas River. It is possible that much of the visible suspended material is less than 0.45 μm, the operational breakoff point for suspended sediment.

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

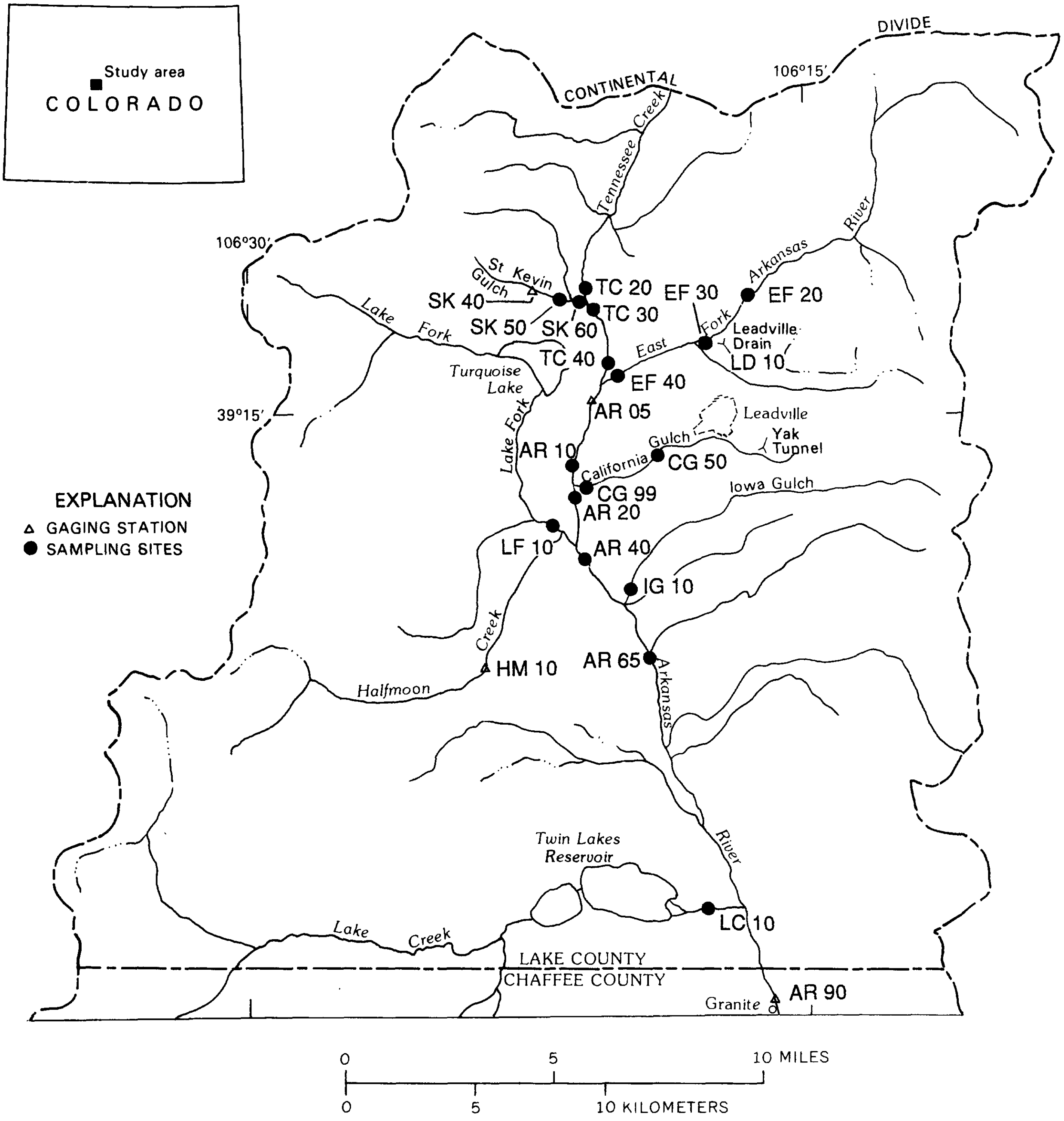

Figure B-4.—Location of sampling transects and location of study area.

The material in the plume from California Gulch is principally colloidal iron hydroxides that would pass through a 0.45-μm filter and not be measured as suspended sediment. With this type of material, a strong nitric-acid treatment should dissolve all the material and allow the determination of its chemical composition. The 0.1-μm filter also may pass part of the colloidal material, so the use of an unfiltered sample and a 0.1-μm filtered sample to define the colloidal chemistry is only an operational scheme. In this paper, metal concentrations in the 0.1-μm filtrate are termed dissolved. Total concentrations are determined from the raw, acidified sample.

RESULTS

Chemical determinations from the samples are listed in table B–1. Each of the transect samples represents an equal-width increment of the

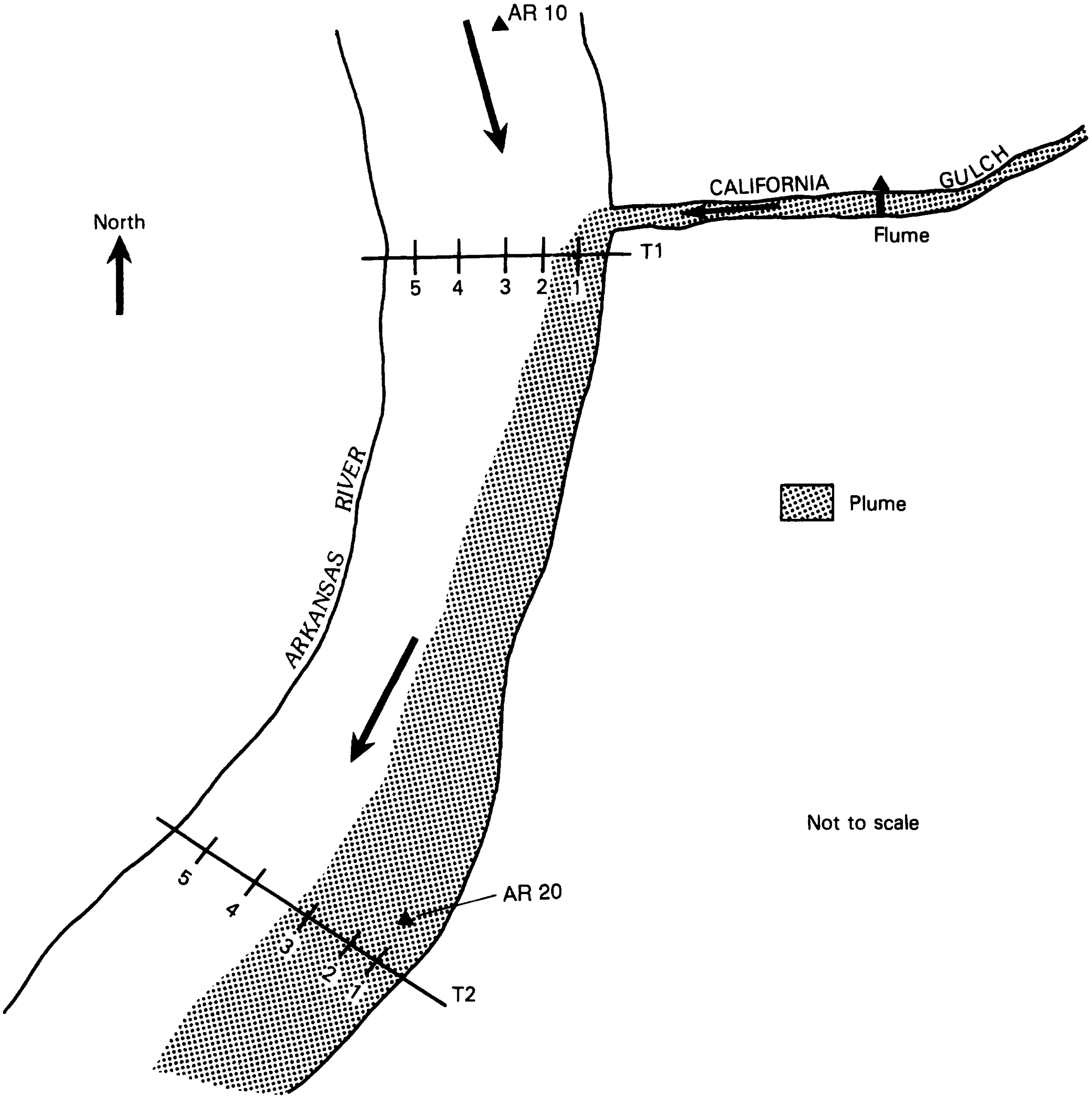

Figure B-5.—Schematic diagram of transects.

stream, not an equal-discharge increment. Without discharge for these increments, only concentrations, in milligrams per liter, rather than mass flow of metals, in milligrams per second, can be discussed. Future sampling of the transects will be done for equal-discharge increments.

At the time of this sampling, pH in California Gulch was 6.96 at site CG99. Some seasonal variation of pH occurs, but this measurement is one of the highest values of pH observed at this site. The plume from California Gulch enters the Arkansas River and immediately mixes with water of about pH 8.0. Dissolved-iron concentrations decrease to less than the detection limit but are larger in the downstream transect. All the metal concentrations decrease across the transects, reflecting the mixing with the Arkansas River water.

Table B-1.—*Chemical determinations of transect samples*

[Site, sampling location in figs. B-4 and B-5; Q, discharge, in cubic feet per second; Ca, calcium; Mg, magnesium; Na, sodium; Cl, chloride; SO4, sulfate; Cd, cadmium; Cu, copper; Fe, iron; Mn, manganese; Zn, zinc; A, 0.1 micrometer; B, unfiltered; <, less than listed value; "--", not determined]

Site	Q	pH	Filter	Ca	Mg	Na	Cl	SO4	Cd	Cu	Fe	Mn	Zn
				Concentration, in milligrams per liter									
AR10	25.6	7.69	A	28.4	10.56	1.95	0.4	31.2	<0.001	0.002	0.028	0.097	0.245
			B	29.0	10.65	2.03	.4	31.2	.003	<.001	.160	.086	.174
CG99	1.5	6.96	A	113.1	72.12	17.22	.9	520.0	.119	.013	.001	21.770	35.590
			B	109.0	70.81	16.20	.9	520.0	.150	.666	19.930	21.130	42.710
TR11	--	7.68	A	53.6	24.26	7.35	4.0	165.0	.028	.003	<.001	6.478	7.439
			B	53.9	24.45	7.20	4.0	165.0	.045	.202	7.139	6.676	11.910
TR12	--	7.69	A	49.9	22.32	6.57	2.2	105.0	.026	.004	.003	5.768	6.505
			B	51.3	22.75	6.69	2.2	105.0	.041	.179	6.150	5.891	10.530
TR13	--	7.74	A	40.7	16.91	4.52	.9	52.8	.012	.004	.007	3.209	3.592
			B	41.2	17.07	4.46	.9	52.8	.021	.098	3.513	3.322	6.028
TR14	--	8.16	A	30.2	11.85	2.46	.9	46.1	.002	<.001	.012	.655	.773
			B	31.6	12.00	2.46	.9	46.1	.004	.015	.754	.695	1.258
TR15	--	8.24	A	28.3	10.84	2.09	.4	32.4	<.001	<.001	.029	.145	.222
			B	29.3	10.93	2.10	.4	32.4	.001	<.001	.168	.111	.207
TR16	--	8.06	A	27.7	10.59	1.95	.4	31.7	.001	<.001	.013	.064	.121
			B	28.9	10.73	1.99	.4	31.7	.002	<.001	.126	.059	.111
TR21	2.6	7.99	A	35.5	14.20	3.46	1.5	69.8	.008	.003	.020	1.794	2.016
			B	35.1	13.94	3.19	1.5	69.8	.010	.050	1.878	1.810	3.295
TR22	4.7	7.99	A	34.3	13.45	3.27	1.4	65.6	.005	.004	.025	1.563	1.648
			B	34.9	13.64	3.34	1.4	65.6	.009	.043	1.602	1.630	2.924
TR23	5.5	8.05	A	32.5	12.83	2.87	1.1	56.5	.005	.004	.022	1.200	1.239
			B	32.6	12.72	2.85	1.1	56.5	.006	.031	1.223	1.224	2.165
TR24	6.5	7.84	A	30.9	12.08	2.65	.9	46.5	.003	.004	.023	.726	.771
			B	31.2	12.04	2.53	.9	46.5	.005	.023	.814	.766	1.359
TR25	6.5	8.09	A	29.7	11.50	2.39	.7	38.8	.001	<.001	.019	.421	.457
			B	30.6	11.53	2.36	.7	38.8	.003	.010	.472	.425	.771
AR20	27.1	8.02	A	31.9	12.00	2.91	.9	60.0	.004	.005	.021	1.160	1.240
			B	33.4	12.00	2.96	.9	60.0	.016	.037	1.240	1.282	2.160
AR40	86.2	8.35	A	18.1	7.04	3.15	1.3	26.1	.002	.002	.064	.211	.135
			B	19.1	7.46	3.24	1.3	26.1	.005	.010	.445	.272	.367
AR65	96.9	8.32	A	25.5	9.82	3.95	1.6	35.9	.003	.003	.039	.200	.156
			B	25.5	9.80	3.86	1.6	35.9	.004	.009	.385	.225	.325

DISCUSSION

The decrease in concentration of metals across both transects is caused principally by dilution. If it is assumed that changes in the concentration of sulfate across the transect are caused by dilution only, then the effect of dilution can be quantified by the relation:

$$X_A = (C_d - C_i)/(C_u - C_i), \qquad (1)$$

where

X_A = the fraction of Arkansas River water in the sample;

C_d = concentration of component downstream from inflow in transect sample, TR11 through TR25;

C_i = concentration of component in inflow, at CG99; and

C_u = concentration of component upstream from inflow, at AR10.

This calculation for sulfate concentrations, after Bencala and others (1987), suggests that the fraction of Arkansas River water across the upstream transect ranges from 0.73 at TR11 to virtually 1.00 at TR15 and TR16 (table B–2). The fraction at the downstream transect ranges from 0.92 at TR21 to 0.98 at TR25.

The reactions of metals in response to the change in pH apparently are very rapid. The variations in dissolved and total metal concentrations are different for the different metals. The extreme patterns are shown for iron (fig. B–6) and manganese (fig. B–7). The concentration of iron in the center of the plume is below the detection limit (sample TR11); virtually all of the iron is part of the size fraction greater than 0.1 μm. A value of less than 0.001 is used in figures B–6, B–7, and B–8 to represent the values below the detection limit.

The concentration pattern of sulfate represents conservative mixing. The concentrations of metals can be compared to the concentration of sulfate to see if they also follow a conservative pattern.

Metals with virtually the same dilution fractions as sulfate are affected by dilution only across the transects. Metals whose dissolved and total concentrations change may participate in chemical reactions that partition metals between aqueous solution and colloids; the metals show reactive, rather than conservative, behavior. The calculations of dilution fractions for cadmium, manganese, and zinc (table B–2) are mostly the same as those for sulfate. Calculations of dilution fractions for copper are limited by the small concentrations of dissolved copper. Iron is the most different with respect to manganese. The dilution fraction for iron suggests that iron is lost from the stream with respect to sulfate. Considering the decrease in iron concentration to below the detection limit in TR11, the dissolved iron most likely is adsorbed onto the surfaces in the presence of colloids with large surface areas and increased pH. Downstream, the colloids are relatively dispersed across the stream, as indicated by the diffusion of the plume and the presence of measurable dissolved iron concentrations.

Conversely, manganese is all in the dissolved phase; the concentration of dissolved manganese exceeds 90 percent of the total manganese concentration across both transects. Downstream from the transects, most manganese continues to be mostly in the dissolved phase, although about 25 percent of the total manganese is adsorbed onto the colloidal phase at AR65.

Cadmium and zinc also seem to be conservative across the transects. In the pH range across the transects (7.7–8.2), both cadmium and zinc are partially partitioned between the dissolved and total concentrations rather than being totally partitioned to one or the other as are iron and manganese (figs. B–8 and B–9). Thus, at the pH of the Arkansas River near California Gulch, these metals will partly be transported by colloids.

Concentrations of copper (fig. B–10) are so close to the detection limit that the small variations detected cannot indicate a conservative or reactive behavior for copper; however, copper virtually is adsorbed onto the colloidal phase.

If the metals are principally transported by colloids, then they can be transported farther and at a higher rate than if they are part of the clay, silt, or sand fractions of river sediment. Thus, the reactive behavior of iron does not necessarily indicate that it will not be transported downstream. Likewise, other metals, if they are reactive downstream, could be transported by colloids. Continued field sampling in this area will try to define the changes that may occur in the transport of these metals downstream; however, the extent of partitioning or adsorption is indicated by initial reactions in the plume of California Gulch.

Table B-2.—*Fraction of Arkansas River water in each transect sample calculated for each dissolved consitituent*

[SO_4, sulfate; Cd, cadmium; Cu, copper; Fe, iron; Mn, manganese; Zn, zinc; —, concentration was below detection limit]

Site	SO_4	Cd	Cu	Fe	Mn	Zn
AR10	1.00	1.00	1.00	1.00	1.00	1.00
CG99	0	0	0	0	0	0
TR11	.73	.77	.91	—	.71	.80
TR12	.85	.79	.82	.07	.74	.82
TR13	.96	.90	.82	.22	.86	.91
TR14	.97	.99	—	.41	.97	.99
TR15	1.00	—	—	1.04	1.00	1.00
TR16	1.00	1.00	—	.44	1.00	1.00
TR21	.92	.94	.91	.70	.92	.95
TR22	.93	.96	.82	.89	.93	.96
TR23	.95	.96	.82	.78	.95	.97
TR24	.97	.98	.82	.81	.97	.99
TR25	.98	1.00	—	.67	.99	.99

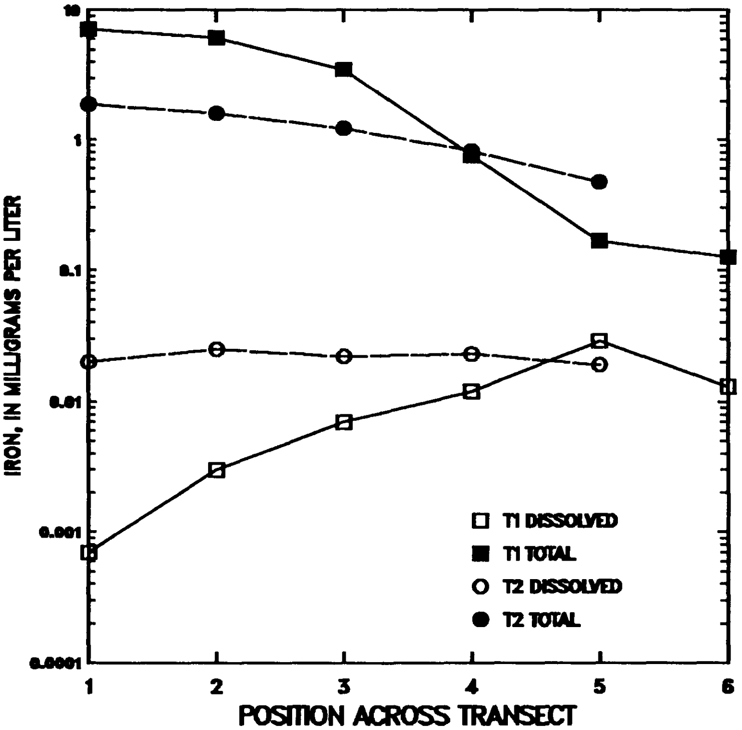

Figure B-6.—Concentrations of dissolved and total iron across the transects.

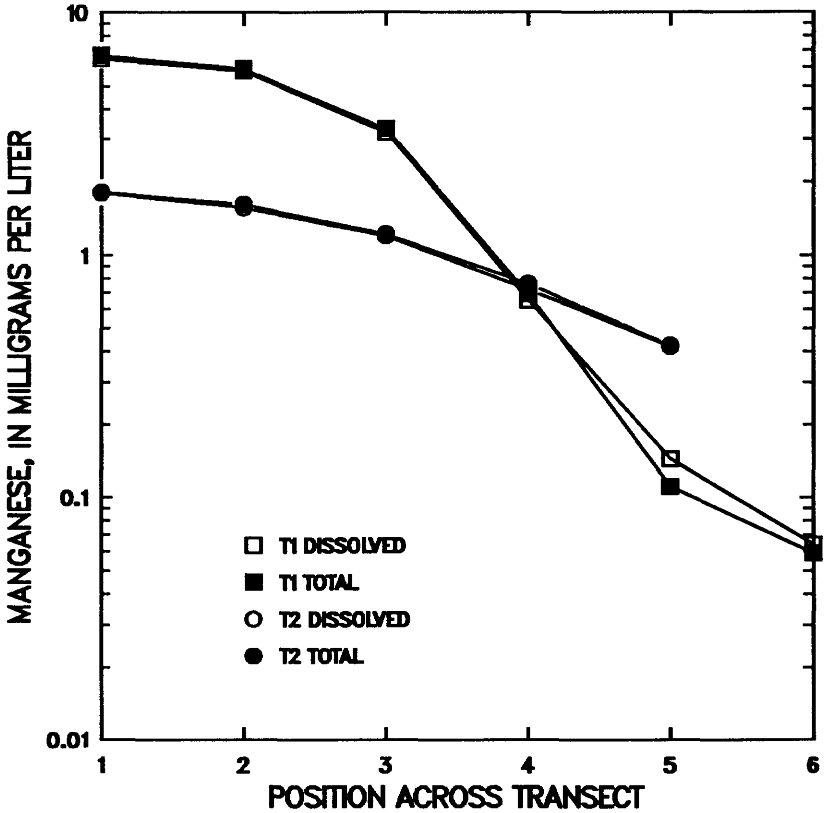

Figure B-7. — Concentrations of dissolved and total manganese across the transects.

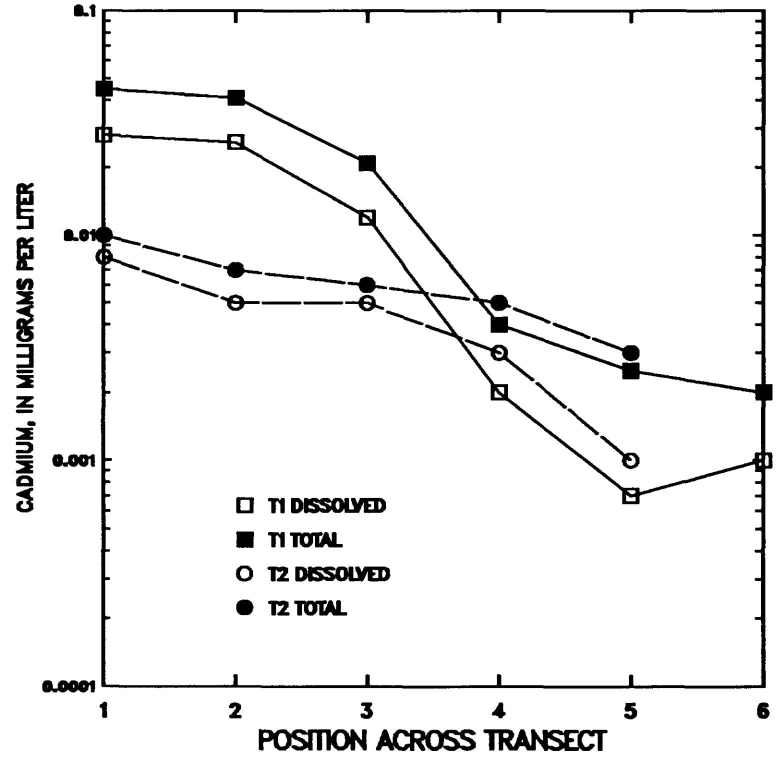

Figure B-8. — Concentrations of dissolved and total cadmium across the transects.

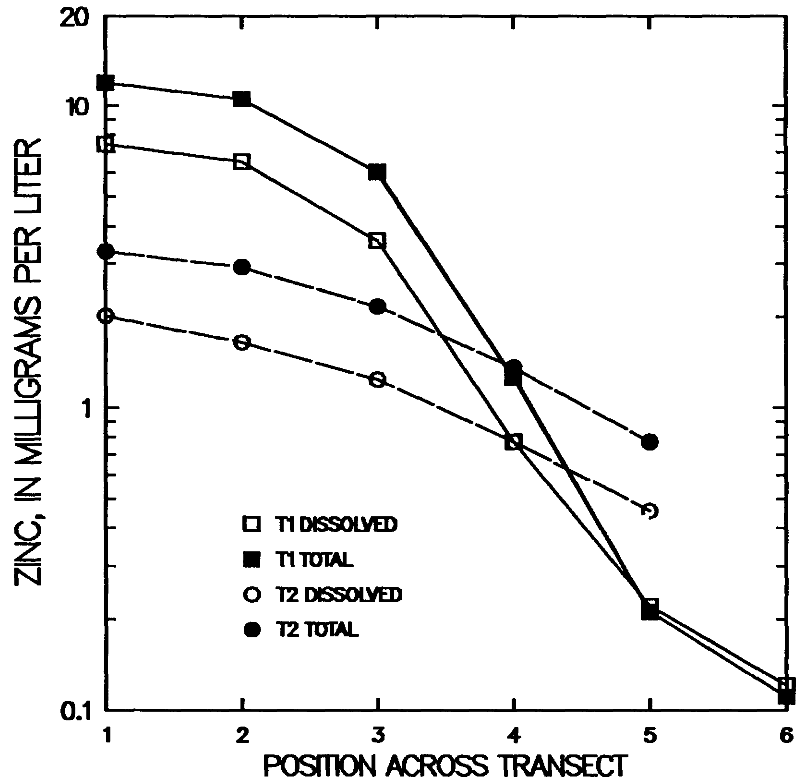

Figure B-9.—Concentrations of dissolved and total zinc across the transects.

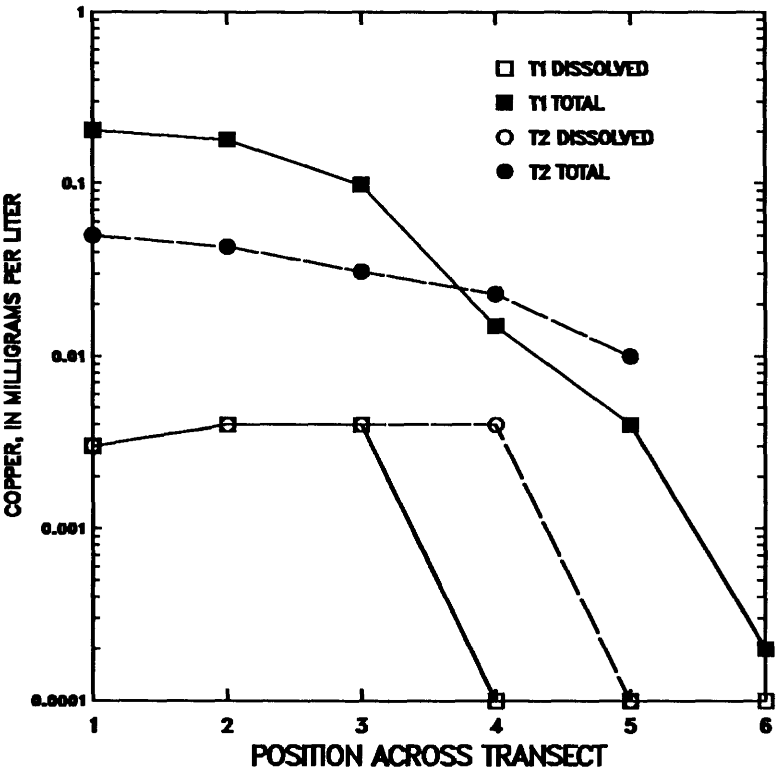

Figure B-10.—Concentrations of dissolved and total copper across the transects.

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(p. 81 follows)

HEAVY-METAL GEOCHEMISTRY OF SEDIMENTS IN THE PUEBLO RESERVOIR, COLORADO

By Edward Callender[1], Walter H. Ficklin[2], Briant A. Kimball[2], and Patrick R. Edelmann[3]

ABSTRACT

Three sediment cores, collected along the axis of Pueblo Reservoir in south-central Colorado, were analyzed for their heavy-metal content. The data were normalized with respect to titanium, an integral component of igneous and sedimentary rocks in the upper Arkansas River basin.

The vertical distribution of normalized heavy-metal data shows some pronounced peaks at depths that record sedimentary riverine inputs during the past 10 years. A core near the river mouth shows normalized copper, zinc, lead, cadmium maxima at depths (14 and 26 centimeters) that correspond to metal discharges from the Leadville mines during 1985 and 1983. The other two cores, located farther from the riverine source, show a pronounced maxima at the 4- to 6-centimeter depth, indicative of contaminant inputs during 1985.

Although the possibility exists that the metal distributions have been affected by sedimentary diagenesis, normalized metal data for riverine suspended sediment and lacustrine bottom sediment suggest that the bottom sediments in Pueblo Reservoir record a history of heavy-metal inputs by acid-mine drainage in the upper Arkansas River basin.

INTRODUCTION

Pueblo Reservoir receives the drainage from the upper Arkansas River basin that extends from Leadville to Pueblo in south-central Colorado (fig. B–11). Water flowing through abandoned mine tailings and from draining adits in the Leadville area contributes large amounts of cadmium (Cd), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), and zinc (Zn) to the upper Arkansas River (Wentz, 1974). Presently (1987–88), an interdisciplinary study of controls on trace-element concentrations in streams of the Leadville area is being conducted. A main objective of this study is to characterize the hydrogeochemical processes that control the transport and distribution of transition metals in streams in the Leadville area.

This paper describes the distribution of these transition metals in sediment cores collected at three sites in the Pueblo Reservoir. Specifically, this paper discusses the effect of heavy-metal (transition metals) inputs to the upper Arkansas River in the Leadville area on a public-supply surface-water reservoir located approximately 190 km (kilometers) downstream; compares the chemistry of Arkansas River suspended sediment with that of Pueblo Reservoir bottom sediment; and examines the distribution of heavy metals down the length of sediment cores.

METHODS

One-meter-long gravity cores were obtained at sites T2B, T5D, and T7B in the reservoir (fig. B–11). Oven-dried (80 °C (degrees Celsius)) sediment samples were digested using a combination of nitric, hydrofluoric, and perchloric acids, and the extracts were analyzed by atomic emission spectrometry-inductively coupled plasma (AES-ICP) (Lichte and others, 1987). The precision of the method, including the dissolution step, is ± 5 to 10 percent relative standard deviation (standard deviation/mean x 100).

Suspended sediment collected from the upper Arkansas River at Portland, Colo. (upstream from the reservoir), was oven-dried at 80 °C and analyzed by direct-current arc emission spectrography and spectrometry (D-C arc spec) (Golightly and others, 1987). The precision of this analytical method is generally ± 15 percent relative standard deviation. Suspended-sediment samples were collected on 1 day in June 1987 and consisted of depth-integrated and point samples.

The analytical detection limits of both techniques (AES-ICP and D-C arc spec) are

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

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

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

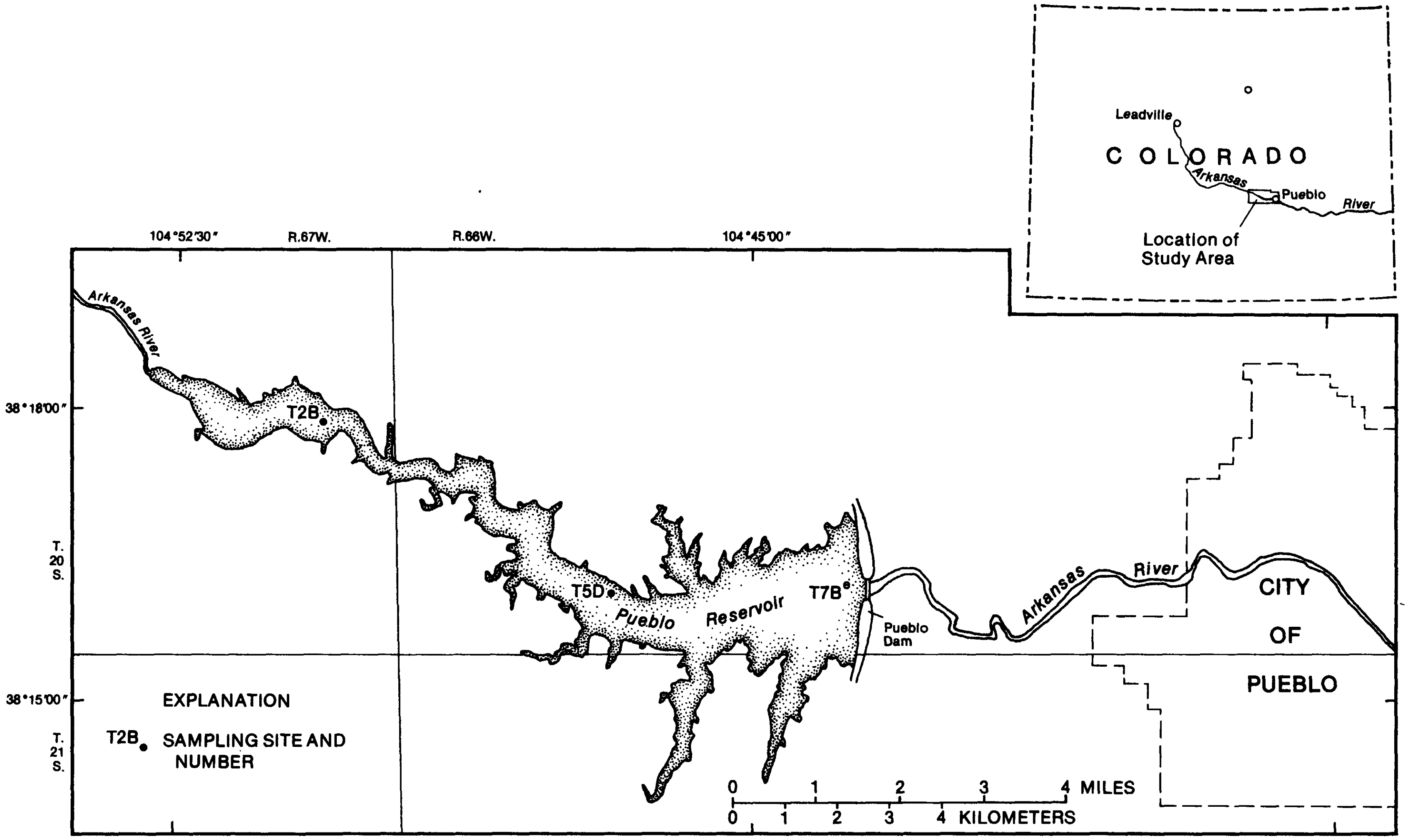

Figure B-11.—Location of Pueblo Reservoir and reservoir sampling sites.

substantially lower (Golightly and others, 1987; Lichte and others, 1987) than the concentrations of Cu, Pb, and Zn in Arkansas River suspended sediment and Pueblo Reservoir bottom sediment.

RESULTS

The total elemental concentration of 1- and 2-cm- (centimeter) long sections of three cores from the Pueblo Reservoir were normalized with respect to titanium (Ti). This element is assumed to be conservative and to have a uniform flux from crustal-rock sources to the reservoir bottom sediments (Horowitz, 1985). In fact, the mean concentrations of Ti in the three cores support this assumption: 3,700 ppm (parts per million) in core T2B from the upper end of the reservoir, 3,535 ppm in core T5D from the middle part of the reservoir, and 3,615 ppm in core T7B from the lower end of the reservoir. The Ti concentration of Arkansas River suspended sediment is 3,590 ppm. The normalized (concentration of metal/concentration of Ti) heavy-metal data are plotted against core depth in figures B-12 through B-18. The data points are joined by lines to show the distributions more clearly.

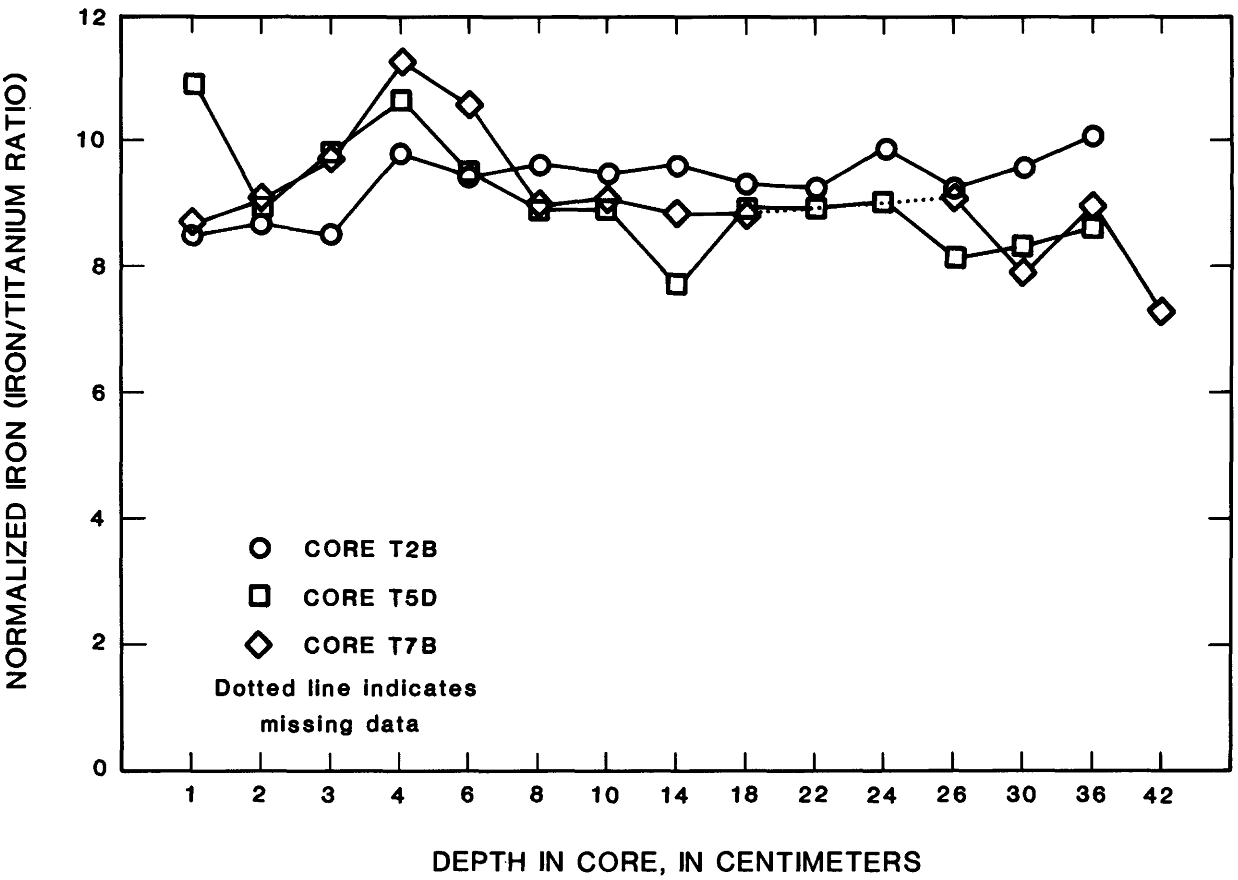

Figure B-12.—Normalized sedmimentary iron distribution in sediment cores.

In figure B–12, the distribution of normalized Fe shows a peak in all three cores at the 4-cm depth. For Mn, the normalized data show a pronounced maxima at 4-cm in cores T5D and T7B (fig. B–13). The absolute concentration of sedimentary Mn is substantially greater in the surficial sections of these cores than in core T2B. With respect to sedimentary Cu, the normalized data show a maxima at depths of 4 to 6 cm.

Below these depths, core T2B exhibits a greater Cu/Ti ratio than do the other two cores (fig. B–14). On the other hand, the normalized sedimentary Ni distribution (fig. B–15) shows maxima at depths of 3 cm in cores T5D and T7B and two maxima in core T5D at depths of 6 and 22 cm.

The normalized sedimentary Zn distribution (fig. B–16) shows distinct maxima at depths of 8, 14, and 26 cm in core T2B; core T5D shows maxima at depths of 4, 24, and 36 cm; core T7B shows maxima at a depth of 4 and possibly at a depth of 24 cm. As was the case for Cu, the Zn content of sediment sections below the 8-cm depth is substantially greater in core T2B than in

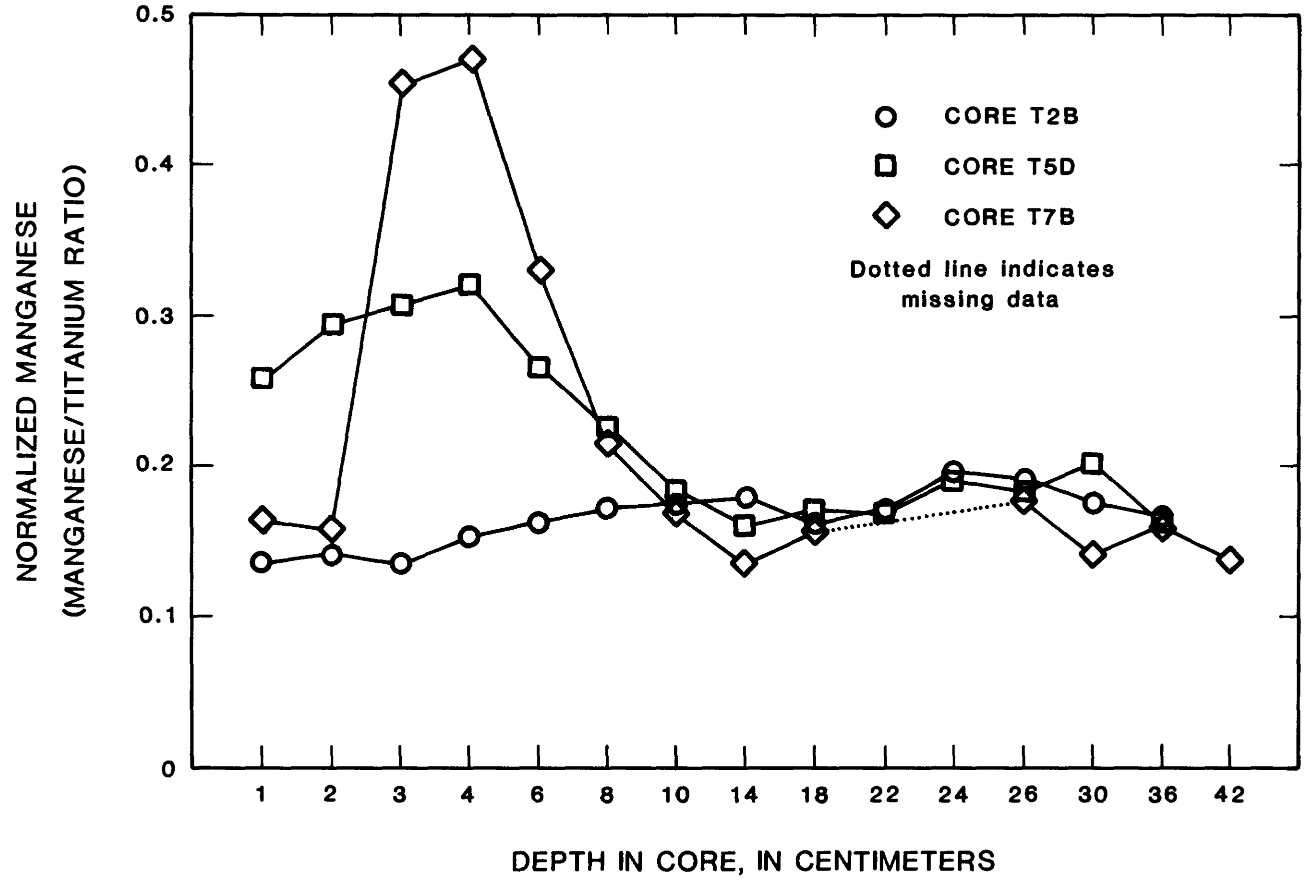

Figure B-13.—Normalized sedimentary manganese distribution in sediment cores.

Table B-3.—*Average normalized heavy-metal ratios for upper Arkansas River suspended sediment and surficial sediments (0-6 centimeters depth) in cores from Pueblo Reservoir*

[Fe/Ti, iron concentration/titanium concentration; Mn/Ti, manganese concentration/titanium concentration; Cu/Ti, copper concentration/titanium concentration; Ni/Ti, nickel concentration/titanium concentration; Zn/Ti, zinc concentration/titanium concentration; Pb/Ti, lead concentration/titanium concentration; Cd/Ti, cadmium concentration/titanium concentration; ND, not dectected]

Normalized heavy metal	Normalized ratios			
	Arkansas River suspended sediment	Core T2B	Core T5D	Core T7B
Fe/Ti	11.1	9.0	10.2	10.1
Mn/Ti	.23	.15	.29	.35
Cu/Ti	.010	.011	.013	.011
Ni/Ti	.006	.010	.019	.008
Zn/Ti	.06	.07	.12	.03
Pb/Ti	.011	.011	.020	.017
Cd/Ti	ND	.0007	.0006	.0004

the other two cores. The distribution of normalized sedimentary Pb (fig. B–17) is similar to that for Zn. The distribution of Pb in cores T5D and T7B shows pronounced maxima at a depth of 4 to 6 cm. The distribution of normalized sedimentary Cd shows distinct maxima at depths of 4 to 6 cm and at a depth of 26 and 36 cm in cores T5D and T7B. Core T2B shows distinct maxima at depths of 6 and 24 cm (fig. B–18).

Table B–3 presents the normalized heavy-metal data for the surficial sediments (0–6 cm depth) in the three reservoir cores and in the suspended sediment in the Arkansas River immediately upstream of the reservoir (fig. B–11). The normalized Fe in suspended sediment appears to be slightly enriched relative to the surficial sediment in core T2B (nearest to the river input) but is similar to the ratios in the other two cores. The suspended Mn is somewhat more concentrated with respect to Ti than surficial sediment in core T2B but is less concentrated than surficial sediment in cores T5D and T7B. Bottom sediments in the middle and lower parts of the reservoir receive suspended-sediment inputs that have fine grain size and contain greater concentrations of organic matter than bottom sediments adjacent to the input of the Arkansas River. Thus, diagenetic remobilization of Mn may be more effective in these sediments, with the result that sedimentary Mn is concentrated at the sediment surface. The normalized Cu, Ni, and Zn are not significantly different in riverine suspended sediment compared to surficial sediment in cores T2B and T7B. The normalized heavy metal data for Cu, Ni, and Zn indicate that the surficial sediments at site T5D are enriched in these metals relative to the other reservoir sites and to the suspended sediment contributed by the Arkansas River (table B–3). Normalized sedimentary Pb data indicate that riverine suspended sediment and the bottom sediments at site T2B contain similar concentrations of this metal, and that the bottom sediments at sites T5D and T7B are enriched by a factor of two relative to sediments contributed by the river. The normalized Cd data (table B–3) show a progressive decrease in Cd in surficial bottom sediments away from the river mouth.

DISCUSSION

As a generality, the normalized ratios of Fe, Mn, Cu, Zn, Pb, and Cd in cores T5D and T7B show a distinct maxima at depths of 4 to 6 cm. In core T2B, Pb and Zn maxima occur at depths of 6 to 10 cm, 14 to 18 cm, and 26 cm. Interstitial-water redox-potential data indicate that surficial sediments are strongly (T2B) to moderately (T7B) oxidizing. Thus, diagenetic remobilization processes may have minimal effect on those metals that are concentrated by iron oxyhydroxides, and the particulate-metal distributions in the sediment cores may reflect the original metal inputs from the river. Visual examination of 13 cores collected at the 3 transects (T2/3, T5, and T7) show that a prereservoir soil horizon occurs at depths that give a calculated sedimentation rate of 5 cm/yr (centimeters per year) for site T2B and a rate from 3 to 4 cm/yr for sites T5D and T7B. With respect to Zn and Pb, the age of the sediment sections that show the pronounced normalized heavy-metal maxima are 2 years and 4 years (or

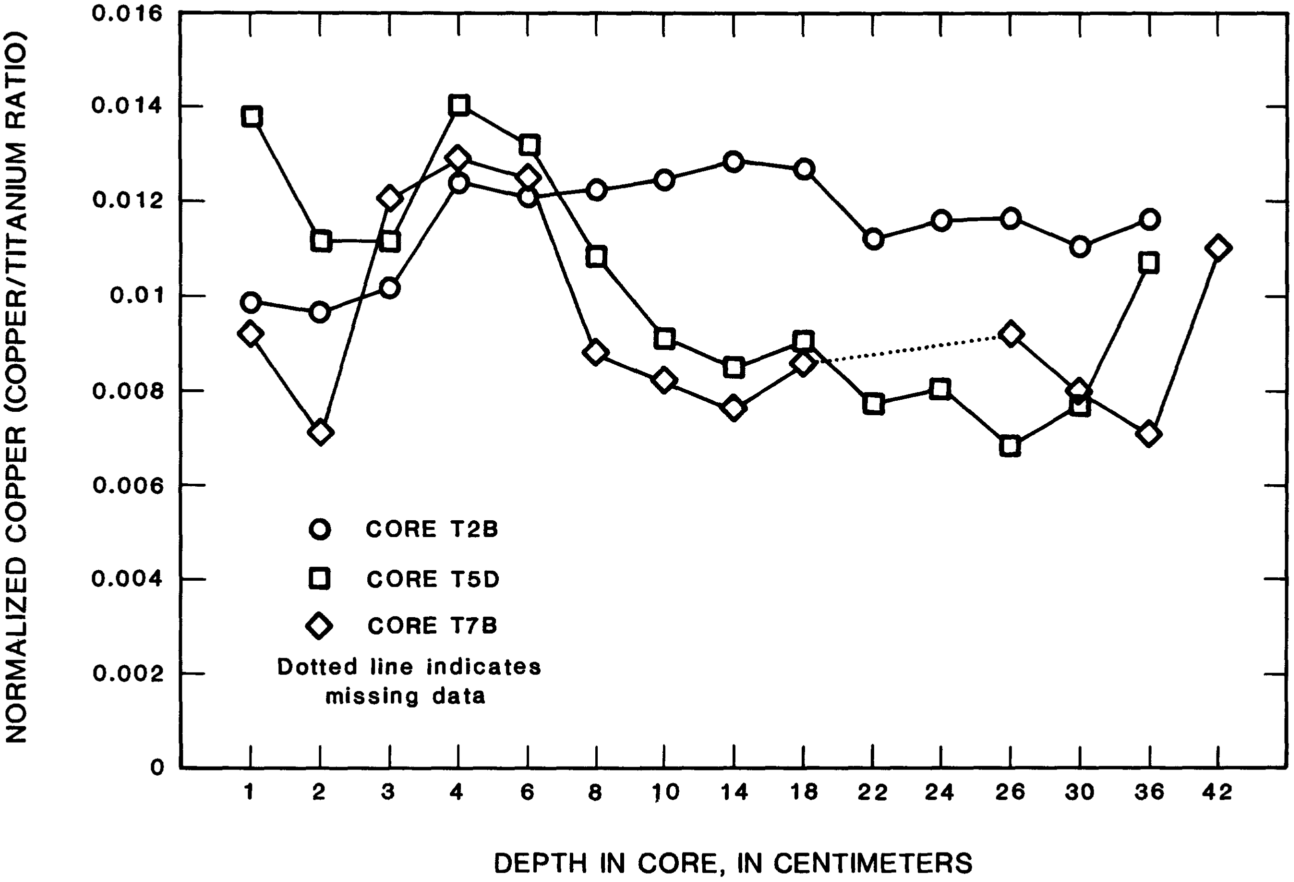

Table B-14.—Normalized sedimentary copper distribution in sediment cores.

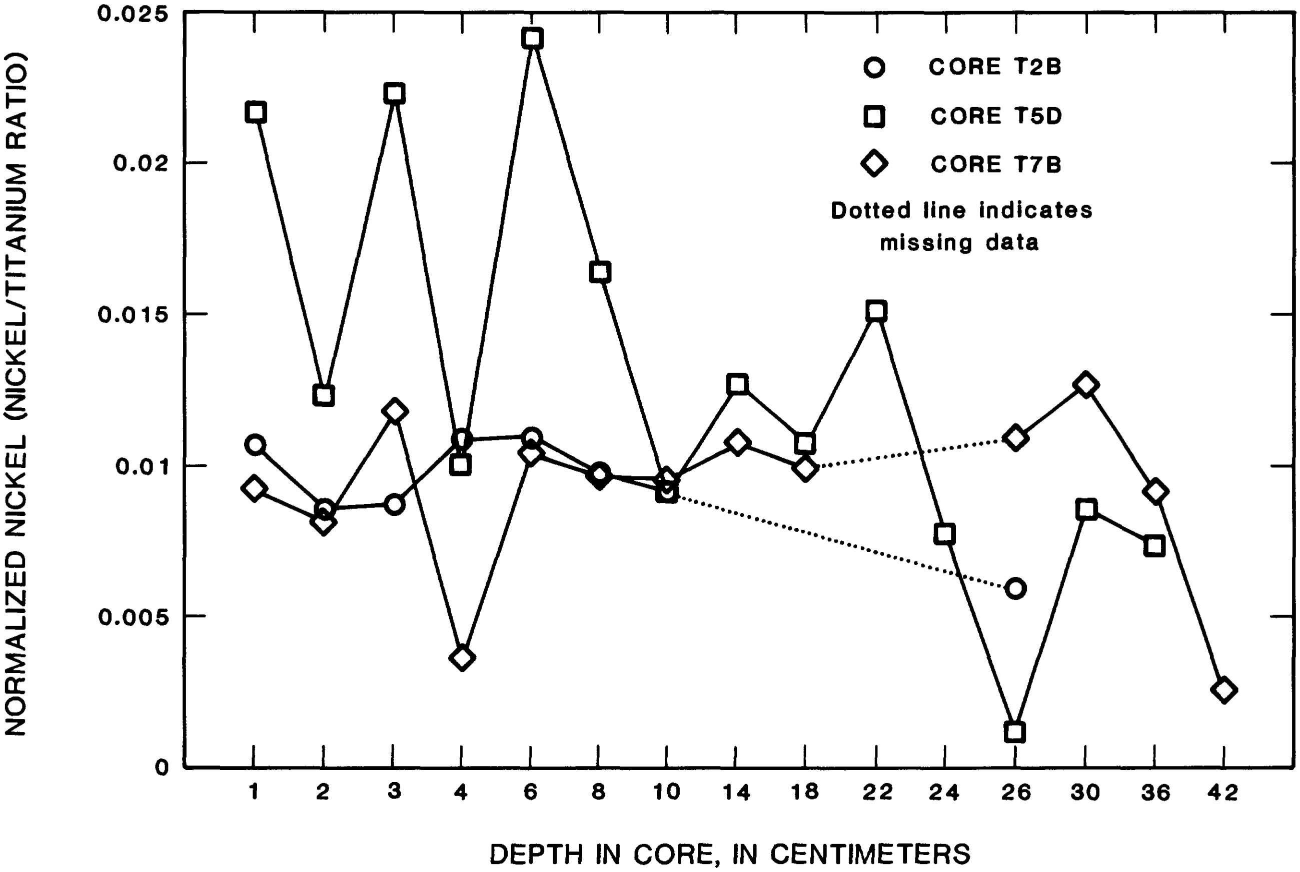

Figure B-15.—Normalized sedimentary nickel distribution in sediment cores.

1985 and 1983) for site T2B (the cores were collected in early October 1987). For sites T5D and T7B, the pronounced maxima for Zn and Pb occur at a depth of 4 to 6 cm, corresponding to a date of 1985. Flooding of mine workings in the Leadville area caused the release ("breakout") of large quantities of heavy metals in October of 1985 and February of 1983 (Engineering Science, 1986).

Considering the normalized sedimentary Zn and Pb distributions in core T2B, the maxima at depths of 14 and 26 cm are interesting. The maxima at the 14-cm depth corresponds to another "breakout" of heavy metals that occurred in the Leadville area in February 1983 (Engineering Science, 1986). The maxima at the 26-cm depth (figs. B–16 and B–17) do not correspond with any reported breakouts of heavy metals from the mining areas near Leadville, Colo. However, the possibility exists that these rapidly accumulating sediments have recorded a previous, undocumented discharge of heavy metals from the Leadville mining area.

Whole-water, total-recoverable-metal data (Fishman and Friedman, 1985) from the upper Arkansas River indicate that, during the spring months when snowmelt runoff is at a peak, the concentrations of particulate Fe, Mn, Cu, and Zn are substantially increased relative to low-flow periods in the winter and summer. The possibility exists that the heavy-metal maxima in the reservoir-sediment cores reflect this increased flux during the snowmelt period. An annual periodicity in the heavy-metal maxima is not apparent in the reservoir-sediment cores (figs. B–13, B–14, B–16, and B–17), except possibly for that of Ni (fig. B–15). Ni is not a major component of the material from the Leadville breakouts and almost all Ni concentrations are below the detection limit in the upper Arkansas River (B.A. Kimball, U.S. Geological Survey, oral commun., 1988). The lack of correlation between Ni and other metals may indicate that the Ni distribution represents a background flux and, perhaps, even an annual variation in runoff inputs. In addition, the heavy-metal data normalized to phosphorus (P) for the suspended sediment in the upper Arkansas River, which feeds the reservoir, shows substantially lower ratios (with respect to P) during springtime than are found in surficial bottom sediment (0- to 10-cm depth), which receives the elevated metal inputs. Like Ti, the total P content of sediment cores does not vary by more than 10 percent and, thus,

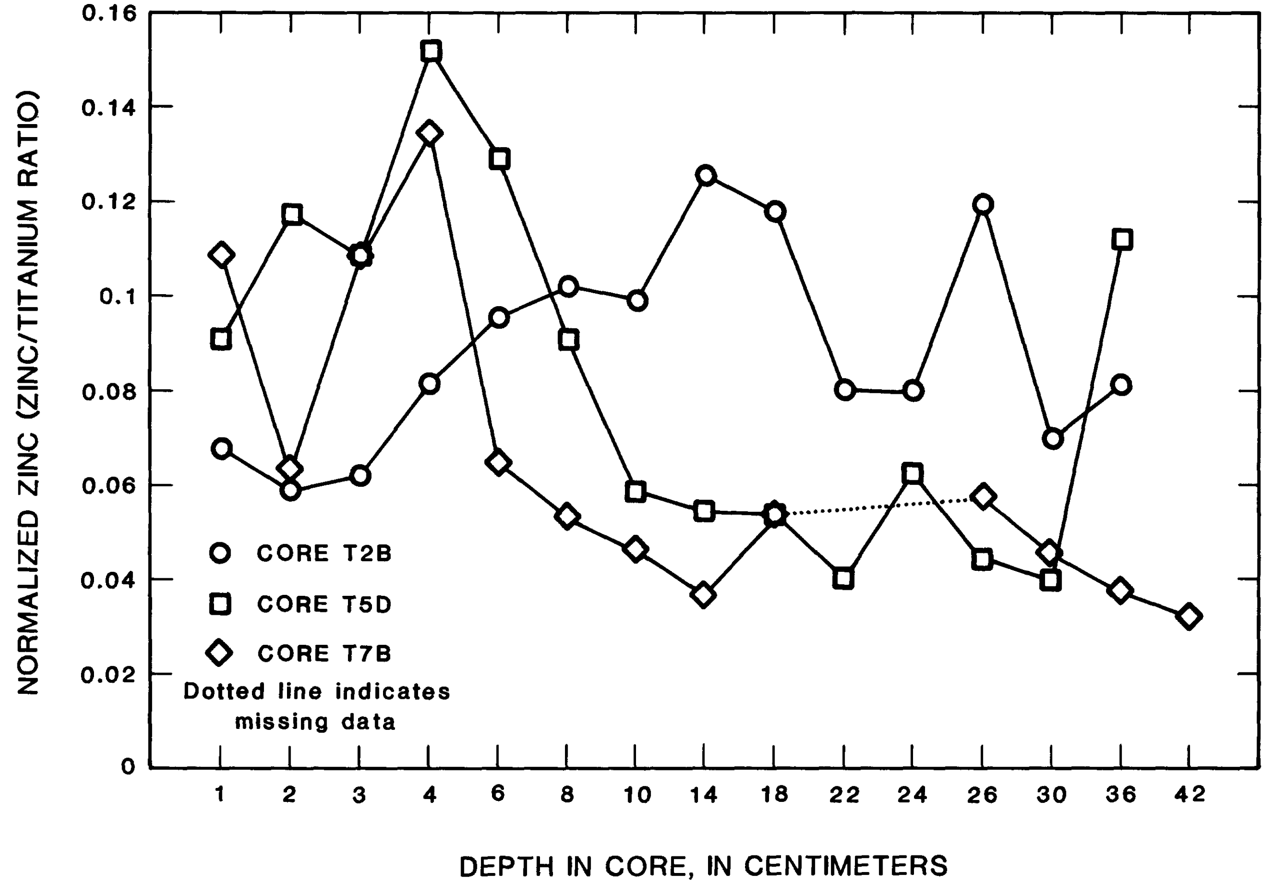

Figure B-16. – Normalized sedimentary zinc distribution in sediment cores.

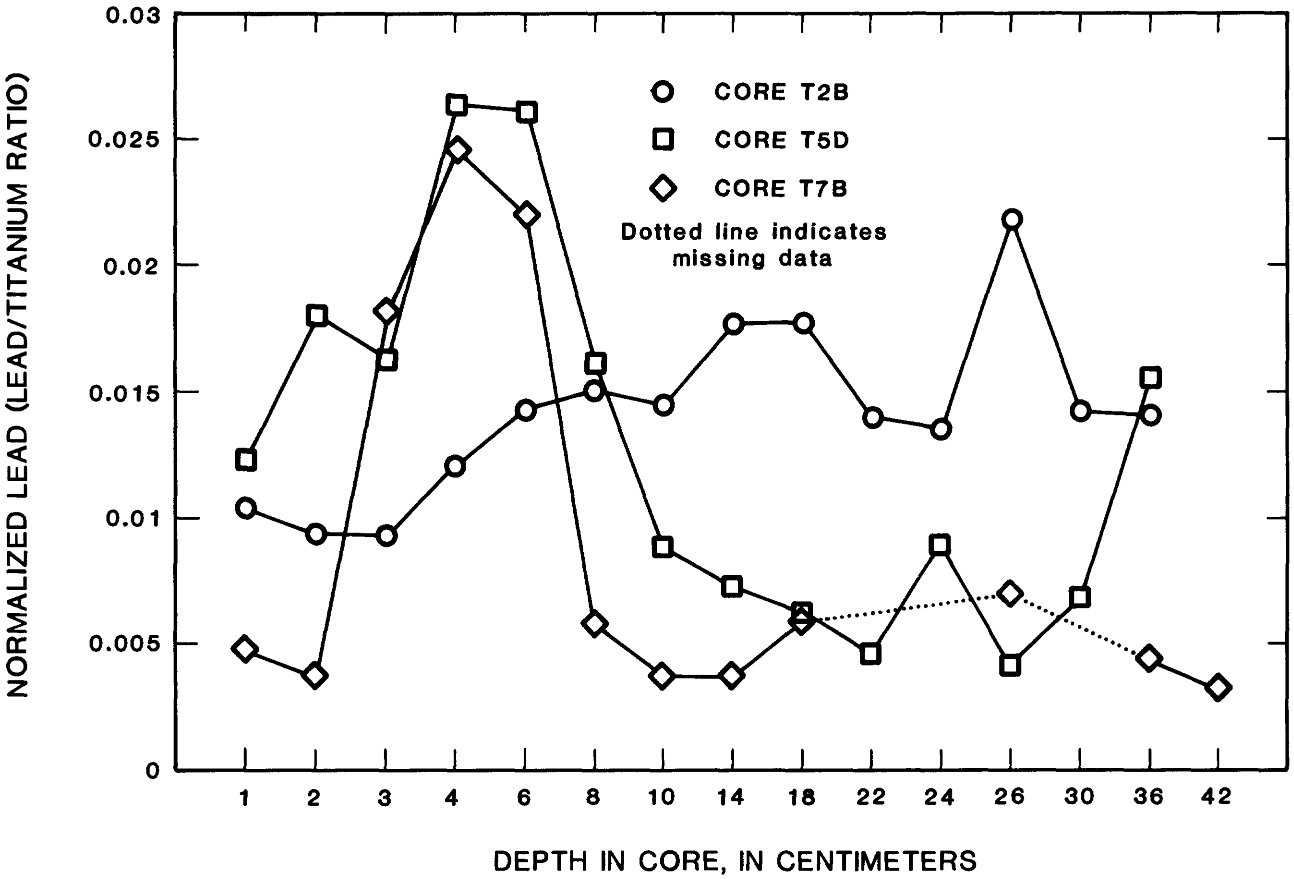

Figure B-17. – Normalized sedimentary lead distribution in sediment cores.

P is another suitable element for metal normalization. Therefore, the hypothesis that Pueblo Reservoir bottom sediments record the history of known heavy-metal releases from abandoned mines in the Leadville, Colo., area is plausible.

It is interesting to speculate as to why the normalized metal maxima are lower in core T2B (closer to the riverine source) than in cores T5D and T7B. The sediments in core T2B consist of coarse silt and fine sand, whereas the other two cores exhibit a silty-clay texture. Generally, there is an inverse relation between grain size and heavy-metal content (Horowitz, 1985). The fine particulate material, which probably contains substantial concentrations of sorbed metals, undoubtedly is transported farther down the reservoir.

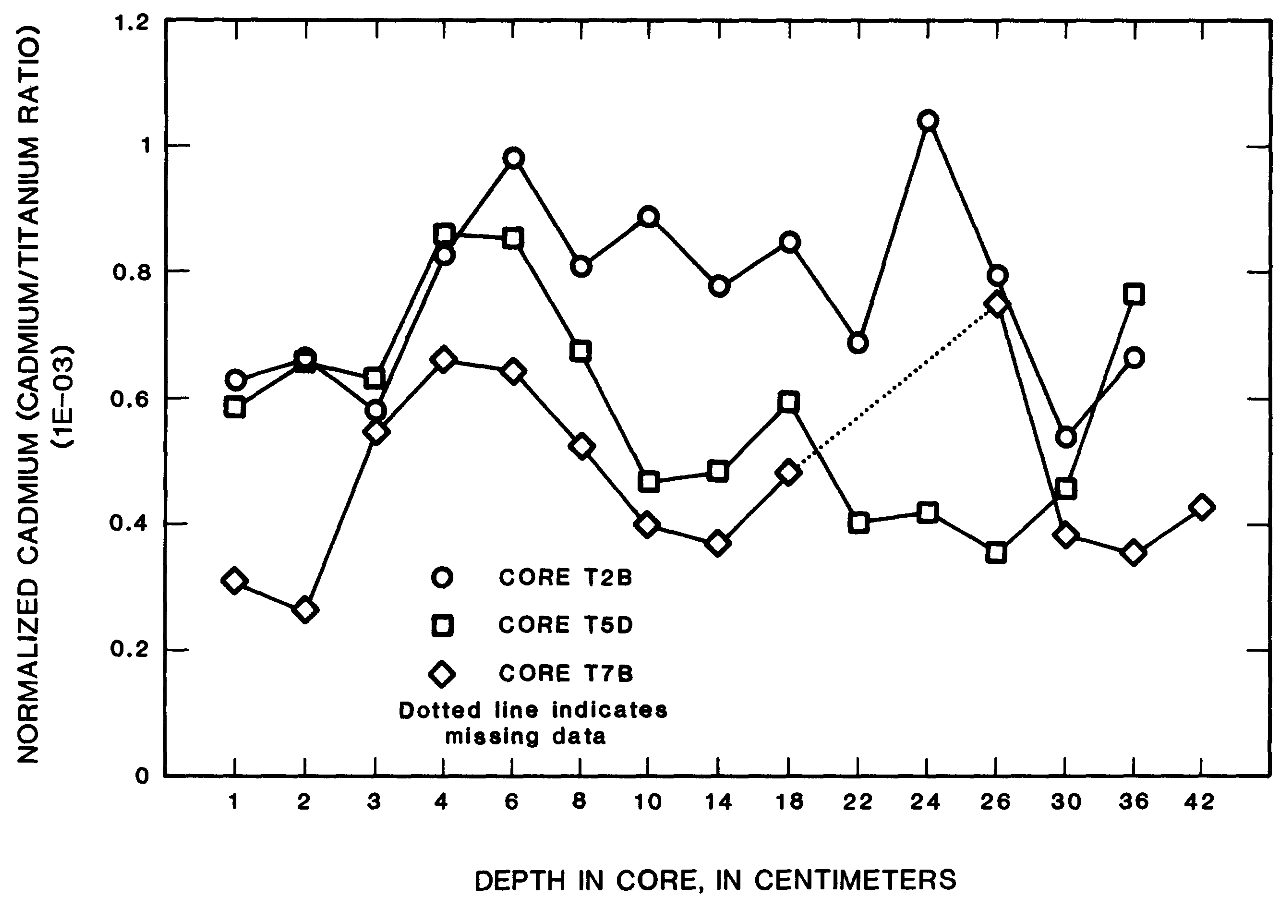

Figure B-18.—Normalized sedimentary cadmium distribution in sediment cores.

CONCLUSIONS

The vertical distribution of normalized heavy-metal concentrations in three sediment cores from the Pueblo Reservoir contain several distinct maxima of Cd, Cu, Pb, and Zn. The location of these maxima in the sediment column and the estimated sedimentation rate indicate that the release of these metals from abandoned mines in the Leadville, Colo., area are recorded in the bottom sediments of the reservoir.

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METAL PARTITIONING AND PHOTOREDUCTION OF IRON IN FILTRATES OF ACID STREAMWATER, ST. KEVIN GULCH, LEADVILLE, COLORADO

By Briant A. Kimball[1] and Diane M. McKnight[1]

ABSTRACT

Onsite experiments in high-altitude acidic mountain streams have indicated that photochemical reactions affect the chemistry of dissolved iron. Previous work defined the rates of daytime photoreduction and nighttime oxidation of iron species in St. Kevin Gulch near Leadville, Colorado, which receives acid mine drainage. This work evaluated the dependence of the photochemical reactions on the presence of stream particulate matter and bacteria in the stream, both of which might catalyze the reaction. The progress of photoreduction with increasing light intensity was monitored by colorimetric determination of ferrous and total iron concentrations in aliquots from an ultrafiltrate (from which bacteria and suspended particulate matter that might catalyze the photoreduction reaction were removed; but smaller organic matter, such as enzymes, may still have been present), from a 0.1-micrometer filtrate and from an unfiltered sample. Concentrations of metals in the different filtrates were evaluated by a chemical-equilibrium model. The initial concentration of ferrous iron in each sample was about 0.2 milligrams per liter; the concentration doubled in the ultrafiltrate, and increased about fourfold in the unfiltered sample. In each sample, the trend of the ferrous- to total-iron ratio was the same, following the trend of light intensity. Although photoreduction proceeded in each sample, it proceeded to a greater extent where additional iron was available.

INTRODUCTION

Many streams in the Rocky Mountains are affected by acidic drainage from mines or mine tailings (Moran and Wentz, 1974). A dominant characteristic of these streams is the presence of iron (Fe) hydroxides, which also can influence the chemistry of other metals by adsorption and coprecipitation reactions. Iron-hydroxide surfaces are present in the form of suspended colloids and as coatings on streambed cobbles and bed sediments. Sorption of other metals by the iron-hydroxide surfaces depends on streamwater pH (Leckie and James, 1974), but pH alone does not account for the variability of iron and other metal concentrations in acidic streams (McKnight and Bencala, in press).

In St. Kevin Gulch, an acidic mountain stream near Leadville, Colo. (fig. B–19), McKnight and others (1988) have studied reactions of dissolved (0.1-μm (micrometer) filterable) ferrous (Fe II) and ferric (Fe III) iron and have shown that iron concentrations vary in response to the diel cycle of light intensity (fig. B–20). All iron concentrations shown in fig. B–20 are 0.1-μm filterable iron. Reactive total iron is that measured by colorimetric determination in which all iron is reduced to Fe (II) by hydroxylamine hydrochloride (Fishman and Friedman, 1985). Ferrous iron (fig. B–20) is measured colorimetrically, without reduction of the sample. ICP iron (fig. B–20) is from a filtered, acidified (concentrated nitric acid) sample. The nitric-acid acidification is more rigorous than the hydroxylamine hydrochloride procedure and appears to dissolve some filterable iron that is not dissolved by hydroxylamine hydrochloride. Sources of Fe (III) include dissolved Fe (III), colloidal Fe (III), and streambed Fe (III). During the first daylight period of a 36-hour experiment (McKnight and others, 1988) the concentrations of reactive iron and Fe (II) increased, which indicates that the source of Fe (III) was suspended colloidal Fe or streambed Fe. During the second daylight period, the concentration of reactive iron did not increase as the concentration of Fe (II) increased; at times it seemed to decrease. The change in concentration of Fe on the second day is consistent with a homogeneous reaction of dissolved Fe (III) rather than a heterogeneous reaction that involves dissolved species and colloidal or surface-bound Fe. The possible reactions can be represented by the following

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

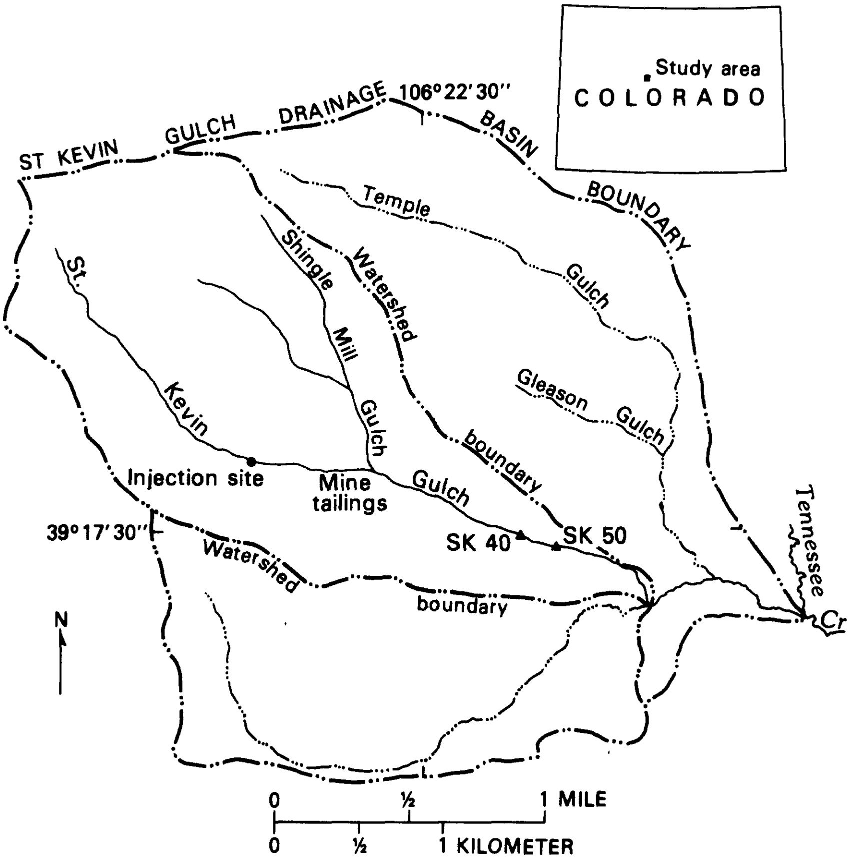

Figure B-19.—Location of St. Kevin Gulch near Leadville, Colorado.

equations (A.C. Sigleo, U.S. Geological Survey, written commun., 1988):

$$\mathrm{FeOH^{2+} + hv \rightarrow Fe^{2+}(II) + {}^{\cdot}OH} \qquad (1)$$

(homogeneous aqueous)

$$\mathrm{Fe(III){:}OH^{-} + hv \rightarrow\ >Fe(II) + {}^{\cdot}OH} \qquad (2a)$$

(heterogeneous surface)

$$\mathrm{>Fe(II) \rightarrow Fe^{2+}} \qquad (2b)$$

where $^{\cdot}$OH = a hydroxide radical, hv = photons of light (250 - 425 nm), and Fe(II) = a surface-bound species.

The first reaction only involves aqueous species whereas the second consists of two steps that involve surface-bound and aqueous species. After the surface-bound Fe (III) is reduced, Fe (II) is released to the stream. The first solution-phase reaction has a greater yield of Fe (II) for a given radiation dose (referred to as quantum yield) than the second heterogeneous reaction. However, because hydrous iron oxides are very abundant in the stream, it is possible that the heterogeneous reaction is the major source of the diurnal increase in Fe (II). This question of the dominance of the homogeneous or the heterogeneous reactions is addressed in the field experiments reported here. This study also addresses the question of whether or not the reaction is exclusively abiotic or bacterially mediated.

METHODS

A streamwater sample was collected from St. Kevin Gulch on July 5, 1987, before dawn and divided for three separate treatments. The first treatment was filtration through a 100,000 molecular-weight filter (approximately 0.01-μm pore size). The second treatment was filtration through a 0.1-μm filter. The filter template for the 0.1-μm filter was frozen closed at 0515 hours; measurements of photoreduction for this treatment were not possible until later in the morning. The third treatment was no filtration, which provided a raw sample. Photoreduction of Fe was followed during a 9-hour period in the morning by

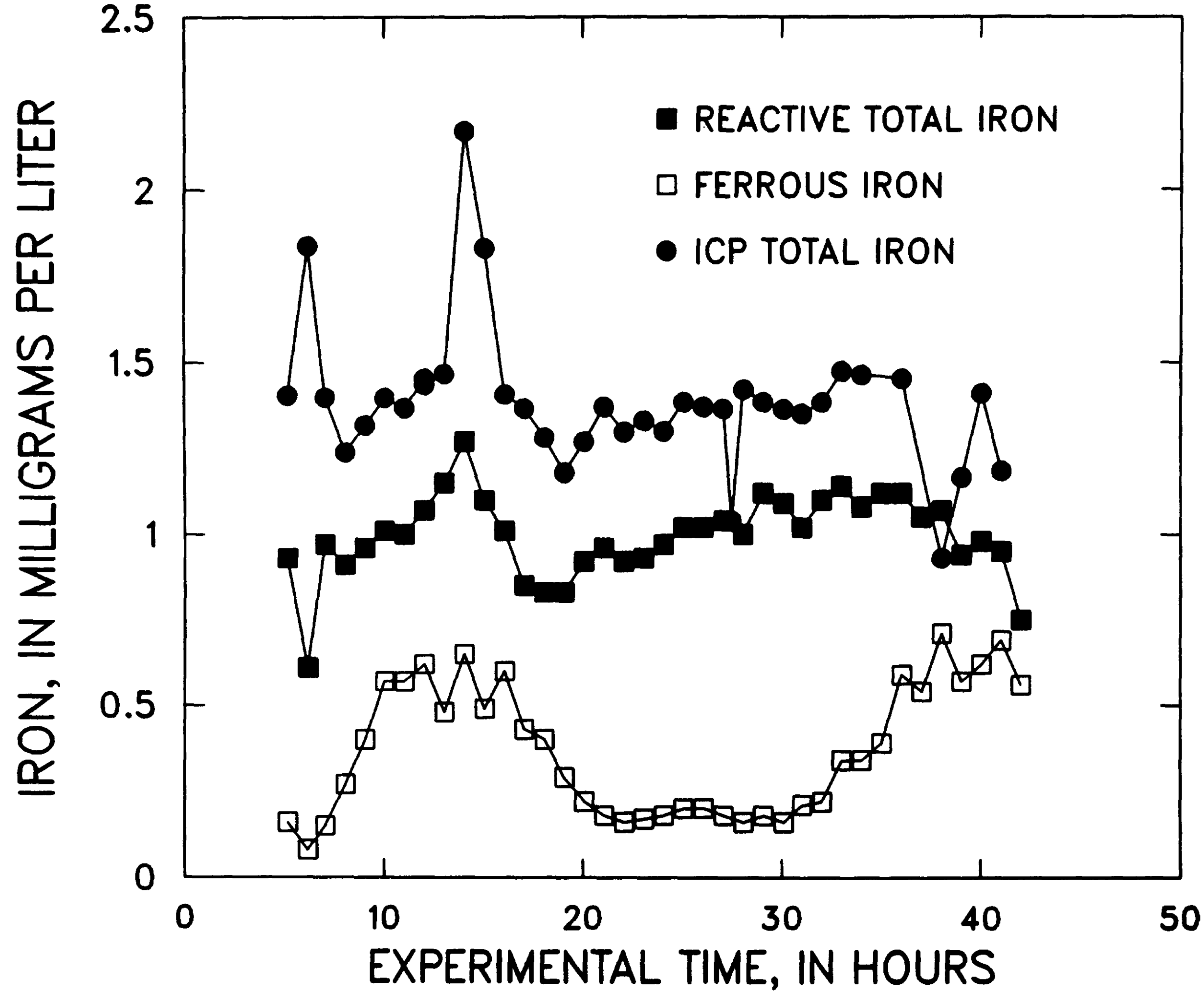

Figure B-20.—Variability of iron at site SK50.

removing aliquots of each treatment and determining Fe speciation by a colorimetric method (Fishman and Friedman, 1985).

RESULTS AND DISCUSSION

Chemical determinations for the three treatments are listed in table B-4 along with results of equilibrium calculations from the computer code WATEQ4F (Ball and Nordstrom, 1987). A calculated pe (redox potential calculated from the Fe^{2+}/Fe^{3+} redox couple) of about 0.6 indicates the dominance of Fe (III) before sunrise. Fe (II) was not completely absent because of an upstream source of Fe (II) at the mine tailings (fig. B-19). This inflow of Fe (II) is not completely oxidized during the nighttime transport to site SK50.

Metal Speciation and Equilibria

Of all the metals, there was a distinct difference in the concentration of Fe among the treatments. Aluminum (Al) concentration is larger in the unfiltered sample than in the ultrafiltrate treatment but not largest in the raw sample. Concentrations of cadmium (Cd), copper (Cu), manganese (Mn), and zinc (Zn) are virtually equal in each of the treatments, which indicates that they are completely dissolved. The dominant aqueous species of these metals, and the percentage of the metal present as these species, suggest a possible reason for this pattern (table B-5): if a metal is present in solution as a hydrated ion or as a sulfate complex, it may be less likely to adsorb to a surface than if the metal

Table B-4.—*Chemical determinations and results of chemical-equilibrium model calculations*

[Water sample had a pH of 4.08, a temperature of 5 degrees Celsius, dissolved organic carbon of 0.5 milligrams per liter; all chemical units are milligrams per liter; pe, redox potential calculated from Fe^{2+}/Fe^{3+} redox couple, dimensionless; SI, saturation index: log-ratio of ion acitivity product over temperature-adjusted equilibrium constant, dimensionless; AP, ion activity product, moles per kilogram water; —, not determined]

Constituent	Filter size (micrometers)		
	<0.01	0.0	>0.1
Calcium	10.1	10.2	10.0
Magnesium	3.5	3.5	3.4
Sodium	2.1	2.2	2.0
Chloride	.3	.3	.3
Sulfate	73.8	76.7	76.7
Aluminum	.940	1.240	1.030
Cadmium	.044	.040	.040
Copper	.086	.100	.080
Iron (II)	.028	.028	.028
Iron (III)	.402	.722	1.632
Iron (total)	.430	.750	1.660
Manganese	2.900	2.950	2.900
Zinc	6.470	6.710	6.530
pe	.599	.626	—
SI (allunite)	-.732	-.604	—
SI (ferrihydrite)	-.777	-.283	—
AP (ferrihydrite)	-37.89	-37.39	—

Table B-5.—*Speciation of metals in the ultrafiltrate treatment*

Metal	Dominant species	Percentage of element
Aluminum	Al^{3+}	75
	$AlSO_4{}^{+}$	22
	$AlOH^{2+}$	2
Cadmium	Cd^{2+}	89
	$CdSO_4{}^{o}$	10
Copper	Cu^{2+}	99
Iron	$Fe\ (II)^{2+}$	62
	$Fe\ (III)(OH)_2{}^{+}$	32
	$Fe\ (II)SO_4{}^{o}$	3
	$Fe\ (III)OH^{2+}$	3
Manganese	Mn^{2+}	94
	$MnSO_4{}^{o}$	6
Zinc	Zn^{2+}	92
	$ZnSO_4{}^{o}$	8

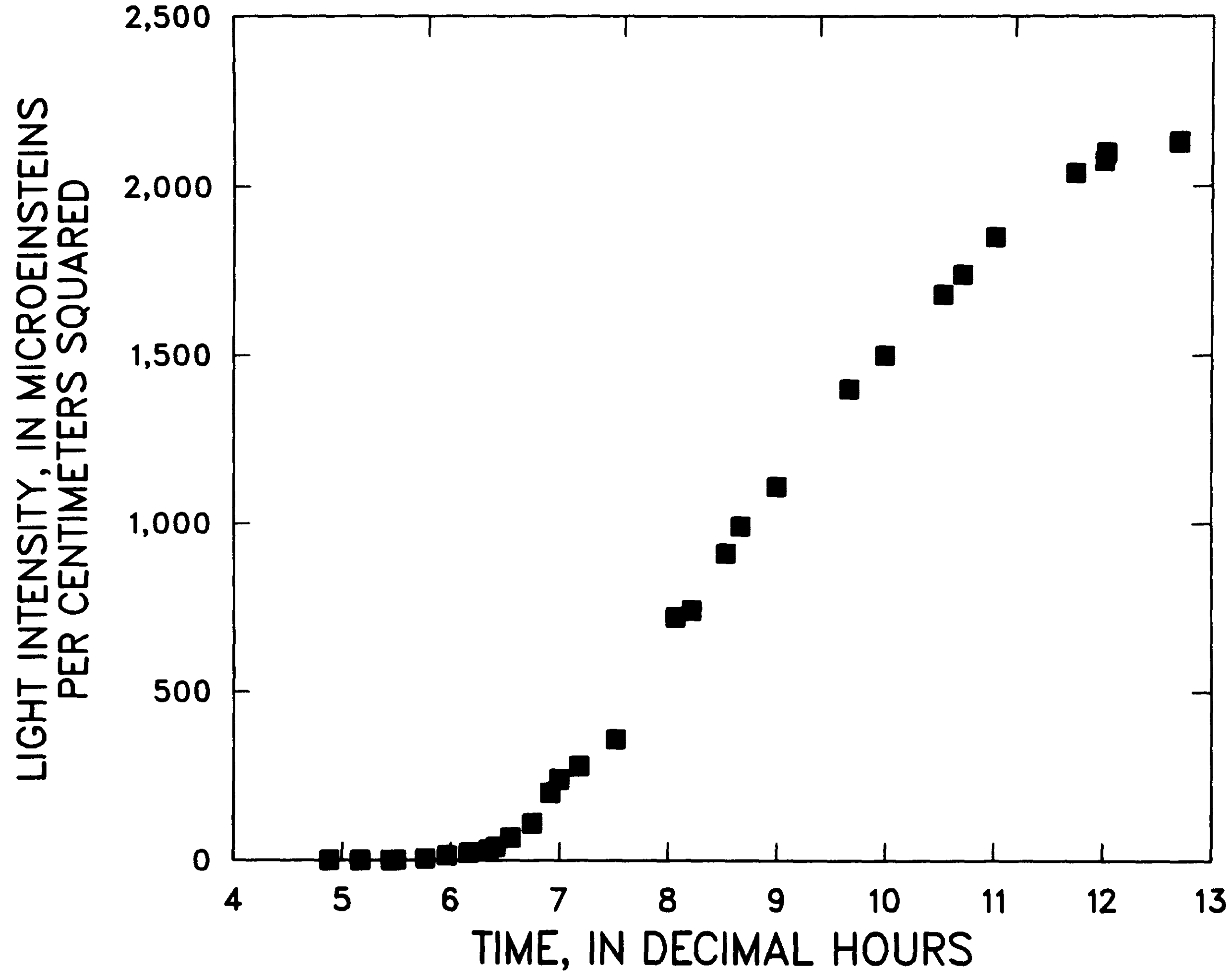

Figure B-21. – Variability of light intensity with time.

is present as an hydroxide complex. Al, Cd, Cu, Mn, and Zn are present as hydrated, free ions and sulfate complexes; they are not adsorbed to the Fe-hydroxide surfaces at a pH of 4.08. It seems that the partitioning of iron to the dissolved aqueous phase generally reflects the dominant speciation of the particular metal. About 34 percent of the iron is present as a hydroxide complex, and Fe appears to be the element most affected by surface reactions at this pH.

At higher pH the speciation of all the metals would change rapidly. The pH at which about half of each of these metals would be present as hydroxide complexes (in the absence of sulfate) is:

Metal	pH	Metal	pH
Al	5.0	Fe	6.7
Cd	10.1	Mn	10.9
Cu	7.7	Zn	7.7

These pH values equal the negative log of the hydrolysis constants for the first hydrolysis of each metal (Lindsay, 1979). If this first hydrolysis reaction is related to the adsorption of metals on the Fe hydroxide surfaces, then the pK values of the first hydrolysis constants suggest an order in which the metals should be affected by a greater pH.

Larger concentrations of Fe in the 0.1-μm filtrate affects the ion activity product of ferrihydrite. This mineral phase has been identified in St. Kevin Gulch (J.J. Fitzpatrick, U.S. Geological Survey, written commun., 1988). At pH 4.08, ferrihydrite is slightly undersaturated in the ultrafiltrate and is nearly saturated in the 0.1-μm filtrate. It is apparent that filter pore size is critical to accurately determine the state of saturation with respect to Fe phases.

Photoreduction in the Filtrates

The variation of light intensity during the 9-hour period was measured as the mean during 10-minute intervals (fig. B–21), and

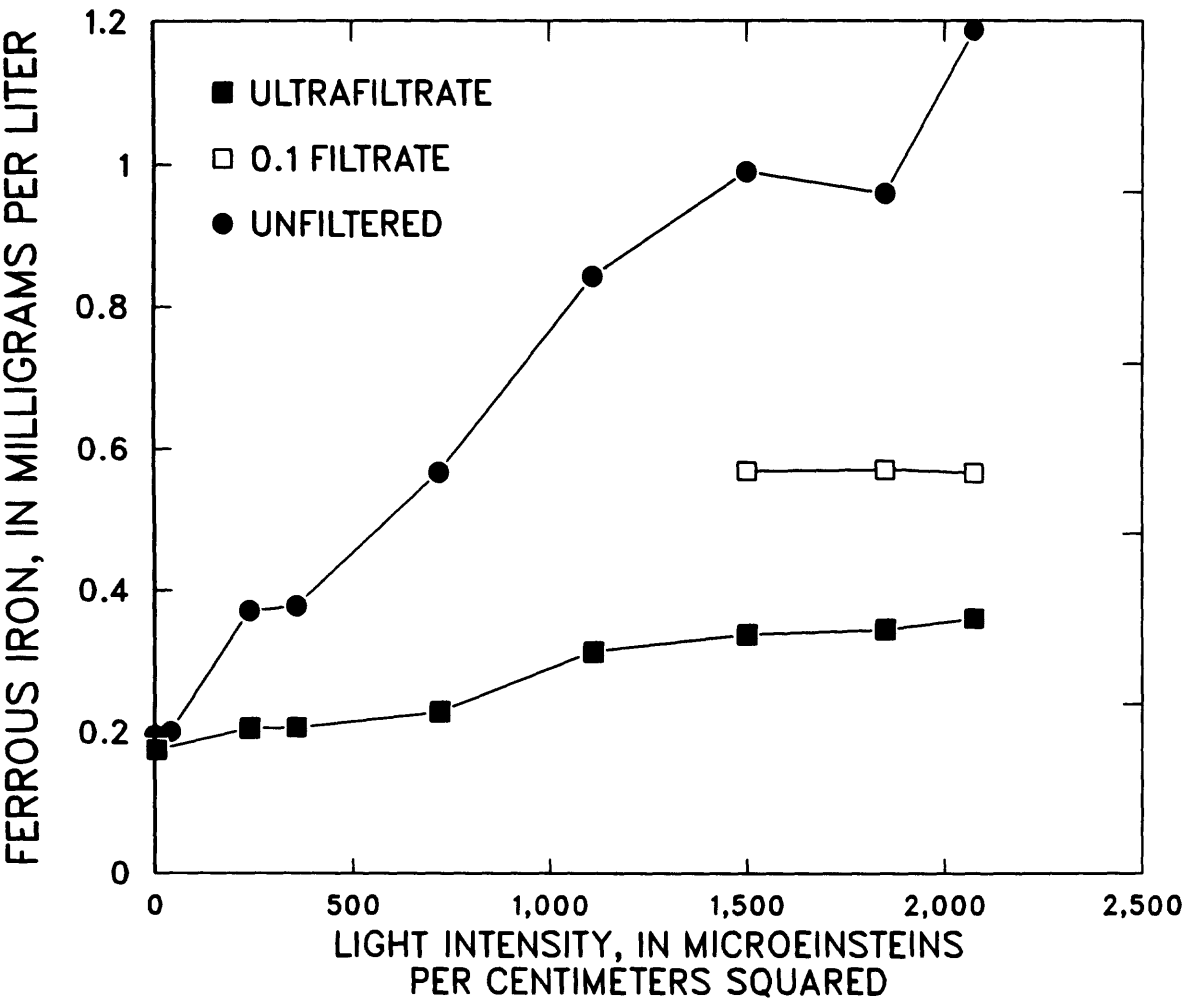

Figure B-22. – Variability of iron (II) concentration with light intensity.

photoreduction was tracked during this time. Light intensity increased from about 0630 to 1200 hours and then became almost constant at 1200 hours. The effect of light intensity on Fe (II) concentrations is shown in fig. B–22. The extent of increase of Fe (II) depends on the total concentration of Fe (III) available, as indicated by the change of the ratio of Fe (II) to total Fe (fig. B–23). In each treatment, the Fe (II) production seems to proceed until all the available Fe is converted to Fe (II) and the ratio is virtually 1.

The increase in the Fe (II):total Fe ratio for the ultrafiltrate initially is rapid – more rapid than for the unfiltered sample. This more rapid increase is indicative of a homogeneous aqueous reaction (reaction 1) rather than a heterogeneous reaction (reaction 2) involving colloidal Fe (III). This result is consistent with the results of laboratory experiments using well defined media and oxide phases, which showed that the homogeneous reaction has a greater quantum yield than the heterogeneous reaction. In addition to this difference in the true quantum yields, which are based on actual adsorption of near ultraviolet radiation, the greater light scattering in the unfiltered sample may have limited the extent of the heterogeneous reaction, especially at the lesser light intensities of the early morning.

These results lead to a conclusion that both the homogeneous and heterogeneous reactions contribute to the diurnal increase in Fe (II) in St. Kevin Gulch. Because at night the concentration of dissolved Fe (III) is less than the concentrations of colloidal and particulate hydrous iron oxides, the Fe (II) produced by the heterogeneous reaction may be quantitatively greater. These results also show that photoreduction occurs in the absence of bacteria in the ultrafiltrate. The results from the 0.1-μm filtrate also indicate that the heterogeneous photoreduction reaction is not dependent upon bacteria

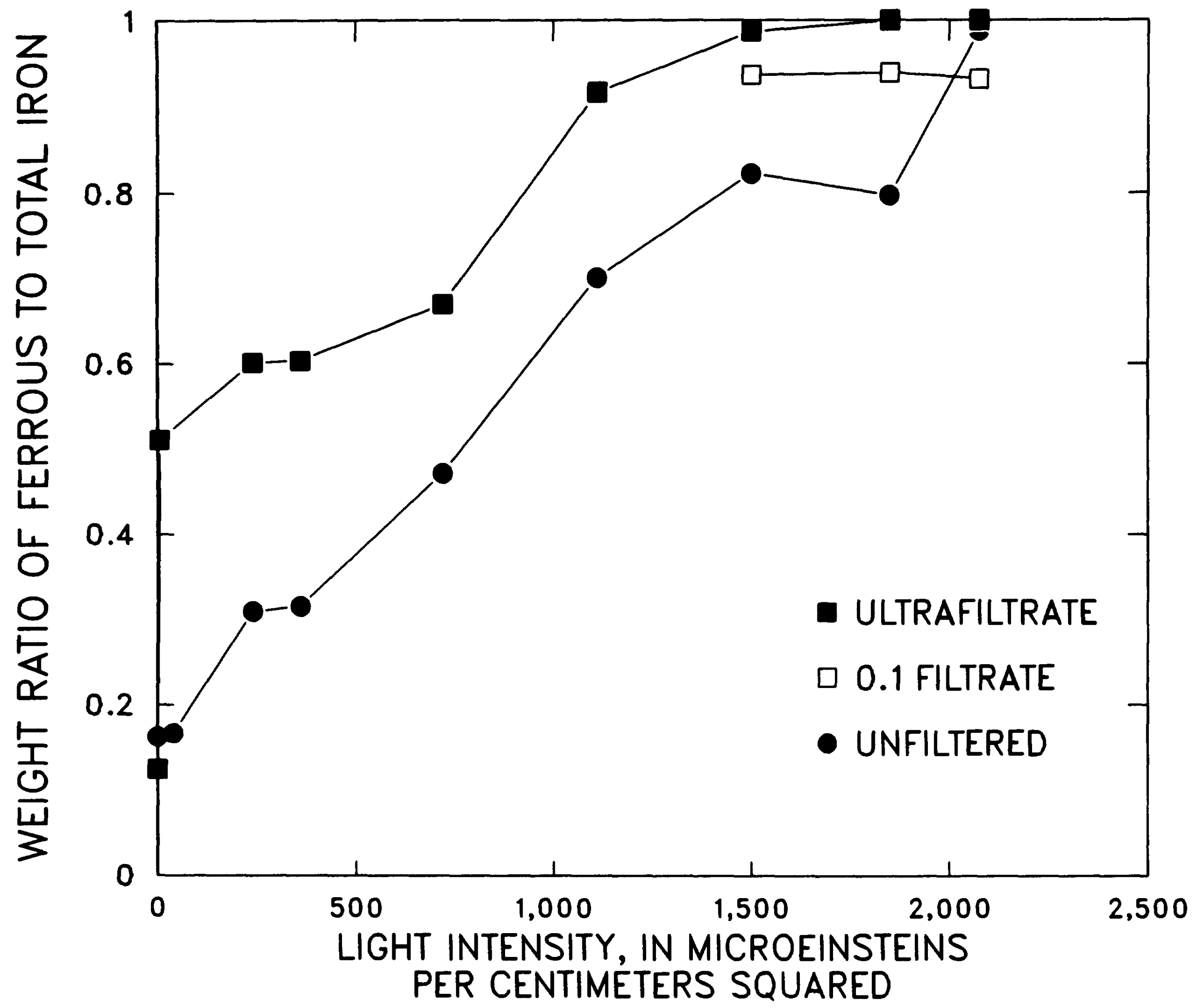

Figure B-23. – Variability of iron (II) to total iron ratio with light intensity.

associated with an iron oxide floc. The ultrafiltrate treatment still has 0.5 mg/L (milligrams per liter) organic carbon and organic material, such as sorbed humic substances, is probably associated with the colloidal and particulate oxides. Such organic material may be essential in reacting with the hydroxyl radical, and limiting the reoxidation of the ferrous iron.

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PARTITIONING OF METALS BETWEEN WATER AND FLOCCULATED BED MATERIAL IN A STREAM CONTAMINATED BY ACID MINE DRAINAGE NEAR LEADVILLE, COLORADO

By Kathleen S. Smith[1,2], Donald L. Macalady[2], and Paul H. Briggs[1]

ABSTRACT

Onsite metal-partitioning studies were performed in August 1987 using mixtures of flocculated iron oxyhydroxide material (floc) and streamwater collected from St. Kevin Gulch, a central Colorado mountain stream contaminated by acid mine drainage. The pH was varied between ambient (about 3.5) and 6 by the addition of $NaHCO_3$ *to aliquots of unfiltered streamwater and floc/streamwater mixtures. Iron and aluminum aqueous concentrations seem to be controlled primarily by solubility reactions, whereas zinc, manganese, copper, and cadmium concentrations are controlled by sorption reactions. The sorption reactions are pH dependent, with a sorption edge between pH 5 and 6 for zinc, and between pH 3.5 and 4.5 for copper. Cadmium does not appear to have a well-defined sorption edge up to pH 6, and the manganese concentration gradually decreases over the pH range tested. Flocculated iron oxyhydroxide material does not seem to be an effective sink for trace metals in St. Kevin Gulch at the ambient pH of about 3.5. Although pH-dependent solubility and sorption reactions drive metal partitioning to the solid phase at higher pH, aqueous concentrations of manganese, zinc, and cadmium at pH 6 are still significant.*

INTRODUCTION

Acid mine drainage is a potential threat to the quality and ecology of receiving waters. Treatment of these metal-rich waters is hampered by a lack of understanding of the processes that control metal mobility in acidic systems. A detailed understanding of this metal chemistry is necessary if successful mitigation procedures are to be adopted.

This paper describes research that examined metal partitioning between flocculated iron oxyhydroxide(s) (floc) and streamwater in an acid mine drainage system. Jenne (1968) emphasized the importance of amorphous hydrous iron oxides in the sorption of metals in natural systems. It has been reported that hydrous iron oxides have a high affinity for the binding of copper (Cu), cadmium (Cd), and zinc (Zn) (Benjamin and Leckie, 1981). Tessier and others (1985) found the sorption of trace metals onto low-pH, iron oxyhydroxide-rich lake sediments to be greater than predicted by simple models. Controls on metal-partitioning processes may be significant in the determination of metal transport in aquatic systems affected by acid mine drainage.

St. Kevin Gulch is a small subalpine stream located 7 km (kilometers) northwest of Leadville, Colo. (fig. B–24). St. Kevin Gulch receives acidic, metal-rich tailings effluent, which produces elevated concentrations of sulfate and several metals including iron (Fe), manganese (Mn), aluminum (Al), Zn, Cu, and Cd (McKnight and others, 1988).

The questions considered in this paper include: (1) Is the floc that coats streambed pebbles in St. Kevin Gulch an important sink for metals? (2) How does metal partitioning between streamwater and floc change as the pH of the stream changes?

An onsite metal-partitioning study was performed with unfiltered streamwaters and floc/streamwater mixtures collected from St. Kevin Gulch in early August 1987. The pH was varied in these experiments, and the corresponding equilibrated aqueous metal concentrations were determined. The experiments were designed to simulate seasonal pH changes and pH changes encountered at confluences of acidic waters with nonacidic waters.

EXPERIMENTAL METHODS

Experiments were performed to determine the time period for rapid-step sorption reactions

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

[2] Colorado School of Mines, Golden, Colo.

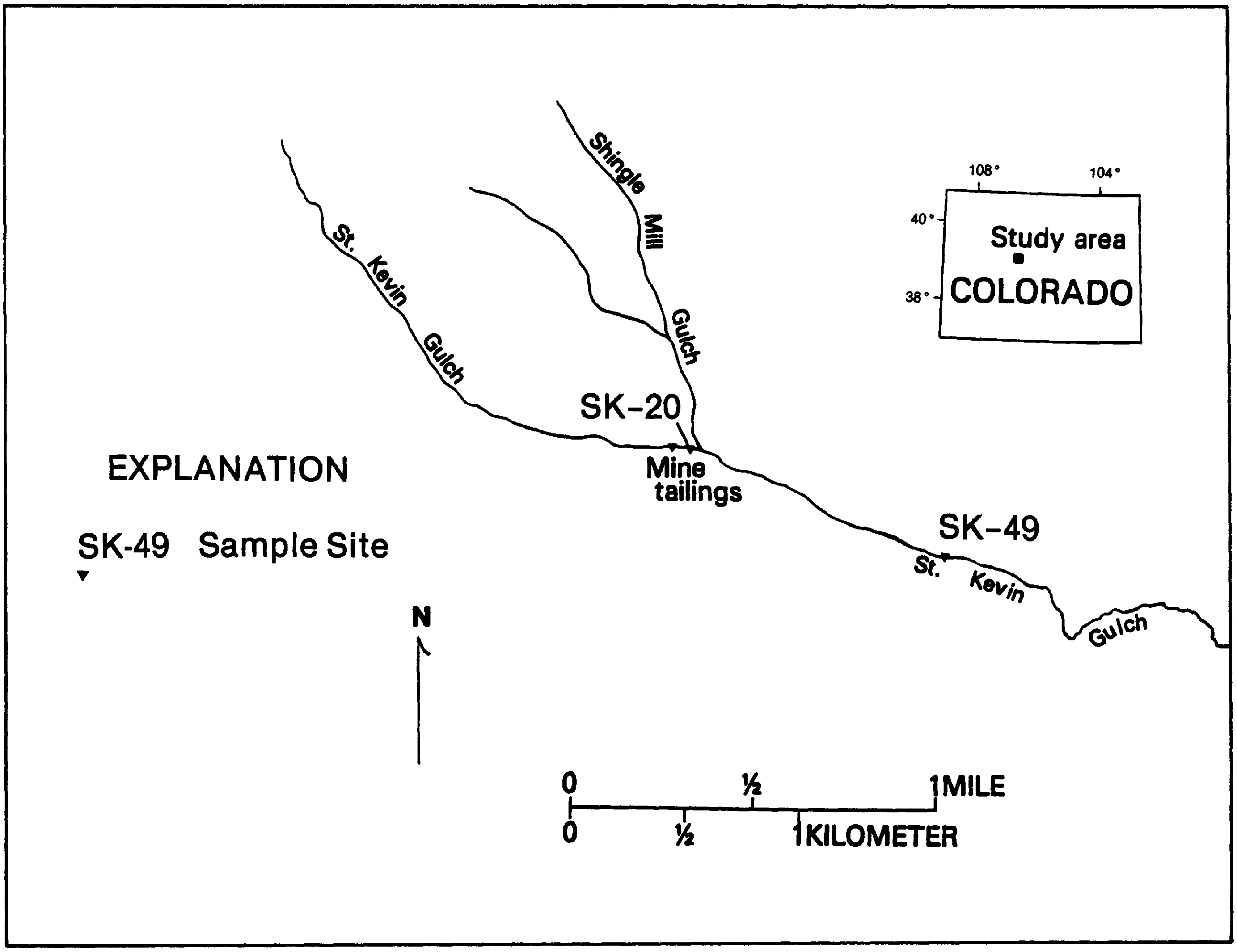

Figure B-24. – Sampling sites along St. Kevin Gulch (from McKnight and others, 1988).

to reach completion. Floc was collected from St. Kevin Gulch sites SK–20 and SK–49 (fig. B–24) by agitating floc-coated streambed pebbles in a closed polyethylene container to obtain a floc/streamwater mixture. Enough 0.5 M $NaHCO_3$ was added to these floc suspensions to raise the pH to 6. Aliquots of the mixture were removed and filtered at various time intervals over a 1-day period. Analyses of these aliquots indicated that a time period of 2 hours was adequate for rapid-step sorption reactions to reach completion.

Metal-partitioning experiments were conducted with unfiltered streamwaters and floc/streamwater mixtures collected from sites SK–20 and SK–49 (fig. B–24). A 40-mL (milliliter) subsample of each suspension was titrated to determine the amount of base necessary to raise the pH to 6. Forty-mL aliquots of unfiltered streamwaters and floc/streamwater mixtures were pipetted into a series of 60-mL polyethylene bottles. The pH of the aliquots was adjusted to several values between ambient (about 3.5) and 6 using either 0.1 M or 0.5 M $NaHCO_3$. The contents of the bottles were equilibrated at streamwater temperature with occasional shaking for 2 hours after which final pH values were determined and aliquots were filtered through 0.1-μm (micrometer) nitrocellulose filters. The filtrates were collected for analysis.

Most metal concentrations in the filtrates were determined using inductively coupled plasma-atomic emission spectrometry (ICP–AES) (Lichte and others, 1987). Flameless atomic-absorption spectrometry (AAS-graphite furnace) was used to measure Cu and Cd (Perkin-Elmer, 1977).

RESULTS AND DISCUSSION

Rates of Cu and Cd sorption at pH 6 onto floc from sites SK–20 and SK–49 are illustrated in figures B–25a and B–25b. These data show initially very rapid sorption followed by a less well-defined, much slower sorption process. Results from both sites exhibit a slight decrease in the amount of sorption between the initial rapid step and the slower step. On the basis of these data, a time period of 2 hours was deemed adequate for the rapid sorption step to reach completion and was chosen as the equilibration time for metal-partitioning experiments.

In the metal-partitioning experiments, the floc suspension from site SK–20 contained 5.7 g/L (grams per liter) solid floc, and that from site SK–49 contained 7.0 g/L. Surface area of the floc is about 150 m^2/g (square meters per gram) at site SK–20, and 50 m^2/g at site SK–49 (Ranville and others, 1989, this Proceedings). As a consequence, the suspension from site SK–20 contained about 2.4 times more sites than that from site SK–49. Figures B–26a and B–26b illustrate titration curves of equal volumes of floc suspensions using $NaHCO_3$. About 2.5 times more moles of $NaHCO_3$ per unit volume of suspension were required to obtain a pH of 6 in the floc suspension from site SK–20 than in the floc suspension from site SK–49.

Results of the partitioning studies are summarized in figures B–27a, B–27b, B–28a, and

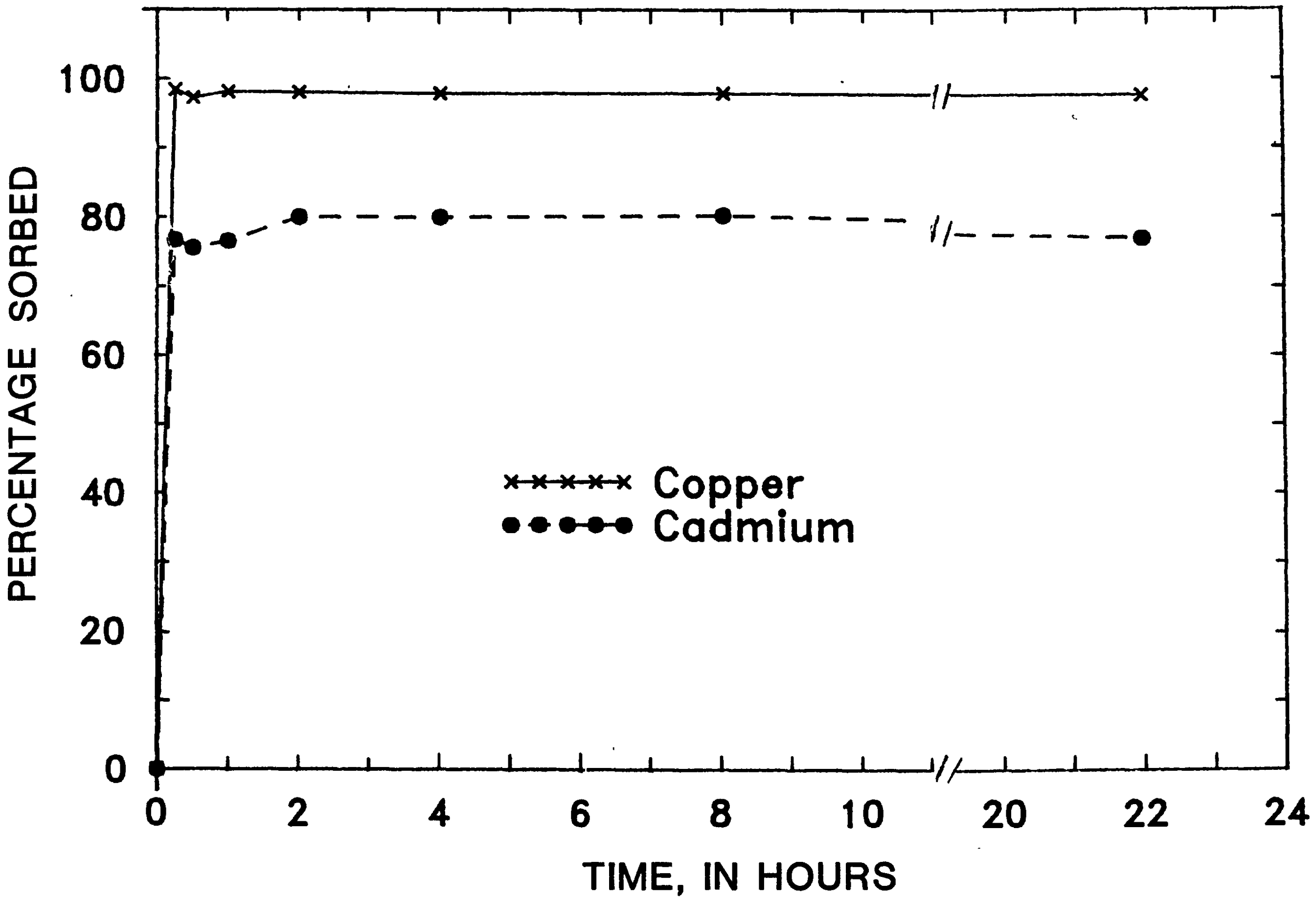

Figure B-25a.—Rates of copper and cadmium sorption at pH 6 onto floc collected from site SK–20.

B–28b. Four bars are shown for each species. The far-left bar represents the species concentration in pH-unaltered unfiltered streamwater collected at the time of floc suspension collection, the middle-left is the species concentration in a pH-unaltered floc-suspension aliquot, the middle-right is the species concentration in an unfiltered streamwater aliquot adjusted to the highest pH measured, and the far-right is the species concentration in a floc-suspension aliquot adjusted to the highest pH measured. These data show that aqueous Fe and Al concentrations in the floc/streamwater mixtures are below the limits of detection of 0.06 ppm (parts per million) and 2 ppm, respectively, at pH 6. The aluminum concentration drops to below detection by pH 4 at both sites whereas the Fe concentration drops to below detection at pH 4 for site SK–49 and at pH 5.9 for site SK–20. Decrease in aqueous Fe concentration between the pH-unaltered unfiltered streamwater and the pH-unaltered floc/streamwater mixture from site SK–20 points to active loss of Fe from the aqueous phase and indicates disequilibrium of Fe at that site. A slight pH decrease was noted in the pH-unaltered mixture. Comparison of results from pH alteration of unfiltered streamwaters with those from pH alteration of floc suspensions reveals that Fe and Al aqueous concentrations are primarily controlled by solubility reactions.

Zn, Mn, Cu, and Cd concentrations appear to be controlled by sorption reactions. The sorption edge is between pH 5 and 6 for Zn, and between pH 3.5 and 4.5 for Cu. Cadmium does not appear to have a well-defined sorption edge up to pH 6, and Mn exhibits a gradual concentration decrease over the pH range tested. This pH-dependent sorption behavior is in agreement with generally accepted trends observed in laboratory studies on simple amorphous iron oxyhydroxide

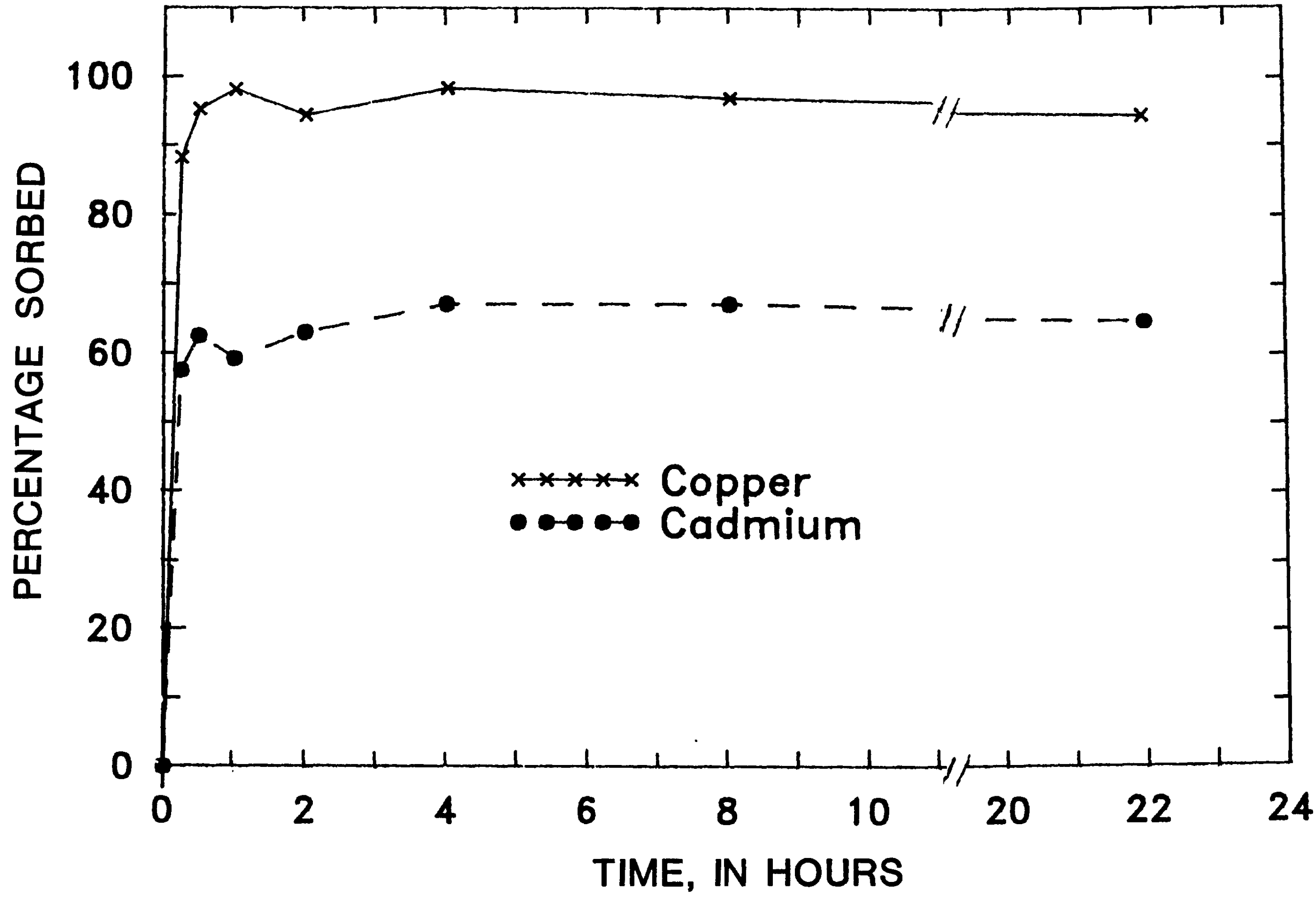

Figure B-25b. – Rates of copper and cadmium sorption at pH 6 onto floc collected from site SK–49.

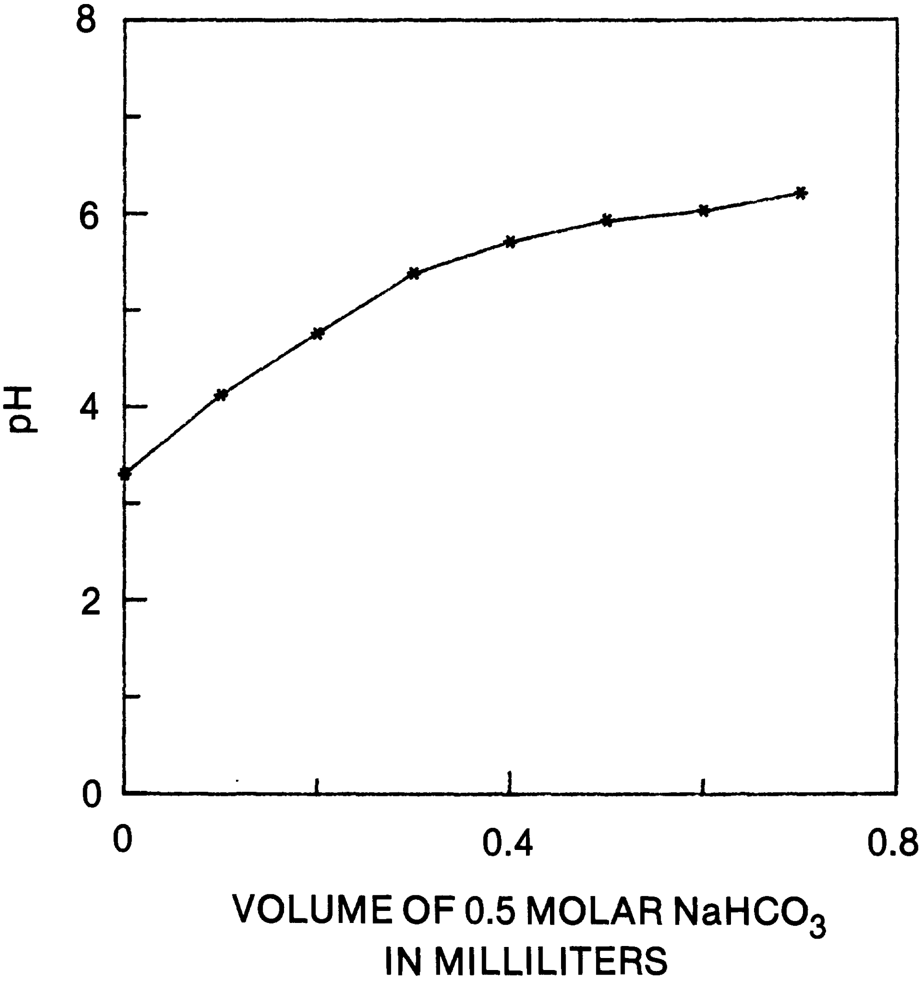

Figure B-26a.—Titration curve for floc suspension collected from site SK–20.

systems (for example see Benjamin and Leckie, 1981).

Conclusions regarding partitioning trends are consistent with data from Shingle Mill Gulch (fig. B–24), a tributary of St. Kevin Gulch with higher pH (6.5). Shingle Mill Gulch has much lower aqueous metal concentrations and, with the exception of Fe, higher solid-phase metal concentrations than does St. Kevin Gulch. These data are discussed in detail by Ranville and others, 1989 (this Proceedings), and indicate that metal partitioning has been driven toward the solid phase in Shingle Mill Gulch.

Adsorption properties of a material are controlled by the surface properties of that material. Coatings and sorption of counterions (for example, sulfate) and/or organics can alter the original surface properties, especially surface charge. Data presented by Ranville and others, 1989 (this Proceedings), illustrate that St. Kevin Gulch floc has a near-neutral surface charge, indicating modifications of the floc surface. Planned research toward understanding the processes that control surface charge will improve understanding of sorption mechanisms and metal-partitioning reactions.

SUMMARY

Results from this study indicate that the flocculated iron oxyhydroxide material that coats streambed pebbles in St. Kevin Gulch is not an effective sink for trace metals at the ambient pH (about 3.5). Floc/water metal partitioning increases as the pH increases, but aqueous concentrations of several metals at pH 6 are still significant.

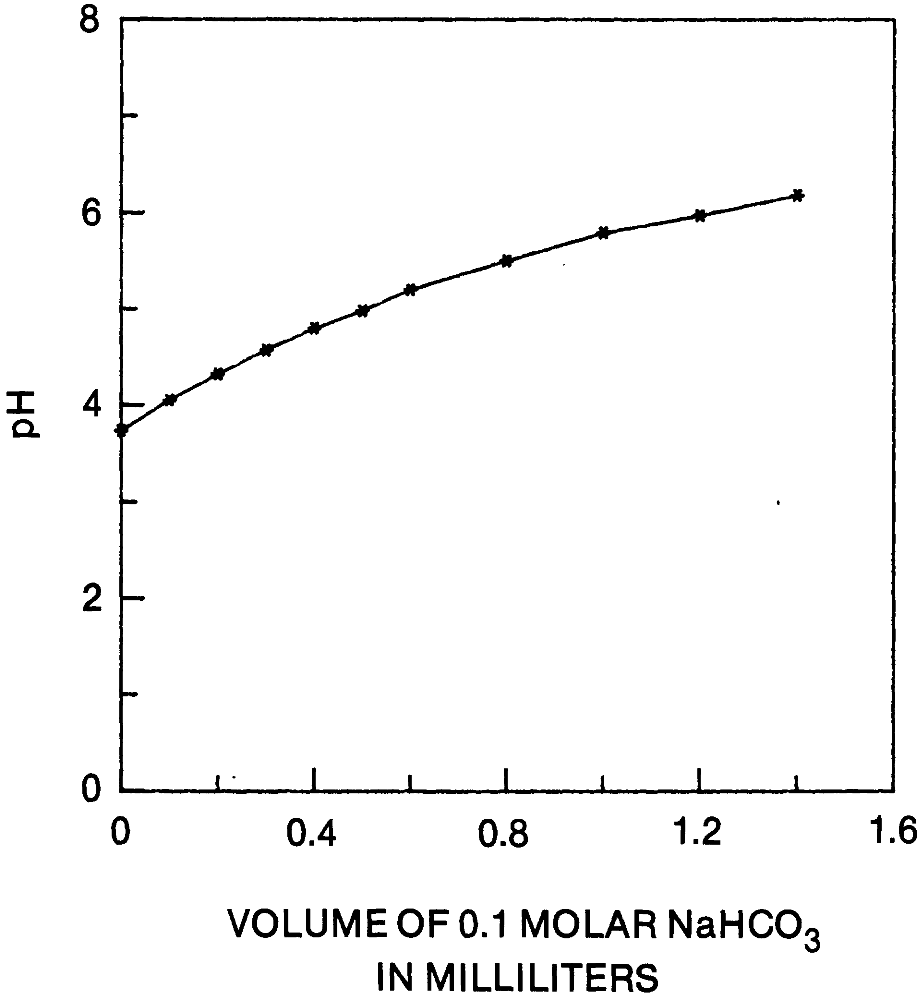

Figure B-26b.—Titration curve for floc suspension collected from site SK-49.

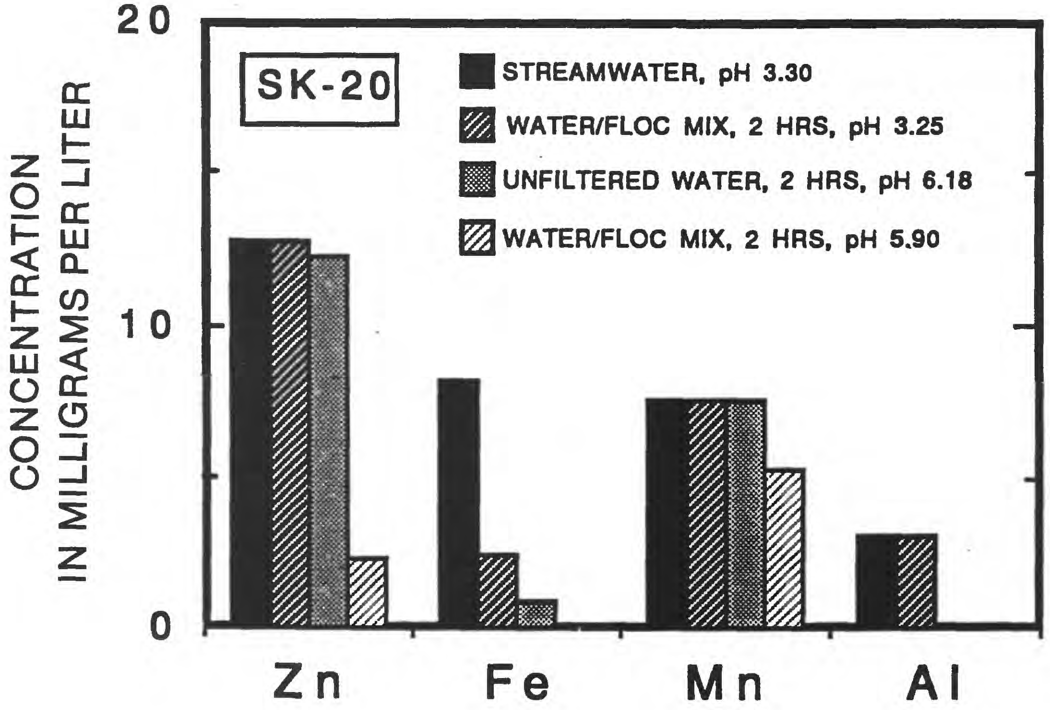

Figure B-27a.—Metal-partitioning for zinc (Zn), iron (Fe), manganese (Mn), and aluminum (Al) at site SK-20.

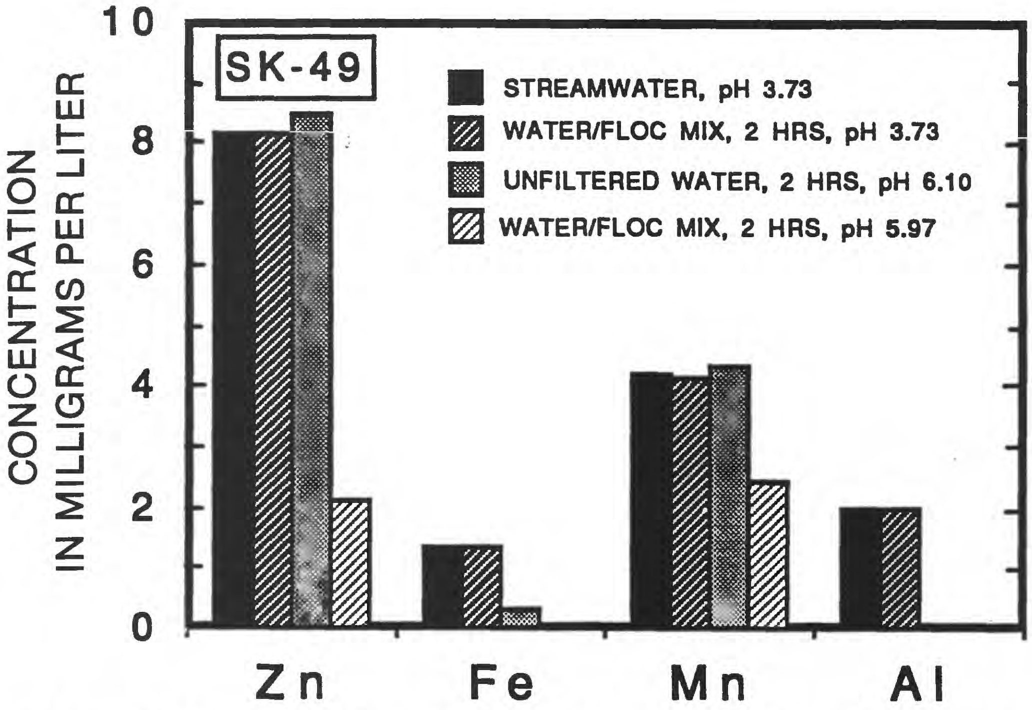

Figure B-27b.—Metal-partitioning for zinc (Zn), iron (Fe), manganese (Mn), and aluminum (Al) at site SK-49.

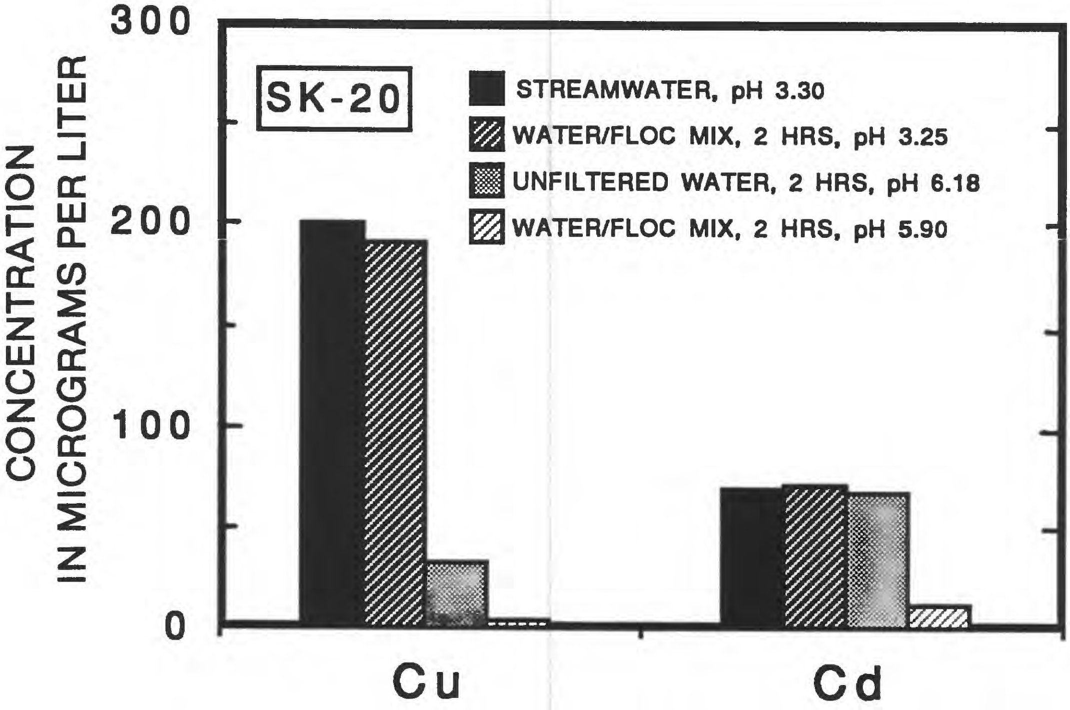

Figure B-28a.—Metal-partitioning for copper (Cu) and cadmium (Cd) at site SK-20.

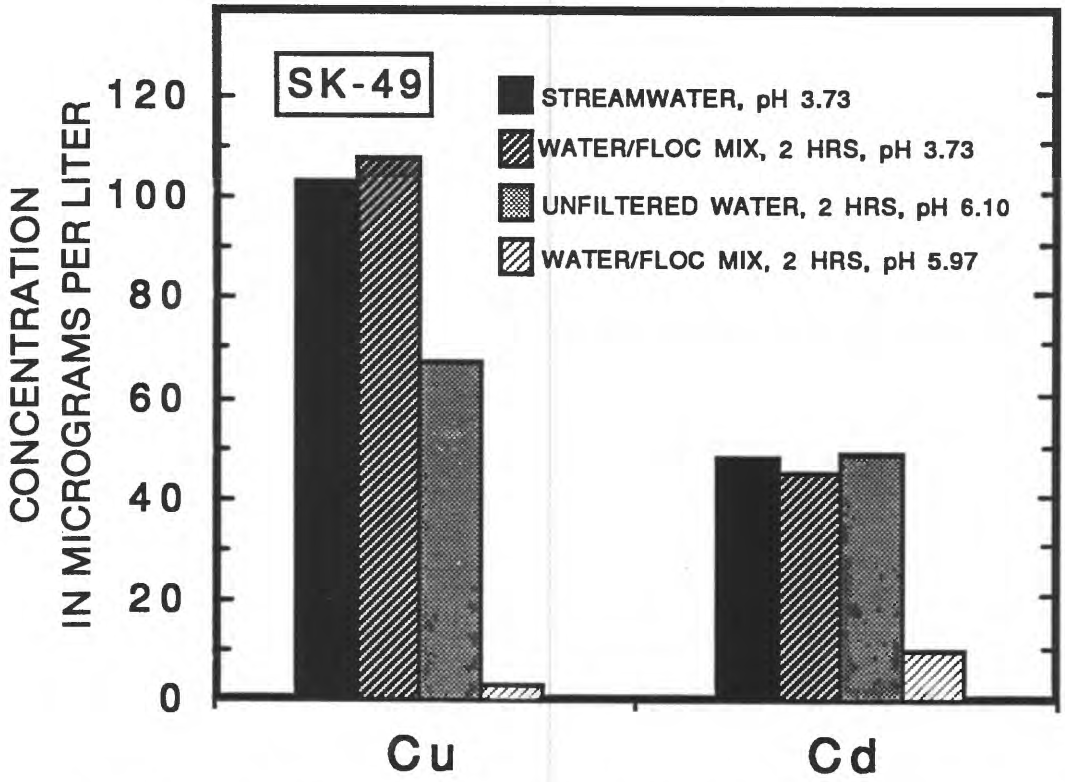

Figure B-28b.—Metal-partitioning for copper (Cu) and cadmium (Cd) at site SK-49.

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(p. 111 follows)

COLLOIDAL PROPERTIES OF FLOCCULATED BED MATERIAL IN A STREAM CONTAMINATED BY ACID MINE DRAINAGE, ST. KEVIN GULCH, COLORADO

By James F. Ranville[1,2], Kathleen S. Smith[1,2], Donald L. Macalady[2], and Terry F. Rees[1]

ABSTRACT

A suite of samples of flocculated iron oxyhydroxide material (floc) was collected along St. Kevin Gulch, a central Colorado metal-rich stream (pH less than 3.8) contaminated by acid mine drainage. Iron is the predominant metal in the floc, with minor amounts of aluminum, zinc, and manganese, and trace amounts of lead, copper, and cadmium. Scanning electron microscopy reveals that the floc is composed of aggregates, generally greater than 1 micrometer in size, of uniformly sized 0.04 micrometer spheroids. Large values of surface area, on the order of 150 square meters per gram, were measured. Electrophoretic mobility measurements, made using a light-scattering technique, indicated a near-neutral charge in the shear plane. Formation of these flocs from iron oxyhydroxide colloids in the stream is consistent with the near-zero charge implied by their electrophoretic mobility. The mechanism(s) of formation of these apparently monodisperse colloids, the physical chemistry responsible for the surface charge neutralization, and the importance of the floc aggregates in metal partitioning in St. Kevin Gulch are under investigation.

INTRODUCTION

St. Kevin Gulch, located 7 km (kilometers) northwest of Leadville, Colo., is a small subalpine stream contaminated by acidic drainage from abandoned mines and mill tailings (McKnight and others, 1988). As a result, the streamwater is acidic (pH less than 3.8) and contains elevated concentrations of sulfate, iron (Fe), aluminum (Al), manganese (Mn), zinc (Zn), and several other trace metals.

Streambed materials in St. Kevin Gulch, as in most streams contaminated by acid mine drainage (AMD), are heavily coated with yellow to orange red precipitates of hydrous Fe oxides. The importance of Fe oxyhydroxides in the removal of dissolved metals by sorption and/or coprecipitation has been extensively examined in laboratory studies (Davis and Leckie, 1978; Benjamin and Leckie, 1981) and field investigations (Jenne, 1968; Robinson, 1981; Lion and others, 1982; Singh and Subramian, 1984; Johnson, 1986). The ability of such material to scavenge metals from solution is strongly controlled by its surface properties—its charge, area, and adsorption site density.

These surface properties, especially charge, also strongly affect the transport of colloidal Fe oxyhydroxides in surface waters. Charge repulsion caused by the electrostatic charge on the particle surfaces is a major mechanism for maintaining the particles in suspension. The development of surface charge on oxides is a result of acid-base reactions on the surface and is therefore strongly pH-dependent. For most Fe oxyhydroxides, the zero point of charge (ZPC) is approximately pH = 6 to 9 (Parks, 1965). At a pH less than the ZPC, the surface is positively charged. At a pH greater than the ZPC, a negative surface charge is expected. When electrophoresis is used to measure surface charge, the point of zero net surface charge is called the isoelectric point (IEP).

Adsorption of organic matter onto particle surfaces has been widely recognized as the major factor in producing a ubiquitous net negative surface charge on particles in natural waters (Hunter and Liss, 1979; Tipping and Cooke, 1982). A study of the Carnon River, England, has shown that, in an AMD contaminated stream with chemistry similar to St. Kevin Gulch, insufficient organic matter to completely coat the Fe oxyhydroxide particles has resulted in positively charged particles (Newton and Liss, 1987).

The goal of this study is to improve an understanding of the role of Fe oxyhydroxide surface chemistry in the transport of Fe and trace

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

[2] Colorado School of Mines, Golden, Colo.

metals in AMD affected streams. This paper reports the results of a preliminary reconnaissance study of Fe oxyhydroxide surface chemistry at St. Kevin Gulch, performed in August 1987.

EXPERIMENTAL METHODS

Four samples of the flocculated material coating the streambed rocks in St. Kevin Gulch were collected in August 1987. The sampling sites were SK-20, SK-25, SK-37, and SK-700 (fig. B-29). This material was yellow to orange red. The floc upstream from the confluence of Shingle Mill Gulch was redder than the floc downstream of the confluence. The floc formed a loosely held coating, the thickness of which differed among the sites, being thickest at site

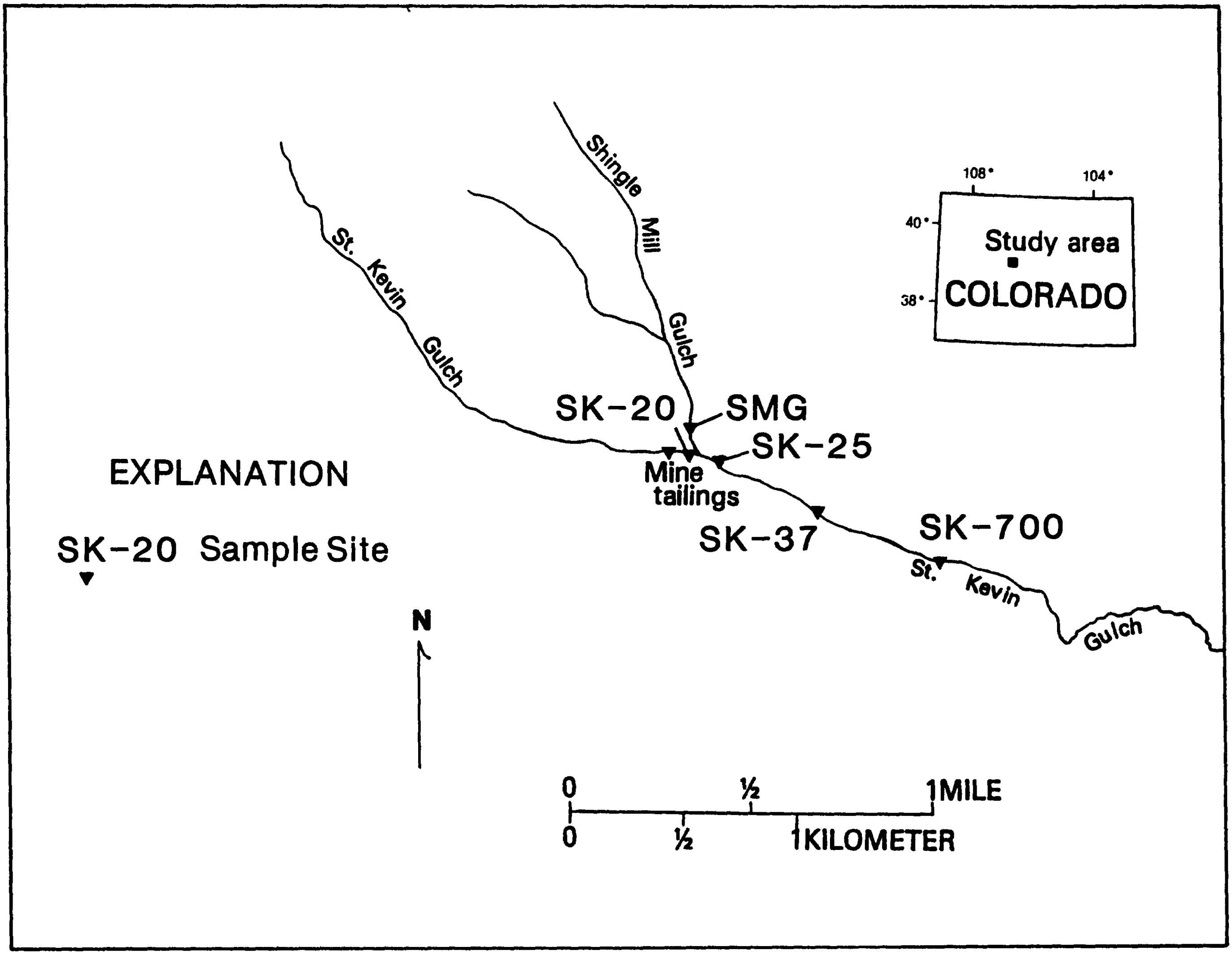

Figure B-29.—Sample-collection locations along St. Kevin Gulch and Shingle Mill Gulch (modified from McKnight and others, 1988, fig. 1).

SK–25. A sediment sample also was collected from Shingle Mill Gulch, a tributary with higher pH and lower dissolved metal concentrations than that of St. Kevin Gulch. This sample was brownish gray and appeared to be clay-rich. Sample materials from St. Kevin Gulch were obtained by collecting streambed pebbles and agitating them with streamwater in a polyethylene bottle. The Shingle Mill Gulch sample was obtained by agitating moss in a similar manner. The resulting concentrated suspensions were transferred to sterile borosilicate glass bottles and kept refrigerated prior to analysis. Measurements of pH and stream temperature were made at the time of sample collection. Dissolved organic carbon analyses were attempted but were unsuccessful because of sample contamination.

Quantitative chemical analysis was performed on a cold nitric acid digestate of air-dried sample using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Percent carbon was measured on air-dried samples by combustion of the sample followed by coulometric titration of the evolved CO_2. Surface area was measured using a single-point N_2 adsorption (BET) technique.

Particle size and morphology were investigated with scanning electron microscopy (SEM). Qualitative chemistry was obtained by energy dispersive X-ray analysis (EDAX). SEM and EDAX analyses were performed on the fine fraction of material obtained by agitating the sample in native streamwater, allowing the suspension to settle for 30 minutes, then filtering a small volume of the supernatant liquid through a 0.1 μm (micrometer) Nucleopore[3] filter.

The surface charge, more properly the electrophoretic mobility, of the fine fraction dispersed in the streamwater was measured using a laser electrophoretic light-scattering technique (ELS). This method involves the measurement of the frequency shift in the light scattered by charged particles moving under the influence of an electric field (Rees, 1987). The magnitude of this shift is proportional to the particle velocity under an applied potential and is a measure of the charge on the region of the double layer known as the shear plane. The shear plane can be defined as the plane that separates solvent molecules and adsorbed ions that drift with the particle under the influence of an applied field from solvent molecules and ions that remain immobile under the field. Some knowledge of the nature of the adsorbed ions in the double layer is necessary to translate electrophoretic mobilities to surface charge values, which are usually determined by potentiometric titration.

RESULTS

Figure B–30a shows the low values and small variation of pH in St. Kevin Gulch. The pH of Shingle Mill Gulch (6.5) is considerably higher than that of St. Kevin Gulch. Inflow of this stream results in a slight increase in the pH of St. Kevin Gulch.

The chemical composition of the St. Kevin Gulch floc and Shingle Mill Gulch sediment, as determined by ICP-AES, is shown in table B–6. Fe is the predominant metal in St. Kevin Gulch floc. The percentage of Fe in the floc is greatest in the sample collected at site SK–25 (just below the confluence with Shingle Mill Gulch) and less in the sample from site SK–20 (above the confluence with Shingle Mill Gulch and immediately below the tailings inflows) and in samples from progressively downstream sites (SK–37 and SK–700). The high Fe content of the floc is in agreement with the dominance of various forms of Fe oxyhydroxides (Fitzpatrick, 1989, this Proceedings). The floc also contains minor amounts of Al, Zn, and Mn. Trace amounts of lead (Pb), copper (Cu), and cadmium (Cd) are present. Concentrations of Al, Mn, and Zn in the floc generally increase downstream. The Shingle Mill Gulch floc sample contains a much lower Fe concentration and higher concentrations of Al, Mn, and Zn than do the St. Kevin Gulch samples. This higher trace-metal content in the Shingle Mill Gulch may reflect increased efficiency of metal scavenging by the streambed materials at higher pH (Smith and others, 1989, this Proceedings). Figure B–30b presents the results of organic carbon analysis of the floc. The percentage of organic carbon is low (less than 1 percent) in the floc and increases downstream. The Shingle Mill Gulch sample is higher in organic carbon. Possible explanations for this increase may be the incorporation of dissolved organic matter into the floc or an increase in the ratio

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

Table B-6.—*Elemental chemistry of the nitric acid soluble fraction of St. Kevin Gulch floc and Shingle Mill Gulch sediment*

[—, below detection; %, weight percent; ppm, milligrams per kilogram]

Constituent[1]	St. Kevin Gulch				Shingle Mill Gulch
	SK-20	SK-25	SK-37	SK-700	SMG
Fe (%)	37.9	43.3	32.8	28.0	10.6
Al (%)	.6	1.1	1.3	1.6	6.8
Mn (%)	.05	.08	2.20	.15	4.80
Zn (%)	.08	.15	.28	.38	2.33
Cu (ppm)	78	136	197	192	993
Pb (ppm)	—	—	575	—	975
Cd (ppm)	35	63	48	50	170

[1] Fe, iron; Al, aluminum; Mn, manganese; Zn, zinc; Cu, copper; Pb, lead; Cd, cadmium.

of organic-matter production to metal precipitation.

The results of the N_2 BET adsorption are shown in figure B–30c. St. Kevin Gulch floc has a large surface area of 50 to 170 m^2/g (square meters per gram). There is a slight increase in surface area at site SK–25 followed by a general decrease in downstream samples. The surface area computed from the observed particle diameter, assuming a spherical shape, is 40 m^2/g. Surface area computed from the unit cell size of 160 angstroms determined for SK–25 floc by Fitzpatrick (1989, this Proceedings) gives a value of 110 m^2/g, a value that is in somewhat better agreement with the BET results than the 40 m^2/g computed value.

Electrophoretic mobility results, shown in figure B–30d, indicate a near-neutral surface charge in the shear plane for all St. Kevin Gulch samples. The sample from Shingle Mill Gulch on the other hand, exhibited a large negative electrophoretic mobility (-1.3 micron centimeter/second volt), indicating negatively charged surfaces.

Direct observation by SEM indicates that the fine fraction of the iron-rich floc is present as 1 to 10 μm aggregates composed of very small, uniformly sized spheroids (0.040 ± 0.008 μm). This is the predominant morphology in samples SK–20 and SK–25. An example of this morphology is shown in figure B–31. SEM examination of the larger fraction, which settled after 30 minutes, showed the presence of aggregates larger than 10 μm also composed of very small spheroids. Similar aggregates are visible in the downstream samples, but they are mixed with other particle types. The sample from Shingle Mill Gulch does not display particles with this characteristic morphology.

DISCUSSION

St. Kevin Gulch floc has a near-zero electrophoretic mobility despite an ambient stream pH well below the expected ZPC for Fe oxyhydroxides. This indicates either incorporation of low-ZPC materials or adsorption of anions at the double layer. Possible anionic species responsible for surface-charge neutralization include sulfate and/or organic matter. The determination of the species responsible for this charge neutralization will be attempted during the 1988 field season. Interpretation of metal partitioning results may be facilitated by this knowledge.

Particle size, determined by SEM, is quite small (0.040 ± 0.008 μm for SK–25) and is expressed in the large measured surface areas (approximately 150 m^2/g). Decrease in surface area per gram downstream could result from increase in the proportions of larger detrital minerals or recrystallization of the Fe floc. A possible consequence of this decrease in surface area may be a general loss of surface adsorption sites downstream.

The formation of these flocs from Fe oxyhydroxide colloids in the stream is consistent with the near-zero charge implied by their electro-

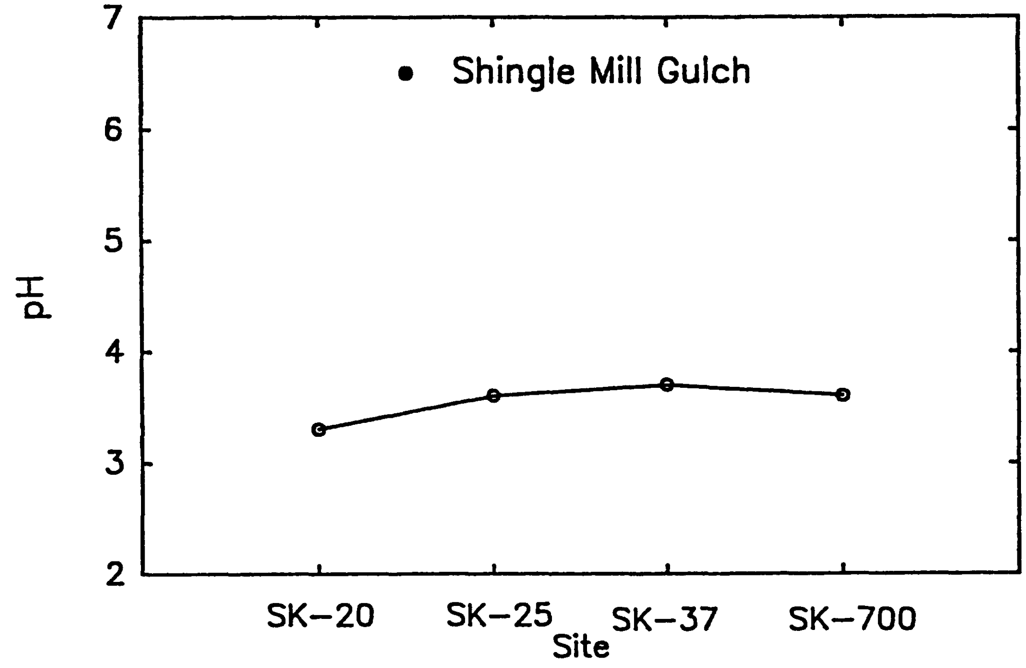

Figure B-30a. – Field-measured pH values in St. Kevin Gulch and Shingle Mill Gulch.

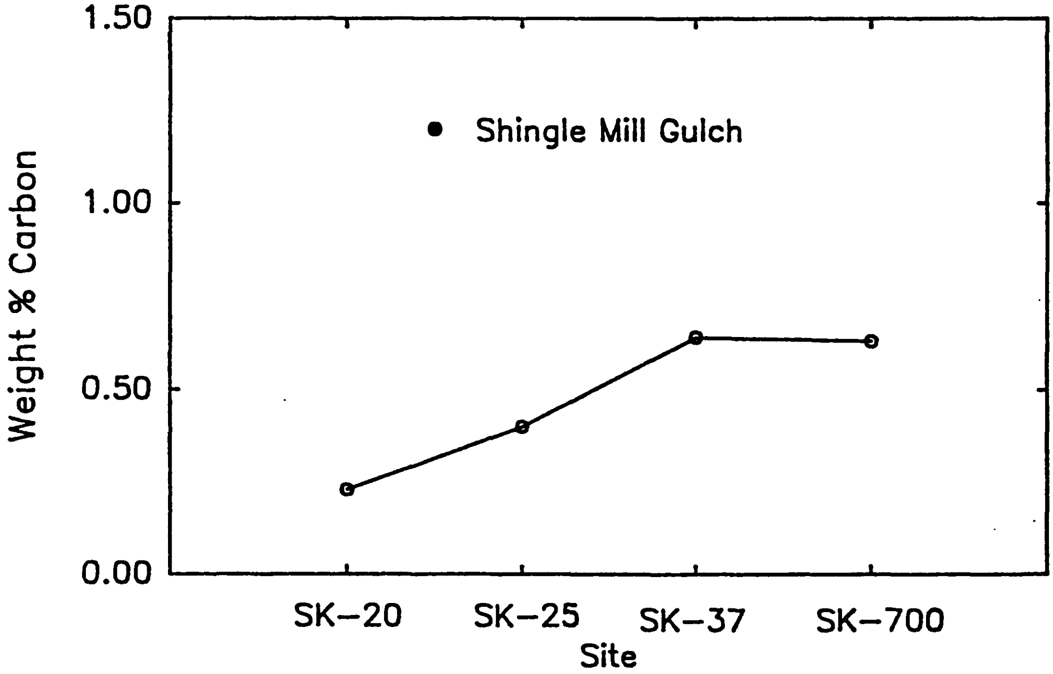

Figure B-30b. – Carbon content of St. Kevin Gulch floc and Shingle Mill Gulch sediment.

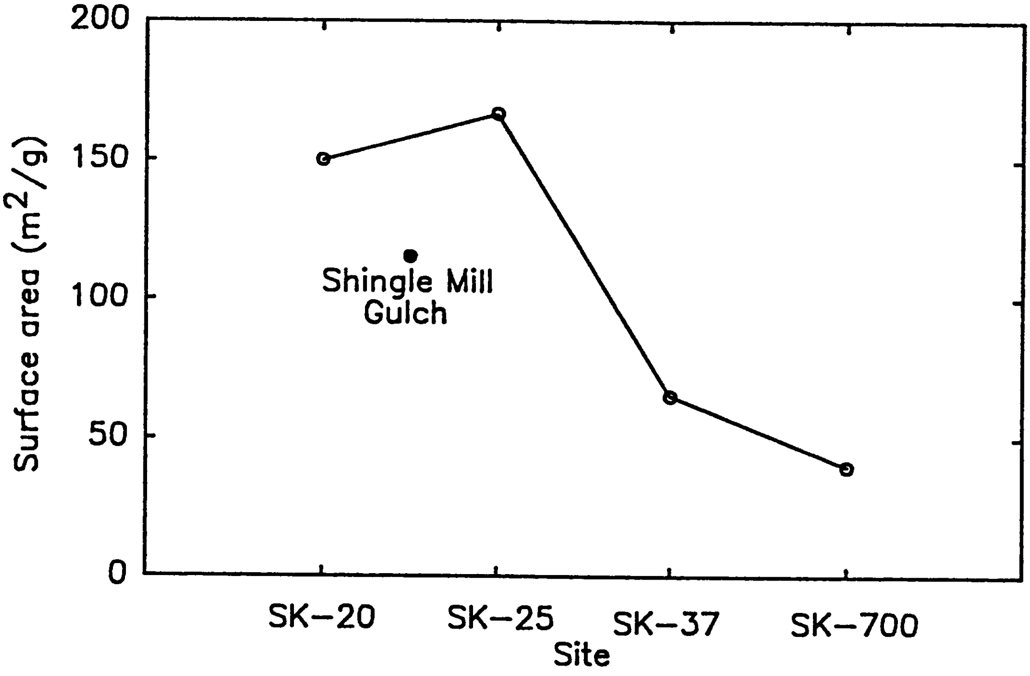

Figure B-30c.—Single-point N_2 adsorption (BET) surface areas of St. Kevin Gulch floc and Shingle Mill Gulch sediment.

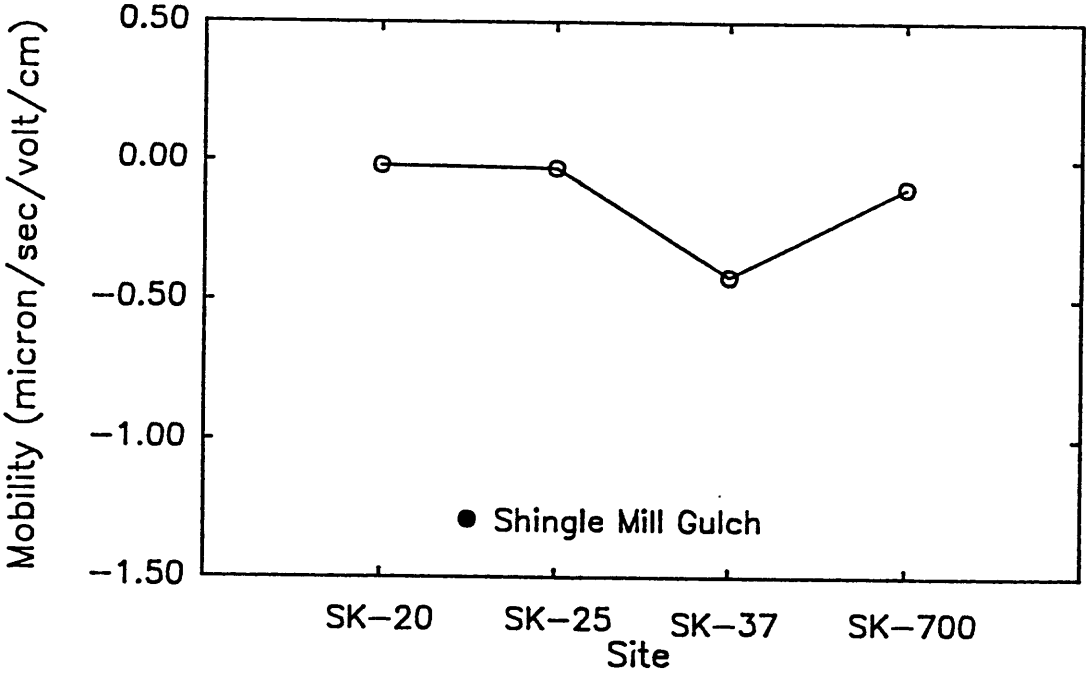

Figure B-30d.—Electrophoretic mobilities of St. Kevin Gulch floc and Shingle Mill Gulch sediment.

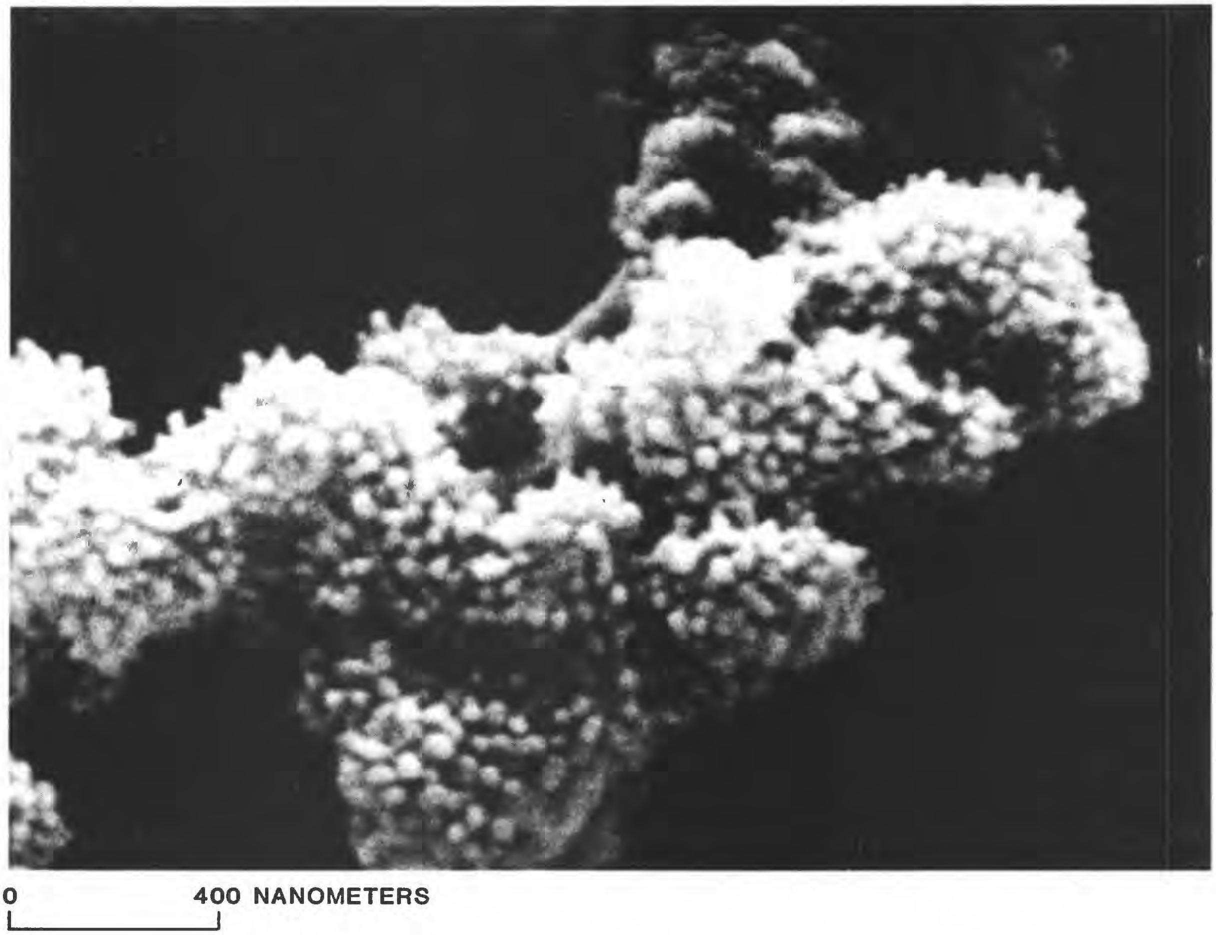

Figure B-31.—SEM photomicrograph of a typical aggregate collected at site SK-25.

phoretic mobility. Such flocculation may be an important process for Fe removal from the stream.

Under the pH conditions (less than 3.8) of St. Kevin Gulch, the floc does not appear to effectively scavenge trace metals (Smith and others, 1989, this Proceedings). Shingle Mill Gulch sediment contains higher concentrations of the minor (Al, Mn, and Zn) and trace (Cu, Pb, and Cd) metals than St. Kevin Gulch floc, perhaps as a consequence of the high pH, high carbon content and/or mineralogy of the Shingle Mill Gulch sediments.

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PRELIMINARY ASSESSMENT OF THE EFFECTS OF ACID MINE DRAINAGE ON GROUND WATER BENEATH A WETLAND NEAR LEADVILLE, COLORADO

By Katherine Walton-Day[1] and Paul H. Briggs[1]

ABSTRACT

St. Kevin Gulch, located west of Leadville, Colorado, is a stream that is affected by acid mine drainage; it drains to the east into a wetland before entering Tennessee Creek and the East Fork of the Arkansas River. Surface- and ground-water samples were collected from the wetland area to allow characterization of the water samples and to determine if ground water has been affected by acid mine drainage. Analyses of the water samples showed that most of the water is a calcium sulfate type, indicating the presence of sulfide mineralization in the study area. Ground-water samples that may have been affected by acid mine drainage are relatively oxidized, contain elevated concentrations of manganese and sulfate relative to other samples, and were collected from the western side of the study area near known areas of mineralization.

INTRODUCTION

Acid mine drainage (AMD) is an environmental problem in the coal mining areas of the Eastern United States and in the base- and precious-metal mining areas of the Western United States. The oxidation of pyrite that commonly is associated with mineral deposits produces elevated concentrations of sulfuric acid, which can mobilize toxic and heavy metals. These metals may drain from the mined areas and enter surface-water systems. In Colorado, 25 watersheds and 450 stream-miles contain no aquatic life and are unfit for beneficial use as a result of toxic drainage from inactive mines (Wentz, 1974).

Recently, several studies conducted in the Eastern United States have shown that routing AMD through natural and manmade wetlands improves the water quality of the AMD (Huntsman and others, 1978; Snyder and Aharrah, 1984; Weider and Lang, 1984; Erickson and others, 1987). Initial studies are being conducted to determine whether the technique will be viable in subalpine environments of the Rocky Mountains (Emerick and Cooper, 1987; Emerick and others, 1987; Wildeman and Laudon, 1988). The results presented here are the initial results from an ongoing study designed to evaluate the treatment effectiveness of a natural wetland receiving AMD in a subalpine environment. Specifically, this paper (1) evaluates the chemical characteristics of some of the surface-water inputs to the wetland and of water in a shallow sand and gravel aquifer beneath the wetland and, (2) assesses whether the ground water has been affected by AMD.

LOCATION AND METHODS

The study area is a wetland approximately 100 acres in size located on the western side of Tennessee Park, northwest of Leadville, Colo. (fig. B–32). The St. Kevin mining district, in the foothills west of the wetland, has been sporadically mined for silver sulfide ore. Tailings piles are located in the valleys containing St. Kevin, Gleason, and Temple Gulches. Although all three gulches have the potential to contribute acid and metals to the wetland, St. Kevin Gulch is the only known source of AMD to the wetland.

In August 1987, 13 shallow observation wells (fig. B–32) were constructed in a sand and gravel aquifer that underlies the wetland. Figure B–33 shows the well design relative to the stratigraphy of the area. The thickness of the peat and clay layers at the site range from 1 to about 4 feet and from zero to 5 feet, respectively. The thickness of the sand and gravel aquifer was not determined. All wells were repeatedly pumped and surged until the water cleared and pH and specific conductance remained constant with continued pumping.

In October 1987, water-quality samples were collected from two of the surface-water sites (Temple and Gleason Gulches), and from 7 of the 13 observation wells (MW-3, MW-5, MW-6, MW-7, MW–8, MW–9, and MW-11). Grab samples were collected from the surface-water sites. Ground-water samples were collected after three-casing volumes were pumped from the wells. Specific conductance and pH were

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

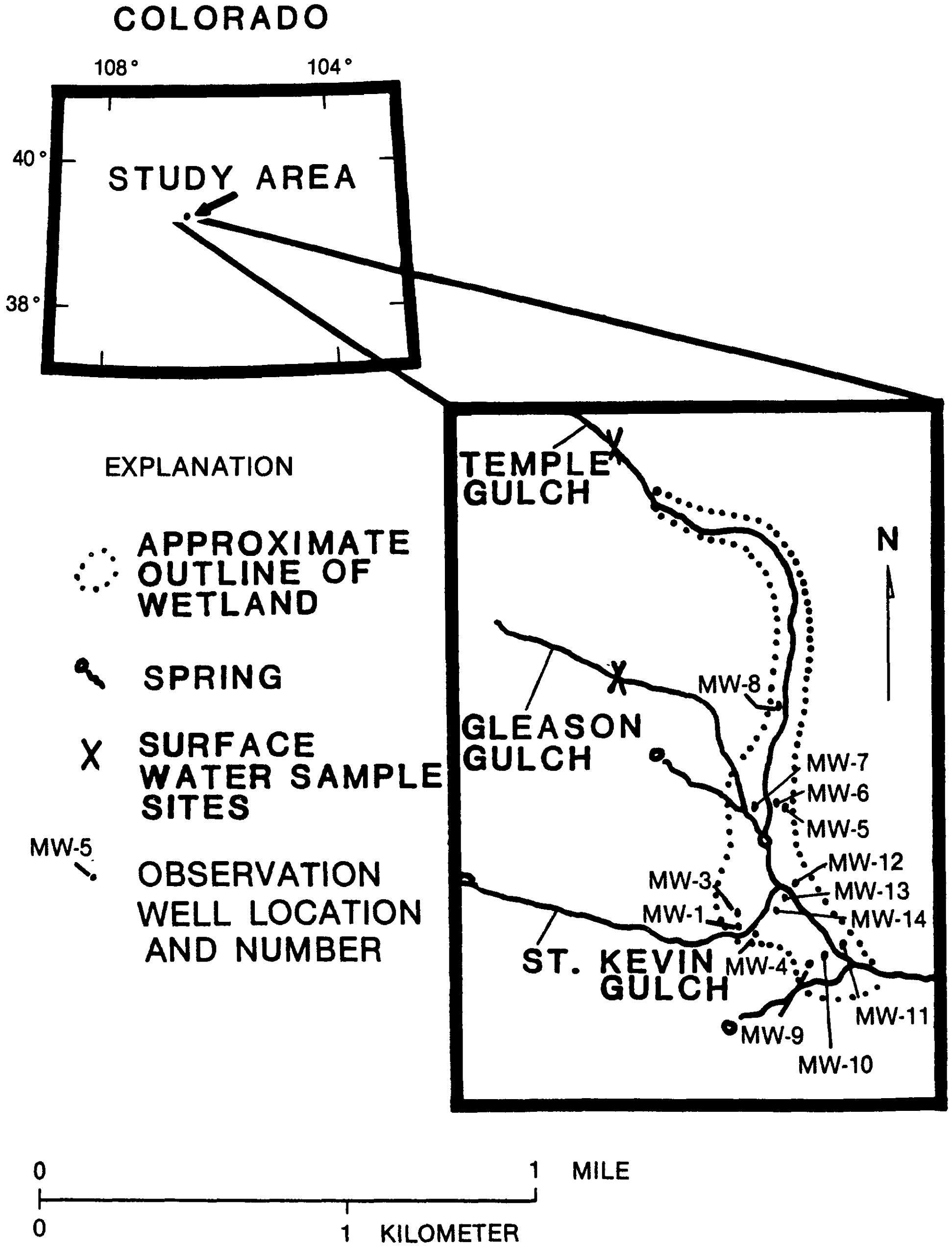

Figure B-32.—Location of study area, surface-water sampling sites, and observation wells.

measured during sample collection. Sample aliquots were filtered through $0.45\text{-}\mu m$ (micrometer) filters for analyses of anions, major cations, and trace metals. Samples for cation and metal analyses were acidified to a pH of less than 2 with nitric acid. Aliquots of raw sample were retained for alkalinity titrations.

Major-cation and trace-metal concentrations were determined using inductively coupled plasma-atomic emission spectrometry. Bicarbonate-ion content was determined using a gran titration (Stumm and Morgan, 1981) the day after sample collection. Other anion concentrations were determined by using an ion chromatograph. Relatively reduced samples were detected by the presence of hydrogen sulfide (H_2S) odor during sample collection.

RESULTS AND DISCUSSION

Analytical results are shown in table B–7 and in figures B–34 and B–35. A Piper plot of the major cations and anions (fig. B–34) shows that there are two types of water in the study area: a calcium sulfate type and a calcium bicarbonate type. Relative cation contents are similar for all samples (fig. B–34). All samples except those

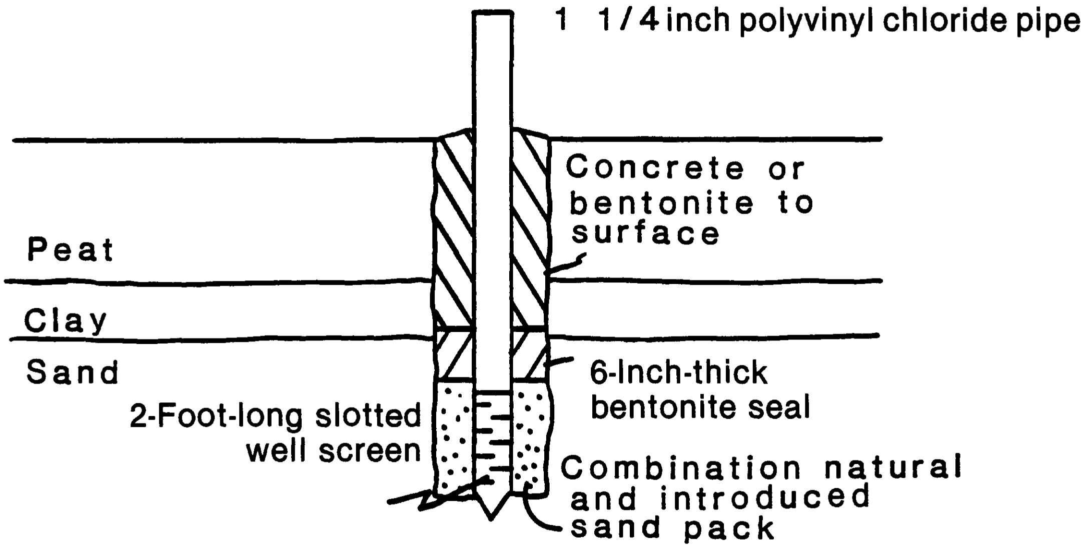

Figure B-33. – Observation-well design at wetland.

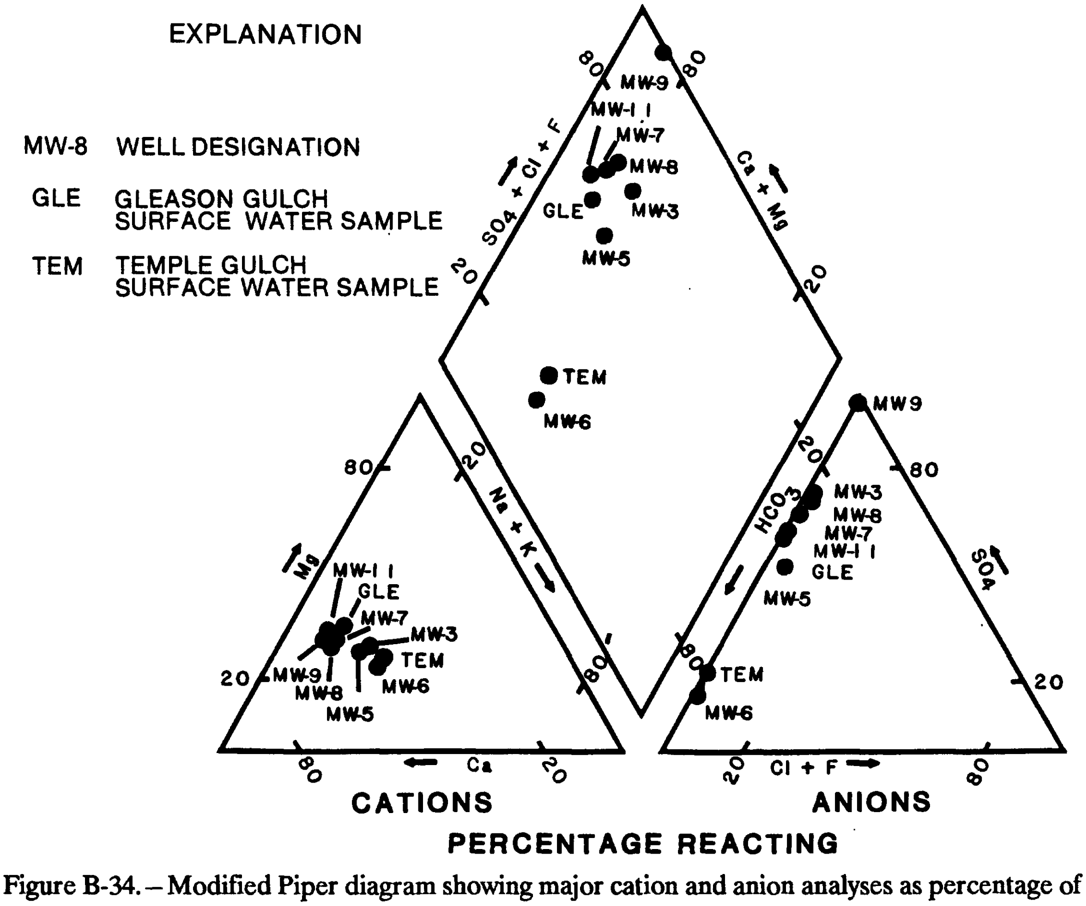

Figure B-34. – Modified Piper diagram showing major cation and anion analyses as percentage of equivalents of total major cation and anion concentrations.

Table B–7. – *Wetland water-quality data, October 1987*

[LD = less than detection; GLE = Gleason Gulch; TEM = Temple Gulch; MW = observation well; cation and trace-metal analyses for MW-6 obtained from sample aliquot filtered through 0.1-µm filter; presence of hydrogen sulfide odor indicated by Y; specific conductance is in microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter]

	Detection limit	Sample								
		GLE	TEM	MW-3	MW-5	MW-6	MW-7	MW-8	MW-9	MW-11
pH		7.23	7.79	6.44	6.34	5.75	5.95	6.06	5.43	6.28
Specific conductance		120	52	350	112	178	278	288	305	225
Calcium, Ca in mg/L	0.02	13.0	4.7	23.1	7.7	14.9	24.7	28.3	26.7	21.5
Magnesium, Mg in mg/L	.01	5.4	1.6	8.1	2.4	4.1	7.9	8.5	8.6	7.1
Sodium, Na, in mg/L	.2	3.5	2.7	11.0	3.4	9.1	6.3	7.3	4.4	3.1
Potassium, K in mg/L	.1	1.3	1.1	1.7	.5	1.1	1.2	1.5	1.9	2.1
Iron, Fe in mg/L	.1	LD	.5	9.8	7.1	13.7	1.1	10.2	.5	4.5
Manganese, Mn, in µg/L	1	2.5	11	749	585	424	18	362	603	541
Aluminum, Al in mg/L	.1	LD	LD	LD	.3	.6	LD	LD	.2	LD
Cadmium, Cd in µg/L	1	LD	LD	LD	LD	LD	LD	LD	LD	LD
Copper, Cu in µg/L	10	LD	LD	LD	LD	LD	LD	LD	LD	LD
Nickel, Ni in µg/L	5	LD	LD	LD	LD	LD	8.9	LD	6.1	LD
Cobalt, Co in µg/L	3	LD	LD	LD	LD	LD	3.4	LD	4.1	LD
Lead, Pb in µg/L	10	LD	LD	LD	LD	LD	LD	LD	LD	LD
Zinc, Zn in µg/L	3	243	12	46	18	11	20	6	188	LD
Sulfate, SO_4 in mg/L	1.0	27.9	4.0	62.0	13.7	5.8	47.0	56.7	70.1	42.1
Chloride, Cl in mg/L	.1	LD	LD	LD	1.0	.1	LD	LD	LD	LD
Fluoride, F in mg/L	.1	LD	LD	LD	LD	.1	.3	LD	LD	LD
Bicarbonate, HCO_3 in mg/L	.5	23.9	18.3	30.1	14.4	41.5	28.5	29.5	.9	31.4
Hydrogen sulfide odor					Y	Y	Y	Y		Y

from Temple Gulch and MW–6 contain greater proportions of sulfate than bicarbonate.

The predominance of sulfate in most of the water samples collected in the area is related to the metal sulfide mineralization occurring in the St. Kevin mining district. The location of the greatest concentrations of sulfate on the southwestern side of the area (fig. B–35), closest to known sulfide mineralization, supports this idea. Sulfate contributions may result from the natural weathering of pyrite-rich mineral deposits in the area or from accelerated weathering of the deposits caused by mining activities. The elevated sulfate concentration in MW–8, upgradient from St. Kevin Gulch, seems anomalous. However, tailings piles in Gleason and Temple Gulches indicate the presence of mineralization and, therefore, sources of sulfate upgradient from MW–8.

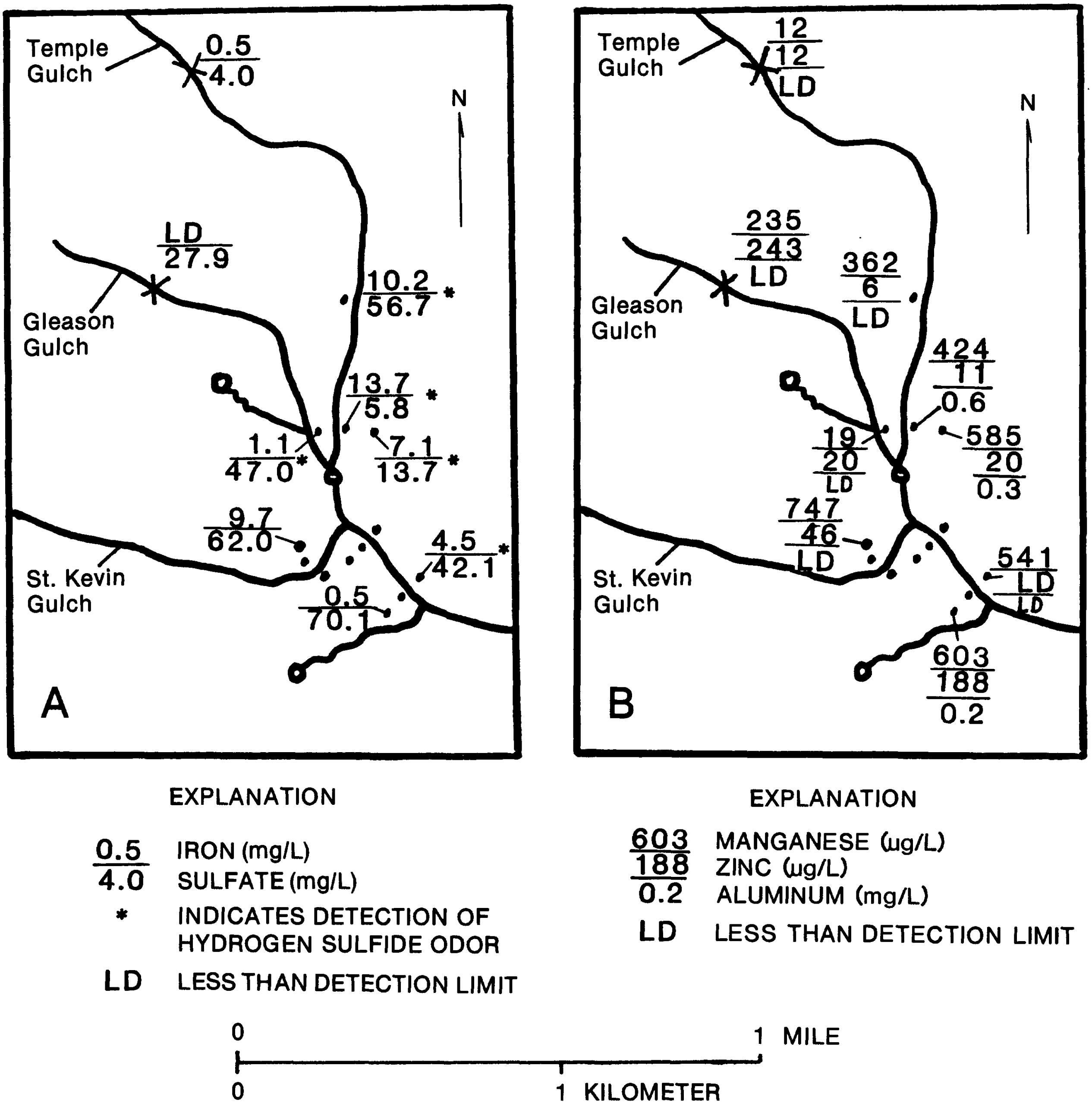

Figure B-35.—Areal distribution of: (A) iron and sulfate concentrations and sites of hydrogen sulfide odor detection, and (B) manganese, zinc, and aluminum concentrations. See figure B–32 and table B–7 for sample locations and data values.

St. Kevin Gulch waters exhibit elevated concentrations of iron, manganese, zinc, aluminum, cadmium, and copper (Kimball and others, 1988). Accordingly, surface and ground waters in the area that are affected by mine drainage from St. Kevin Gulch should have similar metal signatures. However, the greatest iron and manganese concentrations are associated with the relatively reduced samples in the eastern and northern parts of the wetland, rather than in areas near the mining area west of the wetland (fig. B–35). Exceptions to this trend are MW–3, which is relatively oxidized and contains the third highest concentration of iron and the highest concentration of manganese, and MW–9, which is relatively oxidized and contains the second highest manganese concentration. The greatest zinc concentrations are found at Gleason Gulch and MW–9, probably as a result of mining activities. Concentrations of copper and cadmium are below the detection limits of 10 and 1 μg/L (micrograms per liter), respectively, in all samples. The aluminum in MW–9 may indicate that ground water has been contaminated by AMD from St. Kevin Gulch. However, the aluminum in MW–5 and MW–6, which are north of and presumably upgradient from St. Kevin Gulch, probably results from natural weathering processes rather than from contamination of ground water by surface AMD. The proximity of MW–3 to St. Kevin Gulch supports the possibility that the observed metal concentrations result from contamination. Color patterns observed on the land surface between St. Kevin Gulch and MW–9 indicate the presence of shallow ground-water conduits between the two locations. In addition, the low pH, low bicarbonate-ion content, and fairly high specific conductance of water at MW–9 (table B–7) support the hypothesis of ground-water contamination by AMD. Therefore, contamination of ground water in the study area by AMD occurs at MW–3 and MW–9 and is characterized by oxidized waters containing relatively large concentrations of manganese and sulfate; concentrations of other trace metals show no pattern that can be used to relate their concentrations to contamination of ground water by AMD.

CONCLUSIONS

Two types of water occur in the study area: a calcium-sulfate type and a calcium-bicarbonate type. Most of the samples collected from the study area are calcium-sulfate type. The predominance of sulfate indicates the presence of metal-sulfide mineralization in the study area. Ground water that may have been contaminated by AMD from St. Kevin Gulch (1) is present on the western side of the study area, near areas of mineralization, (2) appears to be relatively oxidized, and (3) contains elevated concentrations of sulfate and manganese.

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HYDROXYL RADICAL FORMATION IN ST. KEVIN GULCH, AN IRON-RICH STREAM IN COLORADO

By A.C. Sigleo[1], K.M. Cunningham[1], M.C. Goldberg[1], and Briant A. Kimball[1]

ABSTRACT

Water samples were collected from St. Kevin Gulch, a tributary of Tennessee Creek and the Arkansas River, Colorado. This stream is affected by acid leachates from mine tailings and contains large concentrations of ferric iron that may provide a reactant for the photolytic production of hydroxyl radicals. Water samples were irradiated in a photoreactor with an average incident ultraviolet (300–400 nanometers) photon flux of $4.5x10^{-4}$ Einsteins per minute. Samples containing an iron concentration of 0.03 milligrams per liter had a steady-state hydroxyl radical concentration of $4x10^{-15}$ moles per liter, whereas water containing 11 milligrams per liter iron had a steady-state hydroxyl radical concentration of $2x10^{-13}$ moles per liter. The latter value is unusually large for a natural water sample. The relation between steady-state hydroxyl radical concentration and total dissolved and colloidal iron concentration appears to be linear. These results may indicate that photolytic reduction of ferric iron is a major source of hydroxyl radicals in this stream.

INTRODUCTION

A recent study at St. Kevin Gulch, Colo., a stream affected by acidic effluent from mine tailings, has shown that ferric iron in streamwater can be photolytically reduced to Fe^{+2} (McKnight and others, 1988). Because Fe^{+2} is a soluble species, photochemical iron reduction can increase the concentration of dissolved iron in solution and, thus, increase the stream transport of iron. During abiotic photochemical iron reduction under acidic conditions, a hydroxyl radical [$\cdot OH$] is formed directly or indirectly as shown in the following reactions (David and David, 1976; Waite and Morrell, 1984):

1. Direct photoreduction of $\cdot OH$ from iron species in solution or at mineral surfaces, where $>Fe$ represents a bound iron species at the oxide-solution interface, and hv refers to photon energy:

$$\text{(a)} \qquad FeOH^{+2} + hv \rightarrow \underset{\text{(aqueous)}}{Fe^{+2}} + \cdot OH$$

$$\text{(b)} \quad >Fe(III){:}OH^{-} + hv \rightarrow \underset{\text{(mineral surface)}}{>Fe(II)} + \cdot OH$$

$$>Fe(II) \leftrightarrow \underset{\text{(aqueous).}}{Fe^{+2}}$$

In addition to the direct photoredox reactions above, another source of $\cdot OH$ can be the oxidation of photoreduced Fe^{+2} through the Haber-Weiss reaction sequence, which is accelerated by the presence of Fe^{+3} oxides (Weiss, 1935; Tamura, 1980).

2. Indirect photoreduction of $\cdot OH$, where $>Fe$ represents a bound iron species at the oxide-solution interface, and R^{-} represents a sorbed carboxylate from natural organic materials (Loder and Liss, 1985):

$$>Fe(III){:}R^{-} + hv \rightarrow >Fe(II) + R\cdot$$

$$>Fe(II) \leftrightarrow Fe^{+2}$$

$$Fe^{+2} + O_2 \leftrightarrow Fe^{+3} + O_2^{-} \text{ (slow)}$$

$$Fe^{+2} + O_2^{-} + 2H^{+} \rightarrow Fe^{+3} + H_2O_2 \text{ (fast)}$$

$$2H^{+} + 2O_2^{-} \rightarrow H_2O_2 + O_2$$

$$Fe^{+2} + H_2O_2 \rightarrow \cdot OH + OH^{-} \text{ (slow).}$$

This paper reports the results of measurements of hydroxyl radical using n-butylchloride as a hydroxyl radical probe to give unambiguous evidence of its presence (Haag and Hoigne, 1985). Of the free radical products likely to be found in aquatic environments, the most reactive is the hydroxyl radical, which can extract a hydrogen atom from a carbon-hydrogen bond and add to aromatic rings and double bonds (Farhataziz and Ross, 1977). Recent interest in photochemical reactions by environmental chemists is because of the ability of photochemically induced radicals, such as $\cdot OH$, to degrade organic pollutants (Zepp and others, 1987).

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

SAMPLING STATIONS

Samples were collected October 30, 1987, from three stations along St. Kevin Gulch. Station SK–20 was located just below the confluence of the mine-tailings effluent and the stream (fig. B–36). The effects of acid mine drainage at the second station, SK–50, located about 1 km (kilometer) below the first station, were considerably diluted. The third station, SK–60, was located about 1.5 km below the second station in a marsh just before St. Kevin Gulch enters Tennessee Creek, a tributary of the Arkansas River. The last site shows no apparent effects of acid mine drainage.

METHODS

The samples from St. Kevin Gulch were irradiated for 30 minutes to 6 hours at 20 °C (degrees Celsius) in a water-jacketed Pyrex[2] cell in a Rayonet-type photoreactor with RPR 3500 fluorescence lamps that had a light spectrum in the range of 300 to 400 nm (nanometers). The reactor produced an incident light flux of $4x10^{-4}$ Einsteins per minute. Hydroxyl radicals were measured by adding a radical scavenger compound, n-butylchloride, that reacts rapidly with hydroxyl radicals at a concentration of 2 µmol/L (micromoles per liter) (Haag and Hoigne, 1985). The difference in the initial and final concentrations of the scavenger reflect

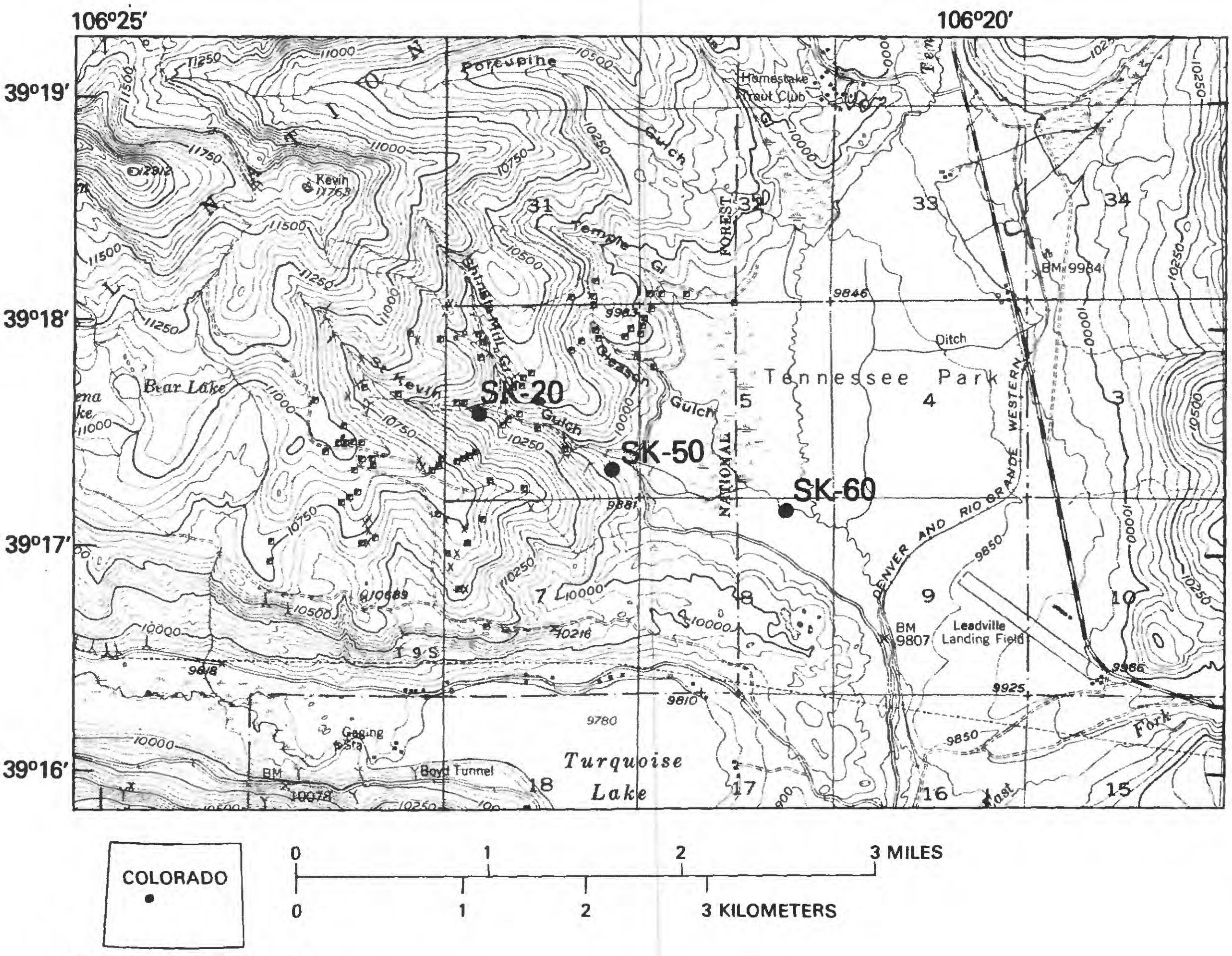

Figure B-36. – Sampling stations.

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

consumption of the scavenger by hydroxyl radicals. The n-butylchloride in this study was measured by gas chromatography using a flame ionization detector after extraction by a purge-and-trap device. Iron was analyzed colorimetrically using 2,2′-bipyridine (Moss and Mellon, 1942).

RESULTS AND DISCUSSION

The concentration of total iron in filtered (0.01 μm (micrometer)) St. Kevin Gulch water is a maximum of 11 mg/L (milligrams per liter) where effluent from mine tailings enters the stream (station SK–20), and rapidly decreases downstream because of precipitation and dilution (table B–8). Precipitation of ferric hydroxides is visually apparent as red-brown coatings on the streambed and by red-brown flocs in the stream. The pH increases from 3.4 at station SK–20 to 6.5 at SK–60 by dilution from incoming streams. Increasing pH affects both the concentration of total dissolved iron, the speciation of dissolved iron, and the nature of surface complexes with ·OH and R˙.

Table B-8.—*Iron (Fe) and hydroxyl radical ($[\cdot OH]_{ss}$) concentrations in St. Kevin Gulch water*

[mg/L, milligrams per liter; mol/L, moles per liter]

Station	Fe total (mg/L)	pH	$[\cdot OH]_{ss}$ (mol/L)
SK–20	10.98	3.4	$2\mathrm{x}10^{-13}$
SK–50	1.18	3.7	$3\mathrm{x}10^{-14}$
SK–60	.03	6.5	$4\mathrm{x}10^{-15}$

The ratio of the initial and final concentrations of the radical trap n-butylchloride as a function of photon irradiation is illustrated in figure B–37 for the three stream samples. The sample from SK–20 had the most rapid decrease in n-butylchloride as a function of absorbed photons, indicating that this sample had the largest concentration of hydroxyl radicals relative to water from the other two stations. The steady-state concentration of photolytically produced hydroxyl radicals ($[\cdot OH]_{ss}$) in waters collected

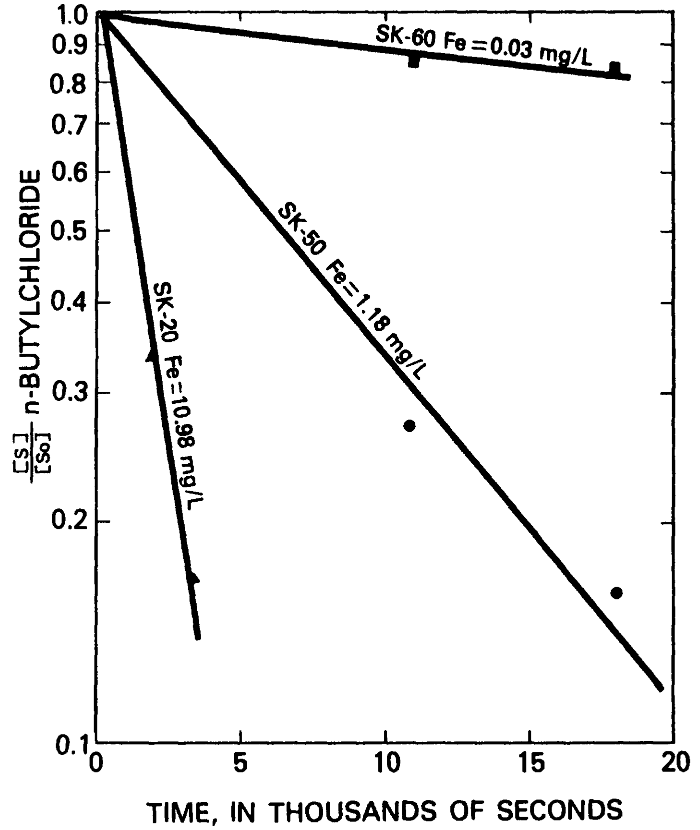

Figure B-37.—The decrease in the scavenger n-butylchloride with respect to time in the irradiated stream samples.

from St. Kevin Gulch ranged from 4x10^{-15} mol/L (moles per liter) in water containing 0.03 mg/L iron to 2x10^{-13} mol/L in a sample containing 11 mg/L iron (table B–8). The latter value of $[\cdot OH]_{ss}$ is unusually large for a natural water sample after ultraviolet-lamp irradiation in the laboratory. Previously, Haag and Hoigne (1985) reported a value of 0.7±0.3x10^{-14} mol/L in Swiss lake water irradiated in the laboratory using n-butylchloride as a radical trap. Mill and others (1980), using 10^{-4} mol/L cumeme as a radical trap reported a $[\cdot OH]_{ss}$ of about 10^{-17} mol/L in lake and river samples, and Russi and others (1982), using 10^{-5} mol/L benzene as a trap, estimated a $[\cdot OH]_{ss}$ of 5x10^{-16} mol/L.

There was an apparent linear relation ($r^2 = 0.995$) between the amount of iron in the sample and the steady-state concentration of hydroxyl radicals in the samples (fig. B–38). A number of solution components not investigated here also influence the production of hydroxyl radicals. These compounds include dissolved nitrate and organic compounds (Zepp and others, 1987). In this stream, nitrates are below the detection limit and organic compounds are present in low concentrations (0.5 mg/L at SK–50), with the possible exception of SK–60, where there was relatively little ·OH production (McKnight and others, 1988). The relation between iron concentrations and $[\cdot OH]_{ss}$ indicate that in streams containing high concentrations of iron, abiotic photolysis, as measured by the steady-state hydroxyl radical concentration, may be correlated with the presence of dissolved and colloidal iron.

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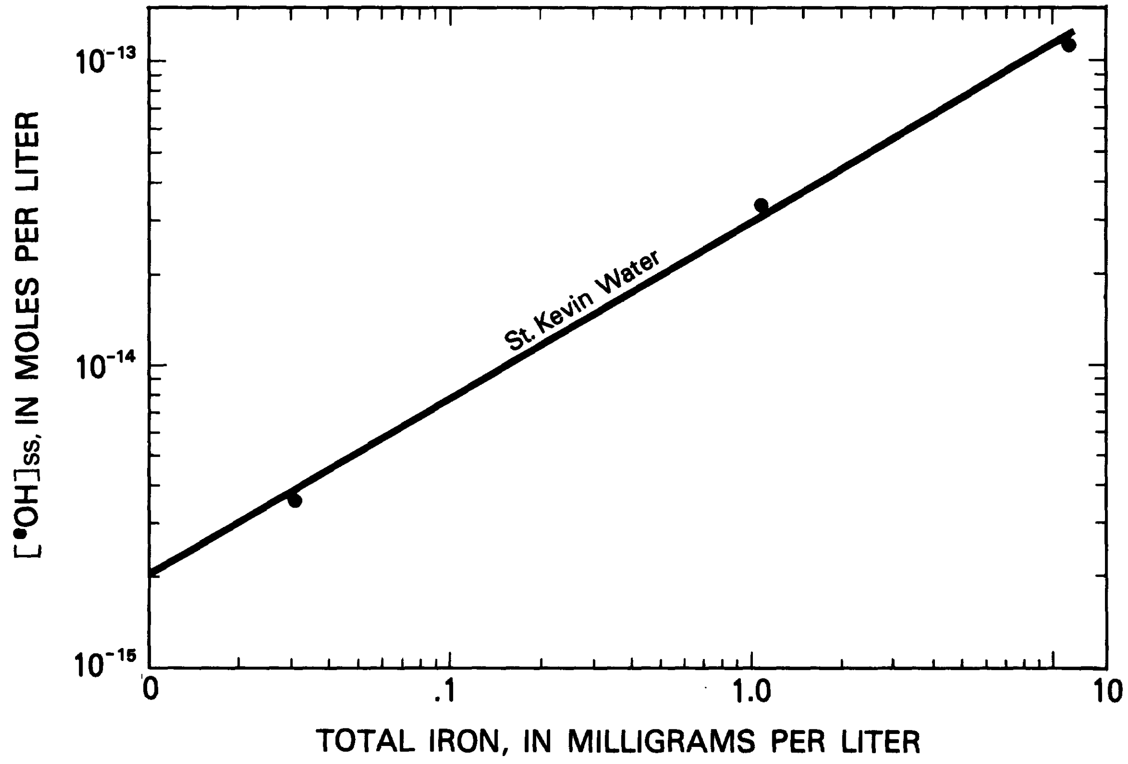

Figure B-38.—Steady-state hydroxyl radical production as a function of iron concentration in water from St. Kevin Gulch.

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(p. 131 follows)

CHAPTER C – SEWAGE-CONTAMINATED GROUND WATER ON CAPE COD, MASSACHUSETTS

(p. 133 follows)

OVERVIEW OF CONTAMINANT HYDROLOGY, GEOCHEMISTRY, AND MICROBIOLOGY AT THE CAPE COD TOXIC WASTE RESEARCH SITE

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

ABSTRACT

An overview of past and current research on contaminant hydrology, geochemistry, and microbiology is presented for the Cape Cod Toxic Waste Research site. Past research efforts have focused on the definition and description of the extent of contaminants in a sewage plume originating from the Otis Air Base sewage treatment facility. Current research at the site includes efforts to use tracer tests and other in situ *measurement techniques to quantify the processes affecting the fate and transport of sewage contaminants in the aquifer.*

INTRODUCTION

The U.S. Geological Survey's Cape Cod Toxic Waste Research site is located in the northern part of Falmouth, Mass., on Cape Cod (fig. C-1). This site is the focus of research on the geologic, hydrologic, and chemical processes that affect the movement of contaminants in a sewage plume originating from Otis Air Base. It was selected for study as part of a nationwide program of the U.S. Geological Survey to describe the fate of contaminants in the subsurface. The purpose of this paper is to review the research effort at the Cape Cod site and to introduce the research topics discussed in the following papers.

SITE DESCRIPTION

The study area is on a broad sand and gravel outwash plain that was formed during the last Pleistocene glacial retreat. The outwash plain slopes southward to Nantucket Sound and is pitted with many kettle holes, some of which contain ponds. The area contains several valleys that transect the plain from north to south. Most of these valleys, which typically are 150 to 270 meters wide and 10 meters deep, do not contain streams but have wetlands at their southern ends.

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

On the basis of measured values for similar sediments on Cape Cod, LeBlanc (1984a) estimated that the horizontal hydraulic conductivity of sand and gravel in the study area ranges from 60 to 90 m/d (meters per day). Results of an aquifer test conducted in the study area in 1984 indicated that the horizontal hydraulic conductivity of the sand and gravel was about 120 m/d (Garabedian, 1987). The horizontal hydraulic conductivity of the fine sand and sandy till is estimated to be about one-tenth that of the sand and gravel (LeBlanc, 1984c). The crystalline bedrock is assumed to have a very low hydraulic conductivity; therefore, the bedrock surface is considered to be the bottom of the regional ground-water flow system.

Ground water in the unconsolidated sediments is under unconfined (water table) conditions in the study area. The water table slopes toward the south, southwest at about 1.5 m/km (meters per kilometer) (fig. C-3). Water-table altitudes shown in figure C-3 are near the average for the period 1963-76. Seasonal variations in aquifer recharge produce an annual water table fluctuation of 0.3 to 0.9 meter; the highest levels are in the spring and lowest are in the fall.

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

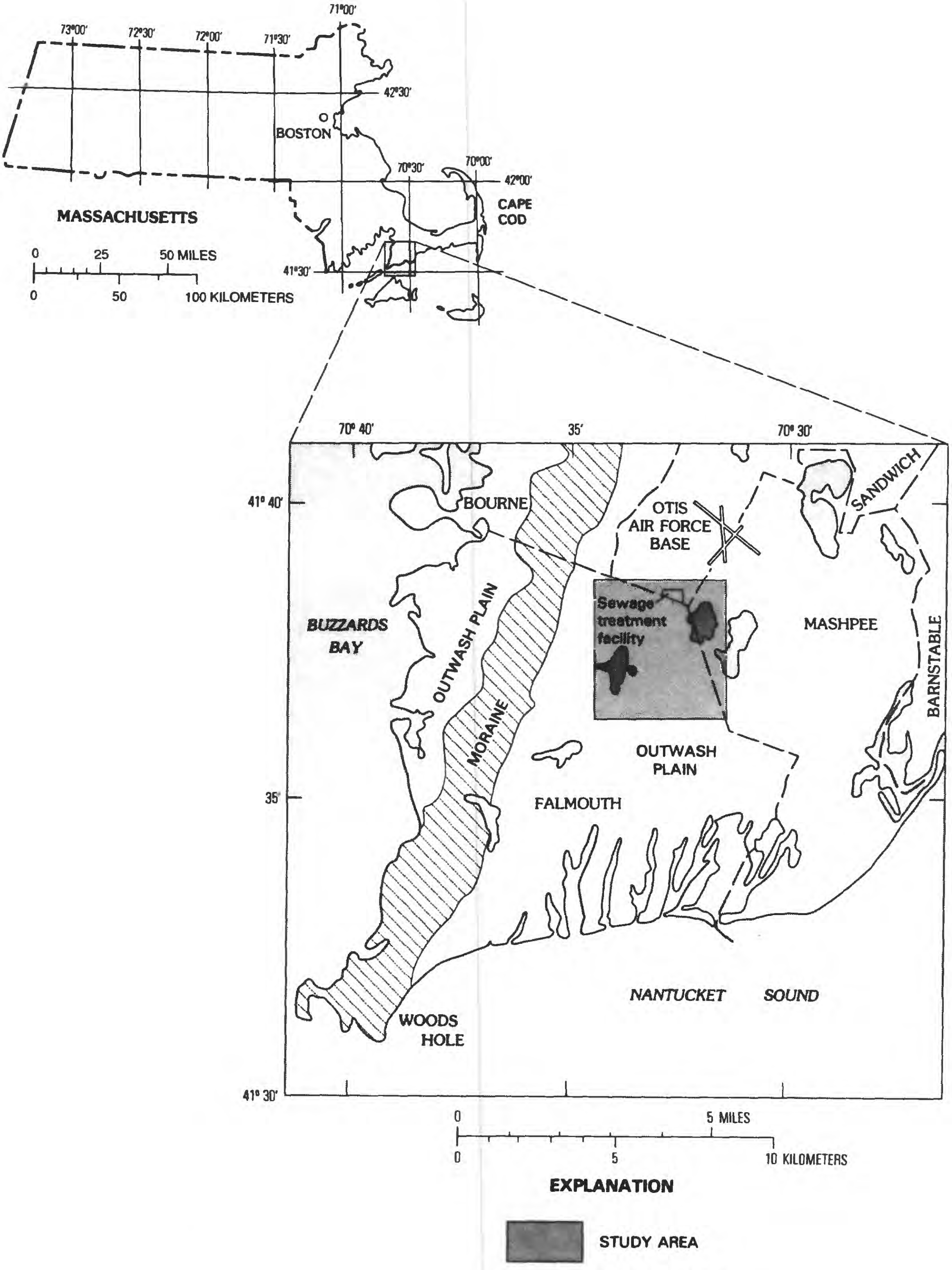

Figure C-1.—Study area.

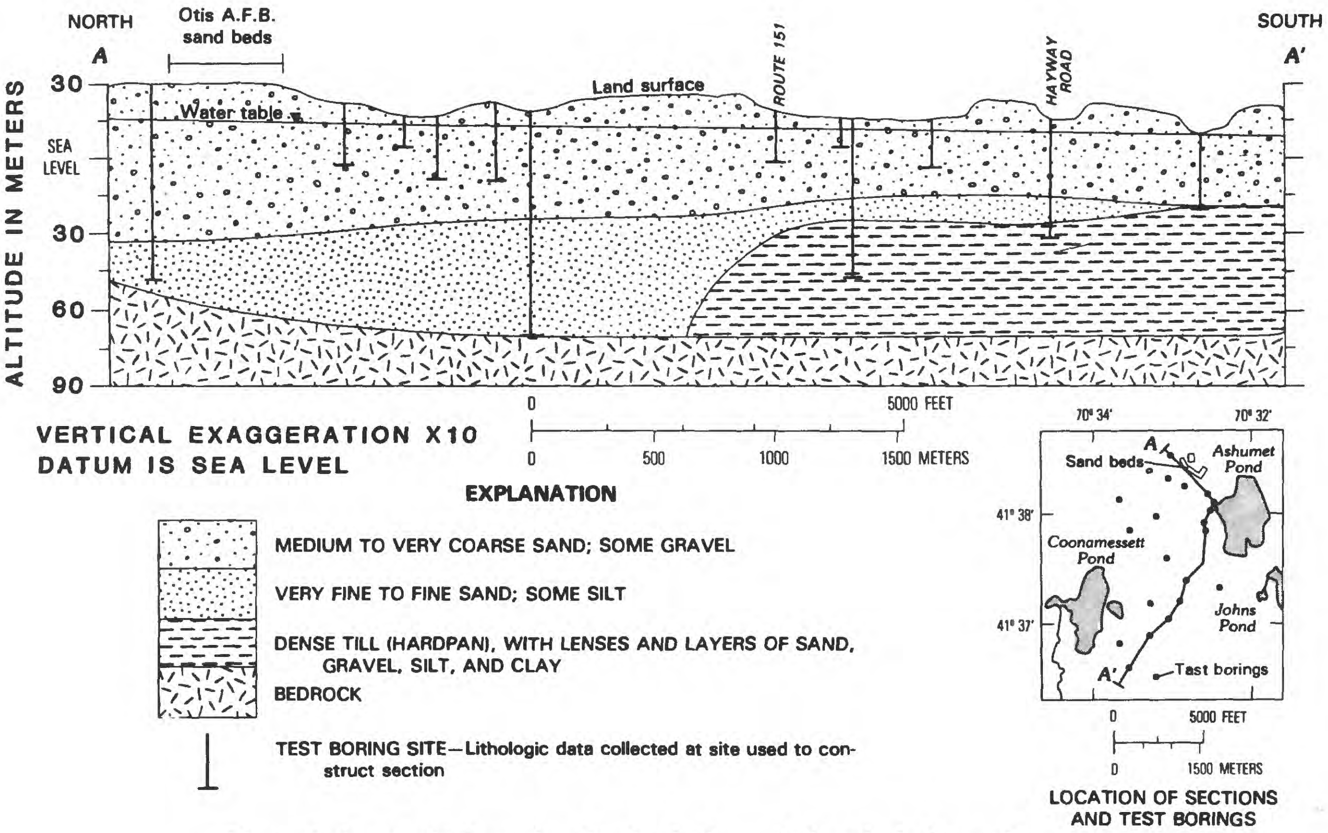

Figure C–2.—Geologic section showing hydrogeologic units in the study area.

Ground-water recharge to the study area occurs primarily from precipitation and underflow from upgradient areas. Little surface-water runoff occurs because the sandy soils are very permeable. Estimated recharge to the aquifer is 0.5 m/yr (meters per year), about 45 percent of the total precipitation (LeBlanc, 1984a). Estimated rates of horizontal ground-water velocity in the sand and gravel range from 0.2 to 0.7 m/d (LeBlanc, 1984a). These estimates are based on an average hydraulic gradient of 1.5 m/km, a hydraulic conductivity from 60 to 90 m/d, and a porosity from 20 to 40 percent.

DESCRIPTION OF SEWAGE PLUME

LeBlanc (1984a) described the extent of contamination in the aquifer caused by sewage disposal at Otis Air Base (fig. C-1). In 1979, the plume of contaminated ground water, formed by the disposal of secondarily treated sewage onto rapid infiltration beds since 1936, was 0.8 to 1.1 km (kilometers) wide, 23 meters thick, and more than 3.4 km long (fig. C-3). The plume moves in the direction of ambient flow to the south and southwest and is overlain by up to 15 meters of uncontaminated ground water derived from precipitation that recharges the aquifer.

The plume of sewage-contaminated ground water is characterized by elevated concentrations of dissolved solids, boron, chloride, sodium, phosphorus, ammonium, nitrate, detergents (LeBlanc, 1984a) and, in some locations, volatile organic compounds (VOC) (Thurman and others, 1984). Boron (fig. C-3), chloride, and sodium appear to be moving conservatively and attenuated primarily by hydrodynamic dispersion. Phosphorus (fig. C-3) movement is greatly retarded by colloidal precipitation (Gschwend and Reynolds, 1987) and adsorption onto the sediments. Although a maximum nitrate concentration of 16 mg/L (milligrams per liter)(as nitrogen (N)) has been detected in the sewage effluent, the concentration in the center of the plume is 3.2 mg/L (Ceazan and others, 1984). Within 1.5 km of the disposal beds, the predominant nitrogen species in the plume is ammonium. At 1.8 km from the beds, the predominant nitrogen species is nitrate. This

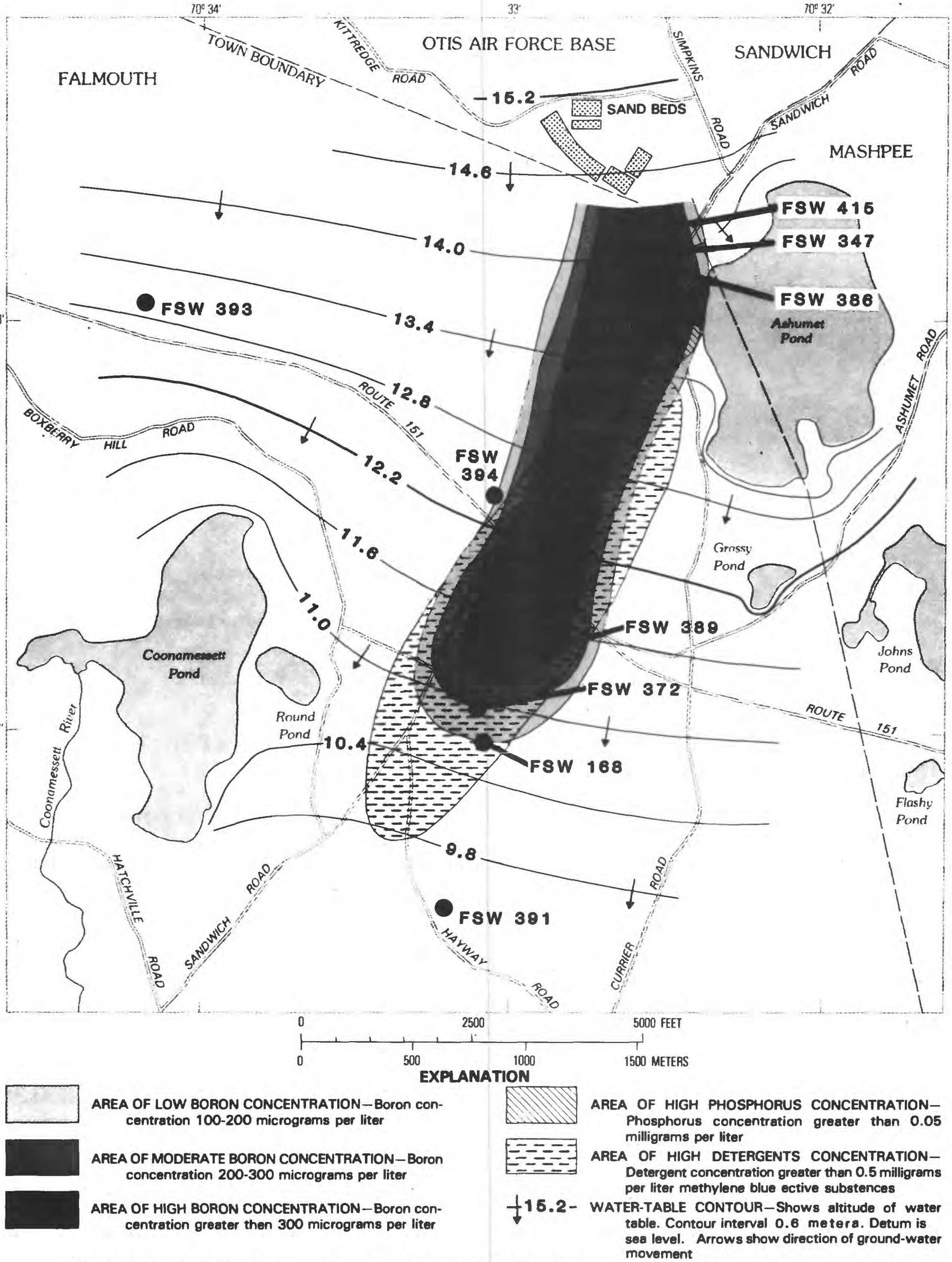

Figure C–3.—Relation between the water table and the distributions of boron, phosphorus, and detergents in the plume in 1978–79. (From LeBlanc, 1984a.)

distribution of ammonium is caused, in part, by adsorption onto the aquifer sediments (Ceazan, 1987), and thus retards the movement of ammonium. Detergent concentrations exceed 0.5 mg/L methylene-blue-active substances (MBAS) from 0.9 to 3.0 km downgradient from the sewage infiltration beds (fig. C-3). This distribution of detergents reflects the use of nonbiodegradable detergents on the base during 1946-64 (LeBlanc, 1984a). Elevated VOC concentrations are present in two zones, one which is immediately downgradient from the disposal beds and the other more than 1 km downgradient. The source of the VOC immediately downgradient from the disposal beds is still under investigation because the VOC are found below the sewage contamination. However, the more downgradient VOC plume is thought to originate from the sewage treatment facility because the VOC are found in the sewage plume itself.

INITIAL PHASE OF RESEARCH

In the first phase of research sponsored by the Toxic Waste Hydrology Program, which is described in LeBlanc (1984b) and Ragone (1988), hypotheses concerning transport of contaminants were proposed and began to be tested. During this phase, transport of boron and detergents was simulated with a two-dimensional numerical model, and wells were drilled and sampled for major inorganic contaminants, organic compounds, and indigenous bacteria.

LeBlanc (1984c) simulated the transport of boron using a two-dimensional method-of-characteristics solute-transport model. Although a comparison of the simulated and the observed plumes indicates that the general flow path was closely matched, the observed and simulated concentrations generally did not agree. This lack of agreement reflects the inadequacy of the two-dimensional model in describing the movement and spreading of contaminants through the aquifer. As precipitation percolates to the water table and recharges the aquifer, the plume sinks with very little vertical mixing. Because the model treats the system as fully mixed over the thickness of the aquifer, it predicts a much more rapid decrease in solute concentration downgradient from the infiltration beds than actually occurs. Accordingly, it was concluded that a three-dimensional model was needed to simulate the transport of contaminants through the aquifer accurately.

Sampling during 1983 and 1984 confirmed the earlier findings by LeBlanc in 1979 for inorganic constituents and identified the presence of VOC in the sewage plume (Thurman and others, 1984). Concentrations of these toxic organic compounds exceeded 50 μg/L (micrograms per liter) in a zone 500 to 2,600 meters from the infiltration beds, which suggested that the VOC are mobile and not readily degraded in the sandy aquifer. Trichloroethene, tetrachloroethene, and dichlorobenzene had traveled farther than did nonylphenol (a semivolatile organic compound) in agreement with estimated retardation rates based on hydrophobicity of the compounds (Barber and others, 1988). However, the relative importance of changes in the concentration of these compounds in the sewage, their retardation by adsorption on the sediments, and their biodegradation were not known. Elevated VOC concentrations were discovered near the sewage beds later in the study (E.C. Jordan, Inc., written commun., 1986).

Bacterial populations were also measured in the plume for the first time in 1983. Bacterial populations were found to be as large as 2 mil/mL (million per milliliter) near the infiltration beds and then decreased to about 250,000 mL (milliliter) 1 km from the beds (Harvey and others, 1984). These numbers appear to correlate with the availability of degradable organic compounds; concentrations of dissolved organic carbon 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 μm (micrometers) in diameter, also suggested that transport and filtering of bacteria is occurring.

Measurements of rates of microbial activity in the plume also were included in the first phase of research (Smith and Duff, 1988a, b). Assays of microbial activity were made of water and sediments because more than 90 percent of bacteria were found to be attached to silt- and clay-sized particles. Results of these efforts have shown that rates of microbially mediated denitrification were greatest in water and sediment samples collected from a 1- to 2-meter-thick zone near the top of the plume.

CURRENT RESEARCH

Observed distributions of contaminants and bacteria were used in the first phase of research to infer major processes that affect the transport and attenuation of contaminants in the plume. Two factors limited adequate testing of these hypotheses: First, the history of chemical quality of the sewage plant effluent is largely unknown; second, methods to measure rates of dispersion and reactions in the aquifer were 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 has focused on the development and use of field tracer experiments and specialized sampling methods to improve an understanding of transport processes.

Sixteen tracer tests have been conducted at the Cape Cod site from 1984 to 1987 (table C-1). These tests have included nine forced-gradient and seven natural-gradient experiments. The forced-gradient tests have included three doublet-well tests, in which the rate of injection in one well and the rate of pumping in the other well were about the same; a convergent test, where the withdrawal rate at the pumped well is large and the injection rate at the injection well is relatively small and of short duration; and five divergent tests, in which the injection rate is high and the withdrawal rate (through sampling ports in a multilevel sampler) are small. The six forced-gradient tests conducted during 1984 were used to obtain estimates of porosity and a qualitative understanding of aquifer heterogeneity, and to develop and test equipment needed for a future, larger-scale tracer test (Garabedian, 1987).

A small-scale natural-gradient test was conducted in early 1985 at the location of the large-scale test to obtain a better estimate of solute velocity for planning of the large-scale test. The large-scale natural-gradient tracer test was conducted from 1985 to 1987 to measure dispersion in the aquifer and to determine geochemical controls on reactive transport in a heterogenous aquifer (Garabedian, 1987; LeBlanc and others, 1987). Bromide, a nonreactive tracer, was monitored with a three-dimensional array of 9,600 sampling points as it moved 280 meters through the aquifer. Statistical analysis of bromide concentrations has shown that dispersivity is about 1.0 meter in the direction of flow, about 0.02 meter in the transverse horizontal direction, and about 0.002 meter in the transverse vertical direction.

Two reactive tracers, lithium and molybdate, also were monitored as part of the large-scale tracer test and were found to be significantly retarded relative to bromide. For lithium, a cation, adsorption occurs both on the mineral surfaces and, more significantly, inside the weathered feldspar grains. Adsorption occurring inside the feldspar grains is controlled by diffusion into the micropores. The result is a skewed distribution of lithium (Wood and others, 1989, this Proceedings). Adsorption of molybdate, an oxyanion of molybdenum, is affected by pH and by the concentration of phosphate, another oxyanion competing for adsorption sites (Stollenwerk and Grove, 1987; Stollenwerk and Kipp, 1989, this Proceedings).

Other tracer tests conducted at the Cape Cod site were used to measure aquifer properties, nutrient mobility, microbial activity, and bacterial transport in the aquifer (table C-1). The results of a test using heat as a tracer were used to calculate aquifer porosity, longitudinal dispersivity for mass and temperature, bulk thermal conductivity, and apparent longitudinal thermal conductivity (Barlow, 1987). Two other tracer tests were conducted at the same site with ammonium and bromide as tracers. Results of these tests showed that ammonium, a cation, is retarded by ion exchange relative to the nonreactive anionic tracer, bromide, causing cations such as calcium, magnesium, and potassium to be released into solution (Ceazan, 1987).

A method to measure directly microbial activity in the aquifer at a site where denitrification is occurring was tested using methane and a chlorofluoromethane as tracers (Smith and others, 1987; Smith and others, 1989, this

Table C-1. – *Tracer tests conducted at the Cape Cod Research Site from 1984-87*

[See fig. C-3 for locations]

Br^- = bromide
Cl^- = chloride
Li^- = lithium
F^- = fluoride
MoO_4^{2-} = molybdate
NH_4^+ = ammonium
NO_3^- = nitrate
K^+ = potassium
CH_4 = methane
$C^{13}H_4$ = carbon 13 labeled methane

Test type	Injection date, month/year	Injection location	Tracers	Maximum travel distance (meters)	Reference
Doublet	6/84	FSW 389	Br^-	3.7	Garabedian, 1987
Doublet	7/84	FSW 386	Br^-	3.7	Garabedian, 1987
Convergent	7/84	FSW 372	Br^-	6.1	Garabedian, 1987
Doublet	8/84	FSW 391	Br^-	3.7	Garabedian, 1987
Divergent	8/84	FSW 394	Br^-	6.1	Garabedian, 1987
Divergent	9/84	FSW 393	Br^-	6.0	Garabedian, 1987
Natural gradient	3/85	FSW 415	Cl^-	10	Garabedian, 1987
Natural gradient	7/85	FSW 415	Br^-,Li^+, F^-,MoO_4^{2-}	280	Garabedian, 1987
Divergent	10/85	FSW 393	Br^-,NH_4^+, bacteria	3.1	Ceazan, 1987
Divergent	6/86	FSW 393	Br^-,NO_3^-, K^+, bacteria microspheres	3.1	Ceazan, 1987, and Harvey and others, in press
Natural gradient	6/86	FSW 347	Cl^-	6.7	Smith and others, 1987
Divergent	8/86	FSW 393	Br^-, heat	3.1	Barlow, 1987
Natural gradient	10/86	FSW 347	CH_4,Cl^-, chlorofluoromethane, microspheres	6.7	Smith, this Proceedings
Natural gradient	6/87	FSW 347	$C^{13}H_4$,Br^-, microspheres	6.7	Smith, this Proceedings
Natural gradient	6/87	FSW 168	Br^-	6.9	Harvey, this Proceedings
Natural gradient	10/87	FSW 347	Br^-, bacteria	6.7	Harvey, this Proceedings

Proceedings). These dissolved gases were transported without retardation, but concentrations of methane apparently decreased because of biodegradation. Five tracer tests conducted at two sites showed that transport of bacteria may be affected by bacterial size and electrical charge on the surfaces of the bacteria (Harvey, 1989, this Proceedings; Harvey and others, in press). In one test, the bacteria moved at the same rate as chloride through about 7 meters of the aquifer under a natural hydraulic gradient. Tracer tests conducted during 1988 include experiments on the effect of complexing ligands on metal transport in aquifers (Davis, 1989, this Proceedings).

A major research thrust at this site has been to relate the dispersion of solutes to the heterogeneity of aquifer hydraulic properties. In particular, it has been found that dispersion of solutes in aquifers is strongly affected by variations in hydraulic conductivity. Hydraulic conductivities are being measured at close intervals in continuous cores of sediments from the large-scale tracer-test site using a constant-head permeameter and are being compared to values determined by analysis of borehole-flowmeter logs. Comparisons of these two methods are made both statistically, using data from different holes, and directly, using information from the same hole. The statistical information includes estimates of means and variances, and variogram analyses (Hess and others, 1989, this Proceedings). The results of statistical analyses and the large-scale tracer-test results will be used to test stochastic theories relating dispersion to variations in hydraulic conductivity.

Other current research topics at the Cape Cod site include an examination of the sediments to determine the primary control of adsorption of organic compounds in the aquifer. Preliminary examination of sediment mineralogy and grain coatings shows 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 by preferential adsorption onto particular mineral surfaces (Barber, 1989, this Proceedings). In addition, about 200 wells were sampled during spring 1988 to define the distribution of organic and inorganic constituents in the sewage plume. This information, along with the results of the tracer and hydraulic tests, will be used to improve an understanding of the movement and fate of these constituents in the sewage plume.

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SPATIAL VARIABILITY OF HYDRAULIC CONDUCTIVITY IN A SAND AND GRAVEL AQUIFER, CAPE COD, MASSACHUSETTS

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

ABSTRACT

Two methods have been used to obtain detailed vertical profiles of hydraulic conductivity in the sand and gravel aquifer on Cape Cod, Massachusetts--a borehole flowmeter and permeameter analysis of cores. The borehole-flowmeter technique has been used to obtain 12-meter-long vertical profiles of horizontal hydraulic conductivity at 19 locations. Laboratory permeameter tests of cores from 16 locations have provided 6-meter-long profiles. These profiles have been used to define the spatial distribution of hydraulic conductivity in the aquifer. Preliminary statistical analyses of results from flowmeter tests conducted at 10 sites, located along a 22-meter-long transect, indicate a geometric mean hydraulic conductivity of 0.097 centimeter per second, a variance in the natural logarithm of hydraulic conductivity of about 0.24, and best estimates of correlation scales of 0.26 meter in the vertical direction and 5.1 meters in the horizontal direction. Permeameter results indicate a geometric mean of 0.03 centimeter per second, a variance of 0.16, a vertical correlation scale of about 0.3 meter and a horizontal correlation scale of approximately 2 meters. These correlation scales are statistical indicators of the length over which hydraulic-conductivity measurements are correlated and were determined by fitting exponential models to the results of variogram analyses of the hydraulic-conductivity profiles. Although the mean hydraulic-conductivity values determined by these two methods differ, the profiles show similar trends with depth in the aquifer. The results of the statistical analysis are being used to test several stochastic theories that relate macrodispersion to the statistical properties of the spatial distribution of hydraulic conductivity within an aquifer. Preliminary calculations indicate a good agreement between the longitudinal dispersivity estimated from these stochastic theories and the dispersivity value observed in a natural-gradient tracer test recently completed at this site.

INTRODUCTION

Improvement in the ability to predict the movement and attenuation of contaminants in the subsurface requires the thorough definition of the effects of spatial variability of aquifer properties on solute-transport processes (Anderson, 1987), and methods for determining that spatial variability need to be developed. Several theories have been developed in recent years that define macrodispersion, or the enhanced spreading of solutes in aquifers, as a function of the statistical properties of the spatial distribution of hydraulic conductivity within an aquifer (Gelhar and Axness, 1983; Dagan, 1984; Neuman and others, 1987). To date, these stochastic theories have been field tested only to a limited degree (Sudicky, 1986). The dispersion studies underway at the U.S. Geological Survey's Cape Cod, Mass., research site are designed to test these theories in a glacial outwash, sand and gravel aquifer. As part of these studies, more than 1,300 measurements of horizontal hydraulic conductivity were obtained by using a borehole flowmeter. A multiple-port permeameter also was used to obtain more than 800 measurements of vertical hydraulic conductivity in cores. These measurements were used to define the variability in horizontal hydraulic conductivity in the sand and gravel aquifer at the site. This paper describes these techniques and the procedures used to verify the resulting hydraulic-conductivity values.

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

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

BOREHOLE FLOWMETER

For this study, nineteen 5-cm (centimeter)-diameter wells were installed near the site of a recently completed natural-gradient tracer test (Garabedian and others, 1987). Figure C-4 shows the location of these wells in the gravel pit immediately south of Otis Air Base (see Garabedian and LeBlanc, this Proceedings, figs. C-1 and C-3 for general location maps). Each well was screened over a 12-meter interval below the water table. Eighteen of these wells were installed by a drive-and-wash technique in order to minimize the disturbance of the aquifer (Morin and others, 1988). One well was installed in an augered hole from which cores were also collected. The network of wells was designed to permit determination of horizontal correlation scales of hydraulic conductivity by variogram analysis (Olea, 1975). Wells were installed at various horizontal separations, ranging from 1 to 22 meters, to obtain a maximum number of comparisons of hydraulic-conductivity values for the variogram analyses. The correlation scales determined by the variogram analysis technique are statistical indicators of the length over which hydraulic-conductivity measurements are correlated.

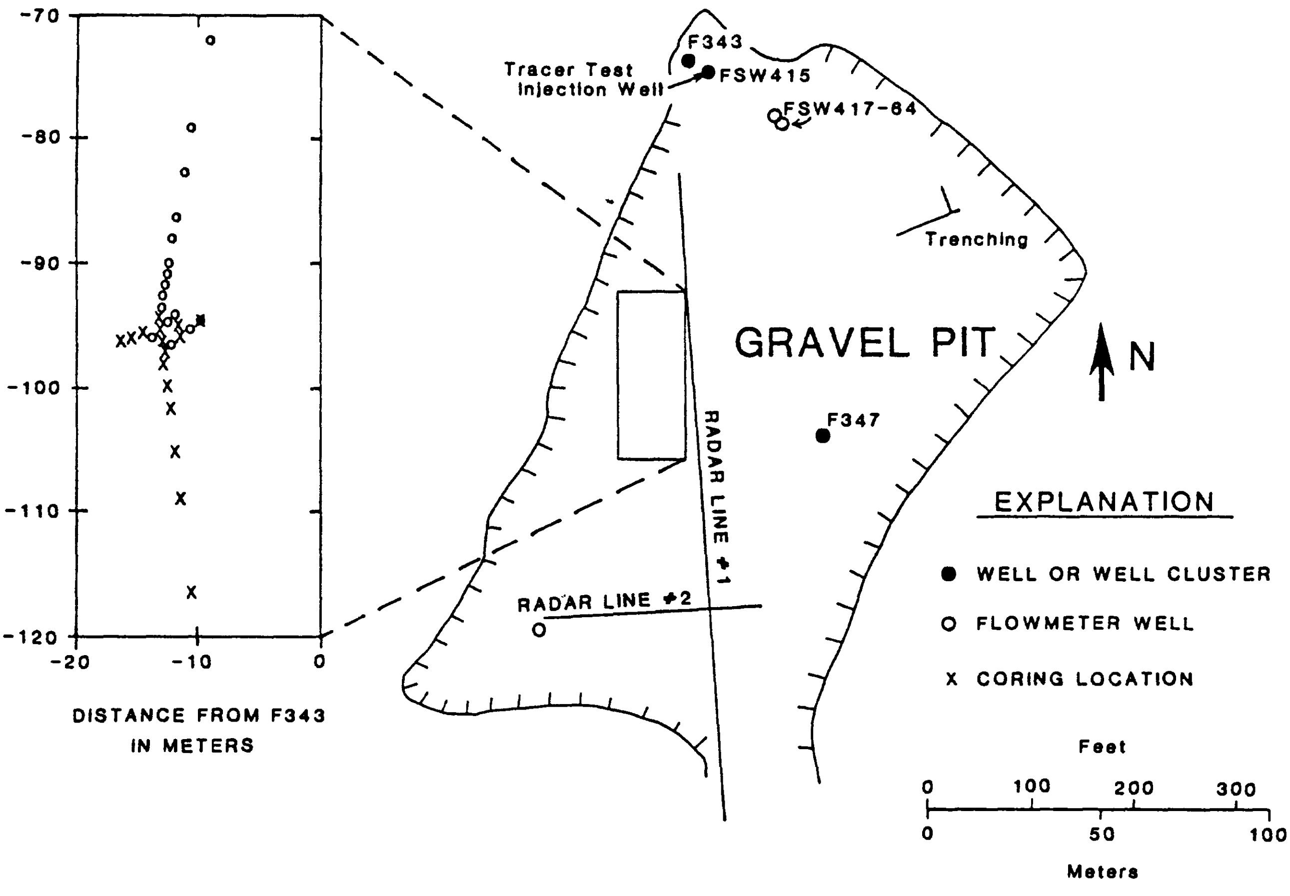

Figure C-4. – Gravel pit south of Otis Air Base, Cape Cod, Massachusetts, showing location of flowmeter wells and coring sites.

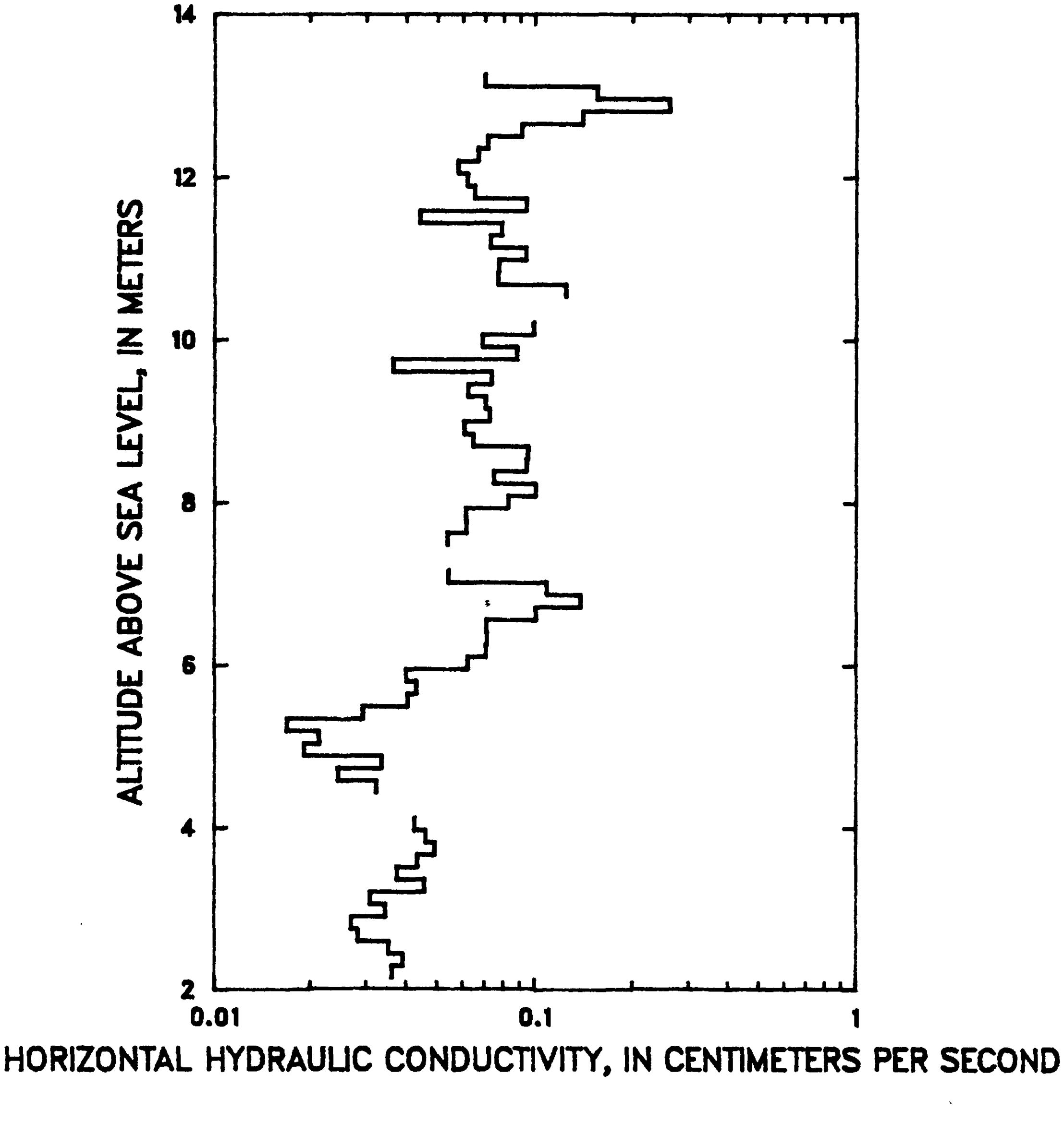

Figure C-5.—Vertical profile of horizontal hydraulic conductivity determined using borehole flowmeter technique in well FSW 417-64, Cape Cod, Massachusetts.

The flowmeter technique, developed by Hufschmied (1986) and refined by Rehfeldt and others, 1989, is a modification of a steady-state aquifer test. The technique involves the pumping of water from the well at a constant rate to establish steady-state flow into the well. An impeller flowmeter is used to measure the velocity of water moving up the well bore at intervals along the well screen. The change in velocity over each interval is used to calculate the amount of water flowing into the well over that interval. (For this study, a constant interval of 15 cm was used.) From these incremental discharges, a profile showing the horizontal hydraulic conductivity over the screened interval is calculated. Other parameters that are needed for the analysis are either known or measured during the test, including pumping rate, drawdown in the well, aquifer temperature, and well characteristics. This technique is analogous to a single-well aquifer test in which the pumped well also serves as the observation well. The difference with the flowmeter technique is that incremental discharges inside the well are measured instead of total discharge from the well. Consequently, a profile of hydraulic conductivity as a function of depth is obtained instead of a single average value. A representative hydraulic-conductivity profile is shown in figure C-5.

Visual comparison of the computed profiles from different wells indicates several patterns of distribution of hydraulic conductivity for the part of the aquifer that was investigated. Each profile indicates that hydraulic conductivity decreases with depth. Several zones having similar hydraulic conductivity over 22 meters in a lateral direction, but less than 1 meter in the vertical direction, also are evident. These observations indicate that the correlation scale in the horizontal direction is much greater than that in the vertical direction.

Preliminary statistical analyses have been performed on profiles from 10 wells located along a transect oriented approximately parallel to the mean direction of ground-water flow, which also is the hypothesized direction of deposition for the sand and gravel outwash. The hydraulic-conductivity values in these 10 profiles range from 0.02 to 0.34 cm/s (centimeter per second), with a geometric mean of 0.097 cm/s and a variance in the natural logarithm of hydraulic conductivity of 0.26. The 95 percent confidence interval around the sample variance is 0.18 to 0.34. Although this preliminary analysis incorporates about 700 data points, the number of uncorrelated data points is estimated to be less than 100. The large uncertainty in the variance reflects, in part, the high degree of correlation within the data.

Correlation scales were determined by fitting exponential models to results of variogram analyses (Olea, 1975), using least square criteria. Figure C-6 shows one possible exponential model fit to the variogram results to determine the vertical correlation scale. Preliminary analyses of the data from 10 wells indicate a vertical correlation scale for the natural logarithm of hydraulic conductivity of 0.12 to 1.1 meters. This range in correlation scale incorporates the uncertainty in the variance discussed above. The best fit exponential model uses a variance of 0.24, which is well within the 95 percent confidence interval about the sample variance, and yields an estimate of the vertical correlation scale of 0.26 meter. Analysis of the correlation structure along the transect of ten wells yields a best fit horizontal correlation scale of 5.1 meters with a range of 2.4 to 9.8 meters.

PERMEAMETER ANALYSIS OF CORES

The other method used extensively at the site to describe the variability in hydraulic conductivity is the permeameter analysis of cores. Cores were collected from 16 locations near the flowmeter wells (fig. C-4) using a wireline piston core barrel described by Zapico and others (1987). Approximately 6 meters of 4.8-cm-diameter core were collected in four or five sections at each location beginning just beneath the water table (Hess and others, 1987; Wolf and others, 1988). Cores were delivered to the laboratory intact and remained in the core liners throughout the study.

In the laboratory, the cores were first examined by X-ray. Sedimentary features such as fine-scale banding were apparent in the X-ray images, indicating that disturbance caused by coring was minimal. A multiple-port, constant-head permeameter similar to that of Raulston

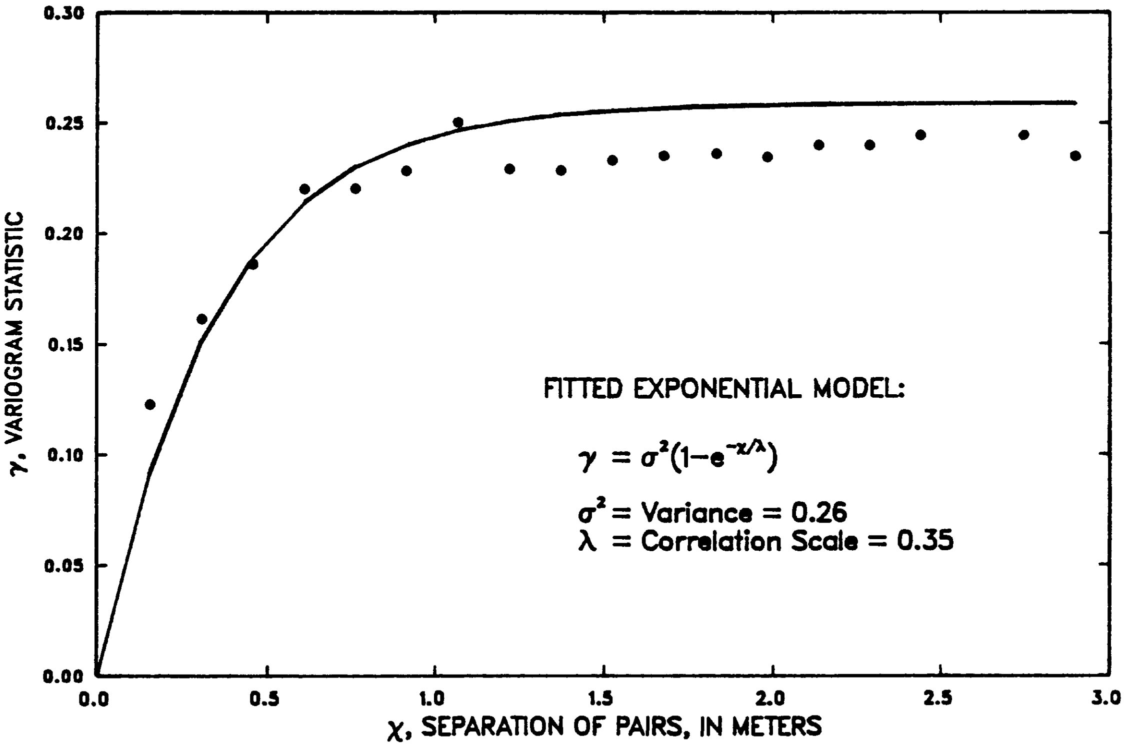

Figure C–6.—Variogram analysis of horizontal hydraulic-conductivity profiles from flowmeter tests in 10 wells on Cape Cod, Massachusetts, to determine vertical correlation scale.

(1986) was used to measure vertical hydraulic conductivity over 5- to 10-cm-long sections of the cores within the original core liners. At each of the 16 coring locations, a profile of hydraulic conductivity as a function of depth was obtained, resulting in a data base of approximately 800 vertical hydraulic-conductivity measurements. The geometric mean of these measurements was 0.03 cm/s at 10 °C (degrees Celsius) with a variance of the natural logarithm of hydraulic conductivity of 0.16. Separation distances between measurements for correlation analysis ranged from 0.05 to 6 meters in the vertical direction and from approximately 1 to 22 meters in the horizontal direction. Preliminary variogram analyses have yielded a vertical correlation scale of approximately 0.3 meter and a horizontal correlation scale of approximately 2 meters.

The permeameter measurements on intact cores have been compared to (1) permeameter measurements on repacked cores, and (2) estimates of hydraulic conductivity from grain-size analysis. Hydraulic-conductivity values from the permeameter measurements on short sections of undisturbed vertical cores are similar to those obtained on repacked cores. This agreement suggests that the media within the cores is isotropic over the scale of these measurements (5 to 10 cm), and that the hydraulic-conductivity values from the vertical cores can be applied to the horizontal direction.

ESTIMATION OF MACRODISPERSIVITY

The preliminary statistical descriptions of the hydraulic-conductivity distribution from the borehole flowmeter data were used to calculate estimates of longitudinal dispersivity by applying the stochastic theory developed by Gelhar and Axness (1983). This theory is one of several recently developed theories which relate dispersivity to the variability of hydraulic properties within the aquifer. Assuming isotropy in the plane of stratification (Gelhar and Axness, 1983, Case 1), a range in longitudinal dispersivity of 0.36 to 2.5 meters is calculated using the range in variance and correlation scales for the borehole flowmeter data presented above. The longitudinal dispersivity calculated using the best fit variance and correlation scales is 0.97 meter. This value agrees with the longitudinal dispersivity value of 0.96 meter calculated in the spatial moments analysis of the natural-gradient tracer test recently completed at this site (Garabedian and others, 1987).

The dispersivity estimates calculated above are based on preliminary analyses of a subset of the flowmeter data. In particular, the hydraulic-conductivity distribution was assumed to be isotropic in the plane of stratification. Evaluation of the complete flowmeter data set will need to be completed before an accurate three-dimensional description of the hydraulic-conductivity distribution is obtained and further estimates of dispersivities are calculated.

COMPARISON OF METHODS

One objective of this study is to provide field verification of the hydraulic-conductivity values determined from the flowmeter data. Use of a flowmeter to determine hydraulic properties of unconsolidated aquifers is a relatively new technique, although it has been used in the past to delineate fractured zones in bedrock. One method of verification is to compare results of the flowmeter technique with values obtained by other methods. One flowmeter well was installed in a borehole from which core had been retrieved. The mean hydraulic-conductivity values obtained at this location by the two methods – permeameter analysis of the cores and borehole flowmeter logging – differ (flowmeter measurements are greater than permeameter measurements), but the profiles show similar trends with depth. This similarity of trends indicates that the variability in hydraulic conductivity computed using the flowmeter data reflects the actual variability in the aquifer. The difference in means may relate to possible compaction of the cores introduced during the coring process and reflected in low permeameter measurements, or it may result from differences in scale between the two measurement techniques – one is a laboratory technique, the other is an *in situ* field technique.

The mean horizontal hydraulic conductivity determined from the flowmeter technique is less than the mean hydraulic conductivity of 0.13 cm/s calculated from an aquifer test conducted in the same aquifer 2 km (kilometers) downgradient (Garabedian, 1987). This discrepancy may be caused by differences in the two measurement techniques or it may reflect an actual difference in hydraulic conductivity between the two sites. To resolve this discrepancy, a long-screened well has been installed at the aquifer-test site so that hydraulic-conductivity values from the borehole flowmeter can be compared directly to the value from the aquifer test.

The flowmeter technique has several advantages over the standard aquifer test in determining hydraulic conductivity. The primary advantage is that a profile showing the variability in horizontal hydraulic conductivity with respect to depth is obtained for each well; with the aquifer test, only the average hydraulic conductivity can be determined. In addition, a flowmeter test can be conducted by one person in less than a day; the aquifer test typically is run over several days and requires a team of several hydrologists. A disadvantage is that the flowmeter has a smaller radius of investigation than the aquifer test, because it imposes less stress on the aquifer. Therefore, disturbances of the aquifer resulting from well installation can influence results from the flowmeter. On the basis of these preliminary tests, the flowmeter technique seems to be effective for making *in situ* measurements of the spatial variability of hydraulic conductivity in a sand and gravel aquifer and may prove to be a useful tool where detailed description of the variability in hydraulic conductivity is needed.

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SIMULATION OF THE RATE-CONTROLLED TRANSPORT OF MOLYBDATE IN COLUMN EXPERIMENTS

By Kenneth G. Stollenwerk[1] and Kenneth L. Kipp[1]

ABSTRACT

Laboratory column experiments were used to identify potential rate-controlling mechanisms that could affect transport of molybdate in the natural-gradient tracer test done at Cape Cod, Massachusetts. Column breakthrough curves for molybdate were simulated by using a one-dimensional solute-transport model that was modified to include four different rate mechanisms: equilibrium sorption, rate-controlled sorption, and two side-pore diffusion models. One side-pore diffusion model was based on an average side-pore concentration of molybdate (mixed side-pore diffusion); the other was based on a concentration profile for the overall side-pore depth (profile side-pore diffusion). The equilibrium model failed to simulate the experimental data, indicating the presence of a rate-controlling mechanism. The rate-controlled sorption model simulated results from one column reasonably well, but could not be applied to other columns that had different input concentrations without changing the rate constant. The mixed side-pore diffusion model also resulted in reasonable correlation with experimental data, and the parameters applied to a variety of input concentrations. The most accurate simulations for the largest variety of input concentrations were achieved by using the profile side-pore diffusion model.

INTRODUCTION

Transport of solutes through porous media can occur under nonequilibrium conditions if ground-water velocities are sufficiently fast to prevent attainment of chemical and physical equilibrium. For example, Fuller and Davis (1987) report that cadmium sorption by a calcareous sand was characterized by multiple reactions, including a recrystallization reaction that proceeded over a period of days. Unless ground-water velocity in such a situation is extremely slow, nonequilibrium transport will occur. Diffusion of a solute through immobile water to a reaction site is also affected by water velocity. The immobile water can occur as a layer on the grain surface (film diffusion), in dead-end pores between tightly packed grains (pore diffusion), or within crevices or pits on the grain surfaces (particle diffusion). Calcium and chloride breakthrough curves from column experiments conducted by James and Rubin (1979) show the effect of flow rate and diffusion on solute transport.

Information about potential rate-controlling mechanisms that could be occurring in the field can often be obtained from carefully conducted laboratory column experiments. The shape of breakthrough curves from column experiments conducted at field ground-water velocities can indicate nonequilibrium transport of a solute, and numerical simulation of these breakthrough curves with a solute-transport model containing the appropriate equations may provide information about the rate mechanism.

Results presented in this paper are from column experiments designed to evaluate potential rate-controlling mechanisms that could affect transport of molybdenum (VI)[Mo(VI)] in the Cape Cod natural gradient tracer test (LeBlanc and others, 1987). The tracer test was conducted to study dispersive transport and chemical processes in the glacial-outwash aquifer affected by recharge of treated sewage (LeBlanc, 1987), and was superimposed on the sewage plume. Molybdate was introduced with other constituents in the initial injection pulse to evaluate transport of a reactive oxyanion. Previous experiments have identified the geochemical parameters that control sorption of Mo(VI) by sediment (Stollenwerk and Grove, 1987; Stollenwerk, 1988).

COLUMN EXPERIMENTS

Sediment and ground water from the sewage contaminated part of the aquifer adjacent to the tracer-test plume were used in the column experiments. Sediment was packed into eight plastic columns 0.302 meter in length and

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

0.025 meter inside diameter. Several pore volumes of Mo(VI)-free ground water were eluted through the columns to establish constant baseline conditions. Influent was then switched to Mo(VI)-spiked ground water; six Mo(VI) concentrations were used, ranging from 0.0016 to 0.096 mmol/L (millimoles per liter). Replicate columns were run for two of the concentrations. After steady-state conditions were achieved (effluent Mo(VI) concentration equal to influent concentration), the influent was switched back to Mo(VI)-free ground water in order to observe the desorption process.

Physical and chemical characteristics for this column are listed in table C-2. Porosity and bulk density were determined gravimetrically, and longitudinal dispersivity was obtained from bromide-breakthrough data. Sorption of Mo(VI) can be described by the Freundlich isotherm. Freundlich constants were calculated from a linear plot of the amount of Mo(VI) sorbed by sediment in each column as a function of input concentration (fig. C-7) according to

where

$$\bar{c} = K_f c^n, \qquad (1)$$

$\bar{c}$ is the amount of Mo(VI) sorbed in millimoles per kilogram;

c is the concentration of Mo(VI) in solution in millimoles per liter;

K_f is the Freundlich adsorption equilibrium constant, in liters per kilogram^{-n}; and

n is the Freundlich exponent (slope of line).

The Freundlich constants used in the solute-transport models are listed in table C-2. The exponent is less than one for these data so this isotherm is nonlinear and predicts a reduction of sorption at higher solution concentrations.

NUMERICAL SIMULATIONS

Modeling results from only one of the column breakthrough curves are presented here. Four different models were used to simulate the shape of the column breakthrough curves. All four models contain a one-dimensional solute-transport equation and use the Freundlich equation to describe sorption. They differ in the type of rate mechanism assumed to control transport of Mo(VI) from flowing phase to solid surface.

Table C-2.–Physical and chemical properties for column experiment

[m, meter; g/cm^3, grams per cubic centimeter; m/d, meter per day; d, day; mmol/L, millimole per liter; L/kg, liters per kilogram]

Length, m	Porosity	Bulk density, g/cm	Interstitial velocity m/d
0.302	0.34	1.75	0.43

Longitudinal dispersivity, m	Time of pulse, d	Input concentration mmol/L
0.0027	4.19	0.0016-0.096

Freundlich isotherm constant (L/kg)	Slope of Freundlich isotherm
0.14	0.72

The essential features of each model are summarized in table C-3.

Table C-3.–Comparison of the four transport models used to simulate column breakthrough of molybdenum(VI)

Model	Features
Local-equilibrium model	Assumes chemical and physical equilibrium conditions throughout column.
Rate-controlled sorption model	Allows for the possibility that the rate of sorption reaction may be too slow for equilibrium to be achieved.
Mixed side-pore diffusion model	Diffusion into immobile water in pores is the rate limiting step. An average concentration is assumed throughout each side pore.
Profile side-pore diffusion model	Diffusion into immobile water in side pores is the rate limiting step. A concentration gradient exists in each side pore.

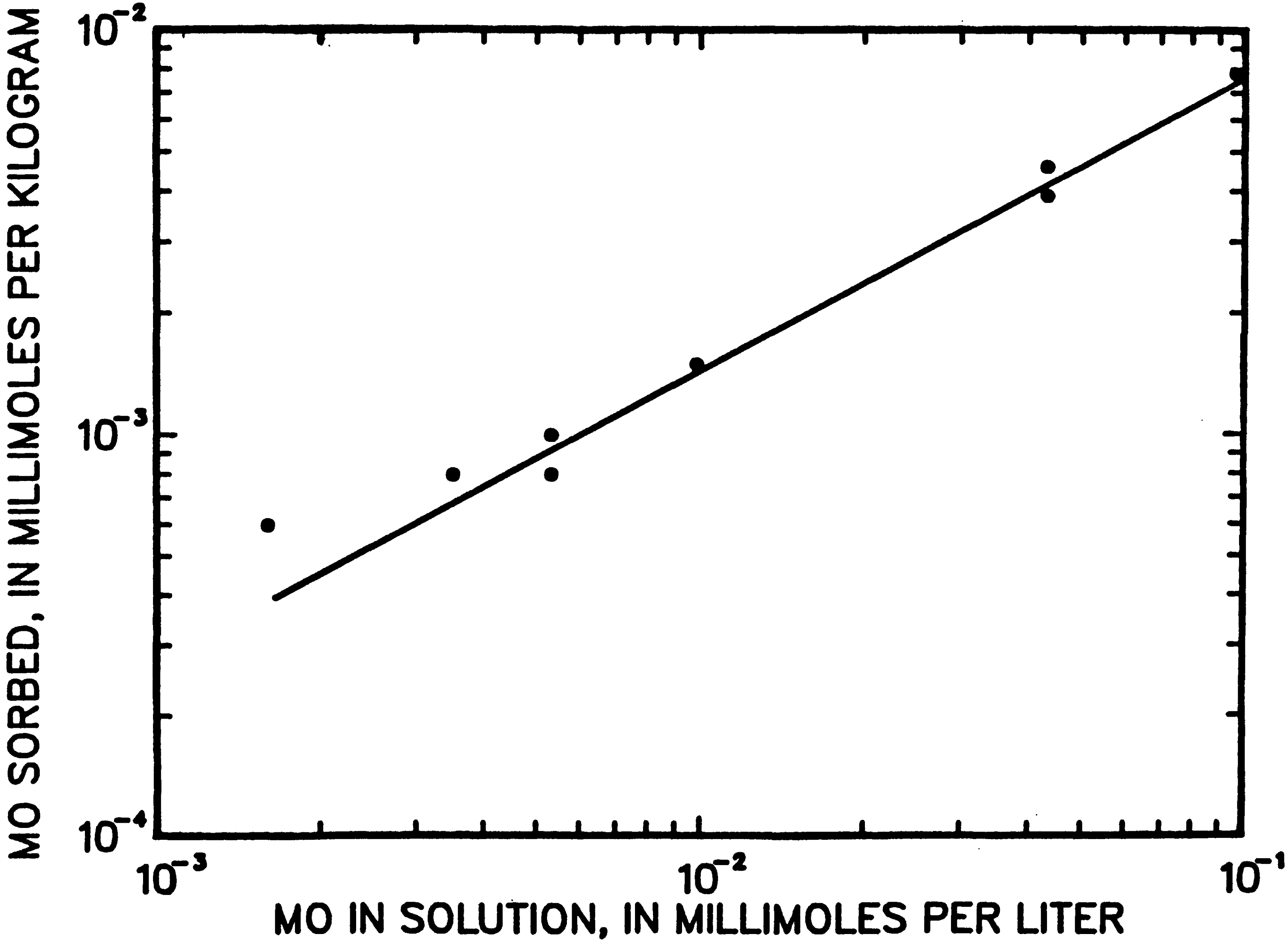

Figure C–7.—Freundlich plot of steady-state sorption parameters from eight column experiments.

The basic equation that describes the transport of solutes in the flowing phase can be expressed as

$$\frac{\partial c}{\partial t} = -V\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2} + \bar{r}. \qquad (2)$$

Accumulation in the sorbed phase is described by

$$\frac{\partial \bar{c}}{\partial t} = -\frac{\theta}{\rho_b}\,\bar{r}, \qquad (3)$$

where

c is the concentration in the flowing phase, in millimoles per liter;

t is time, in days;

x is distance along the column, in meters;

V is the interstitial velocity, in meters per day;

D is the dispersion coefficient, in square meters per day;

θ is the porosity;

ρ_b is the bulk density, in grams per cubic centimeter;

$\bar{r}$ is the rate of addition of solute to the flowing phase from the sorbed phase, in millimoles per liter per day;

$\bar{c}$ is the concentration on the solid phase, in millimoles per kilogram.

All parameters are assumed to be constant and uniform along the column.

The boundary conditions for equation 2 are

$$\text{at } x = 0 \quad -D\frac{\partial c}{\partial x} + Vc = Vc_0(t) \qquad (4a)$$

$$\text{at } x = L \quad \frac{\partial c}{\partial x} = 0, \qquad (4b)$$

where c_0 is the inlet concentration and L is the column length. Solute is introduced to the column as a slug of a given duration, t_s. The initial conditions for equations 2 and 3 are

$$\text{at} \quad t = 0, \quad c = 0 \quad \text{and} \quad \bar{c} = 0. \qquad (4c,d)$$

The first transport model (equilibrium sorption) is formulated by assuming that local equilibrium exists along the column. No immobile-water phase is present. The water velocity is assumed to be slow enough so that sorption rapidly attains equilibrium (Grove and Stollenwerk, 1984).

The second transport model (D.B. Grove, U.S. Geological Survey, written commun., 1988) (rate-controlled sorption) is based on the assumption that the sorption mechanism does not have time to reach equilibrium at each point along the column. Therefore, equation 1 is replaced by the sorption rate expression

$$\bar{r} = \frac{\rho_b}{\theta}\,k_r\,(K_f c^n - \bar{c}) \qquad (5)$$

where k_r is the sorption rate constant, in d^{-1}.

The third and fourth models are based on the assumption of an immobile-water phase in the side pores. This phase can be caused by the existence of crevices or pits on the grain surfaces, and by dead-end pores created by tight packing of the grains. An immobile-water film that could cover entire grain surfaces is not considered. Diffusion of Mo(VI) into the immobile-water phase retards transport because of the capacitance of this phase and also provides a rate-limiting step for sorption on the solid matrix adjacent to the immobile-water phase. For these models, transport of Mo(VI) from the flowing phase can occur by sorption to the solid phase or by diffusion to the immobile-water phase followed by sorption to the solid phase. The sorption from either phase is assumed to be at local equilibrium with the adjacent fluid phase. An additional balance equation for the solid adjacent to the immobile-water phase is as follows:

$$\frac{\partial \bar{c}_s}{\partial t} = -\frac{\theta_s}{\rho_{bs}}\,\bar{r}_s, \qquad (6)$$

where

ρ_{bs} is the dry bulk density adjacent to the immobile-water phase, in grams per cubic centimeter;

θ_s is the porosity of the immobile-water phase;

$\bar{r}_s$ is the transfer rate of addition of solute to the immobile-water phase from the adjacent solid phase, in millimoles per liter per day;

$\bar{c}_s$ is the sorbed concentration adjacent to the immobile-water phase, in millimoles per kilogram.

The total dry bulk density and total porosity in equation 3 must be changed to the values for the flowing and solid phase that are in contact, denoted by ρ_{bf} and θ_f.

The third model (mixed side-pore diffusion) is based on the assumption of an effective average or mixed concentration of solute in the immobile-water phase. This model has no spatial dependence in the immobile-water phase. The balance equation for the immobile-water phase is

$$\frac{\partial c_s}{\partial t} = -\frac{\theta_f}{\theta_s} r_s + \bar{r}_s , \qquad (7)$$

where

c_s is the immobile-water phase concentration, in millimoles per liter; and

r_s is the rate of addition of solute to the flowing phase from the immobile-water side pore phase, in millimoles per liter per day.

The initial condition is

$$\text{at } t = 0, \qquad c_s = 0, \qquad (8)$$

and the transfer rate expression is

$$r_s = -\frac{\theta_s}{\theta_f} k_s A(c - c_s) , \qquad (9)$$

where

k_s is a transfer rate constant, in meters per day, and

A is the effective interfacial area per unit volume of immobile-water phase, in d^{-1}.

Parameters in the mixed side-pore model include V, θ_f, θ_s, ρ_{bf}, ρ_{bs}, k_s, and A. The parameters k_s and A can only be determined as a lumped parameter, k_sA.

The transfer rate in the mixing model is merely proportional to the difference in concentration between the flowing-water and immobile-water phases. The transfer-rate constant k_sA is a characteristic-rate scale factor for diffusion in the immobile-water phase. Without the Freundlich sorption mechanism, this third model is the same as the dead-end pore model of Coats and Smith (1964). Grove and Stollenwerk (1985) present a similar model but with Langnuir sorption and a continuous immobile-water film phase.

The fourth model (profile side-pore diffusion) is similar to the third, but the assumption is made that a concentration profile exists over the thickness of the immobile-water phase. Molecular diffusion of solute is the major transport mechanism in the immobile-water phase. The transfer rate of solute from the flowing to the immobile-water phase is assumed to be described by the diffusional flux at the interface between these phases. Thus, equations 7 and 9 are replaced by

$$\frac{\partial c_s}{\partial t} = D_m \frac{\partial^2 c_s}{\partial y^2} + \bar{r}_s . \qquad (10)$$

The boundary conditions are

$$\text{at } y = 0, \qquad c_s = c \qquad (11a)$$

$$\text{at } y = L_s , \qquad \frac{\partial c_s}{\partial y} = 0 , \qquad (11b)$$

where D_m is the effective molecular diffusivity in the immobile-water zone, in square meters per day; y is distance into side pore from the entrance, in meters; and L_s is length of side pore, in meters. The second boundary condition states that no solute leaves through the back end of the side pore. The transfer-rate expression at the side-pore entrance is

$$r_s = AD_m \frac{\partial c_s}{\partial y} \bigg|_{y=0} \frac{\theta_s}{\theta_f} . \qquad (12)$$

The concentration profile in the immobile-water phase is governed by a diffusional transport mechanism. The transfer rate from the immobile water to the flowing-water phase is the diffusive flux, which depends on the concentration gradient in the immobile-water phase at the interface. Parameters in the profile side-pore model include V, θ_f, θ_s, ρ_{bf}, ρ_{bs}, A, L_s, and D_m. The effective molecular diffusivity, D_m, is estimated from values published in the literature.

The profile side-pore diffusion model is the most complex and perhaps the most realistic of the four models. Without the Freundlich sorption mechanism, it is the same as that of Kipp (1982). Even with shallow dead-end pores or thin immobile-water pockets, the diffusion rates may be so low that a concentration profile is more realistic than an effective average concentration in the immobile-water phase.

Because of the nonlinear Freundlich isotherm in each transport model, finite-difference techniques were used to compute numerical solutions in the form of column breakthrough curves. One hundred nodes were used along the column, and 10 nodes were used in the side-pore direction for the profile model. Tests verified that the truncation errors were acceptable. A predictor-corrector calculation was used at each time step to handle nonlinearity. A line successive overrelaxation solver was used in the direction of the side-pores for the profile model, but a bi-tridiagonal solver was used for the mixed side-pore and rate-controlled sorption models.

MODELING RESULTS

The four potential rate mechanisms were evaluated by calculating column breakthrough curves for various parameter sets in order to obtain the best agreement between observed column breakthrough curves and calculated concentration data. Only the results for the 0.043 mmol/L column are presented here. Physical and chemical parameters common to all four models are listed in table C-2.

Simulation of Mo(VI) breakthrough by the equilibrium sorption model is compared with the experimental data in figure C-8. The model predicts a very steep slope for the adsorption limb of the breakthrough curve and complete site saturation by the second pore volume. Experimental data from the column show that complete breakthrough did not occur until the sixth pore volume, indicating that transport of Mo(VI) was affected by a rate mechanism. The equilibrium simulation also predicted complete rinse-out of Mo(VI) by the 9th pore volume, whereas Mo(VI) in the column effluent did not reach zero until the 15th pore volume, indicating that desorption also was affected by a rate mechanism.

The assumption of rate-controlled sorption resulted in a better simulation of the experimental data (fig. C-9). A sorption rate constant of 1.5 d^{-1} gave the best visual match to the experimental data; however, some discrepancy between the two curves is still present in the shoulder portion of the adsorption curve and the tail portion of the desorption curve. The rate-controlled sorption model was also used to simulate the column breakthrough curves at other input concentrations using the reaction rate constant of 1.5 d^{-1}. Simulation of these breakthrough curves (data not shown) became progressively worse as concentrations deviated from 0.043 mmol/L. Only by using a different rate constant for each concentration could results similar to figure C-9 be achieved. If sorption rate were controlling sorption of Mo(VI), one rate constant should be able to better simulate transport at different concentrations.

The mixed side-pore diffusion model also reasonably simulated the experimental data (fig. C-10) but failed to accurately predict the shoulder of the adsorption portion of the breakthrough curve. This model was more robust than the reaction rate model in simulating breakthrough curves over the range of input concentrations.

The profile side-pore diffusion model simulated the experimental data almost exactly, within the accuracy of the breakthrough data (fig. C-11). Based on the best fit simulation of the experimental data, the immobile-water phase was calculated to be approximately 5 percent of the total porosity. Apparently, diffusion into and out of this volume of immobile water was responsible for the observed shoulder and tail in the experimental data. The profile model also was the most transferable to other inlet concentrations.

CONCLUSIONS

The shape of breakthrough curves from column experiments provided evidence that Mo(VI) transport was not equilibrium controlled. The decrease in slope as the adsorption limb of the breakthrough curve approached steady state, and the decrease in slope of the desorption limb as Mo(VI) was rinsed out of the column, could adequately be simulated only with a solute-transport model that included a rate mechanism. When transport was assumed to be controlled only by the rate of Mo(VI) sorption, experimental data were simulated reasonably well, but the reaction rate constant used in the model was applicable only for the breakthrough curve to which it was fitted.

The concept of Mo(VI) diffusion into and out of side pores containing an immobile-water phase resulted in a better simulation of experimental breakthrough curves over a wider range of concentrations. The mixed side-pore diffusion model could be used to fit a particular

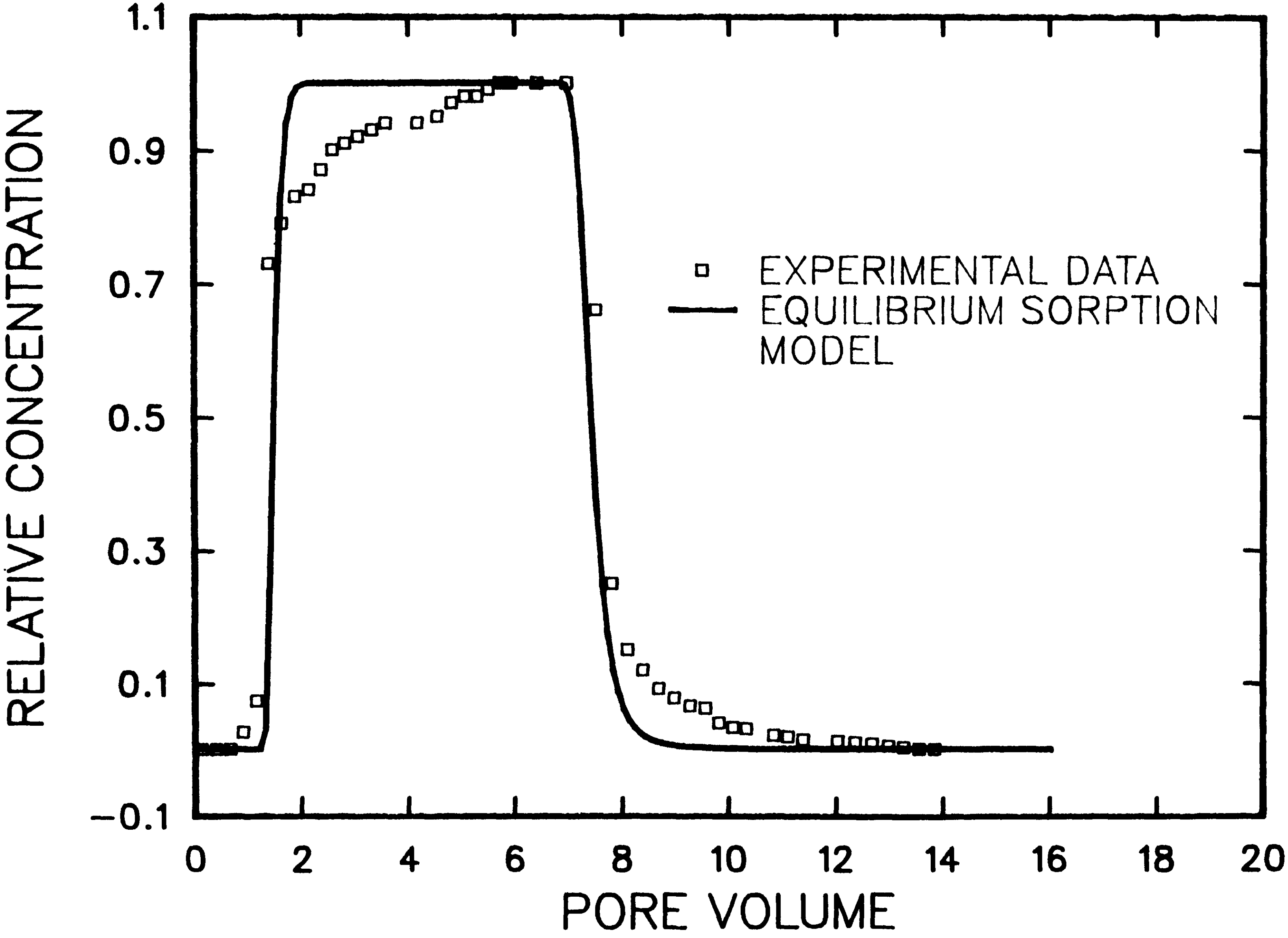

Figure C–8.—Simulation of experimental data with the equilibrium sorption model.

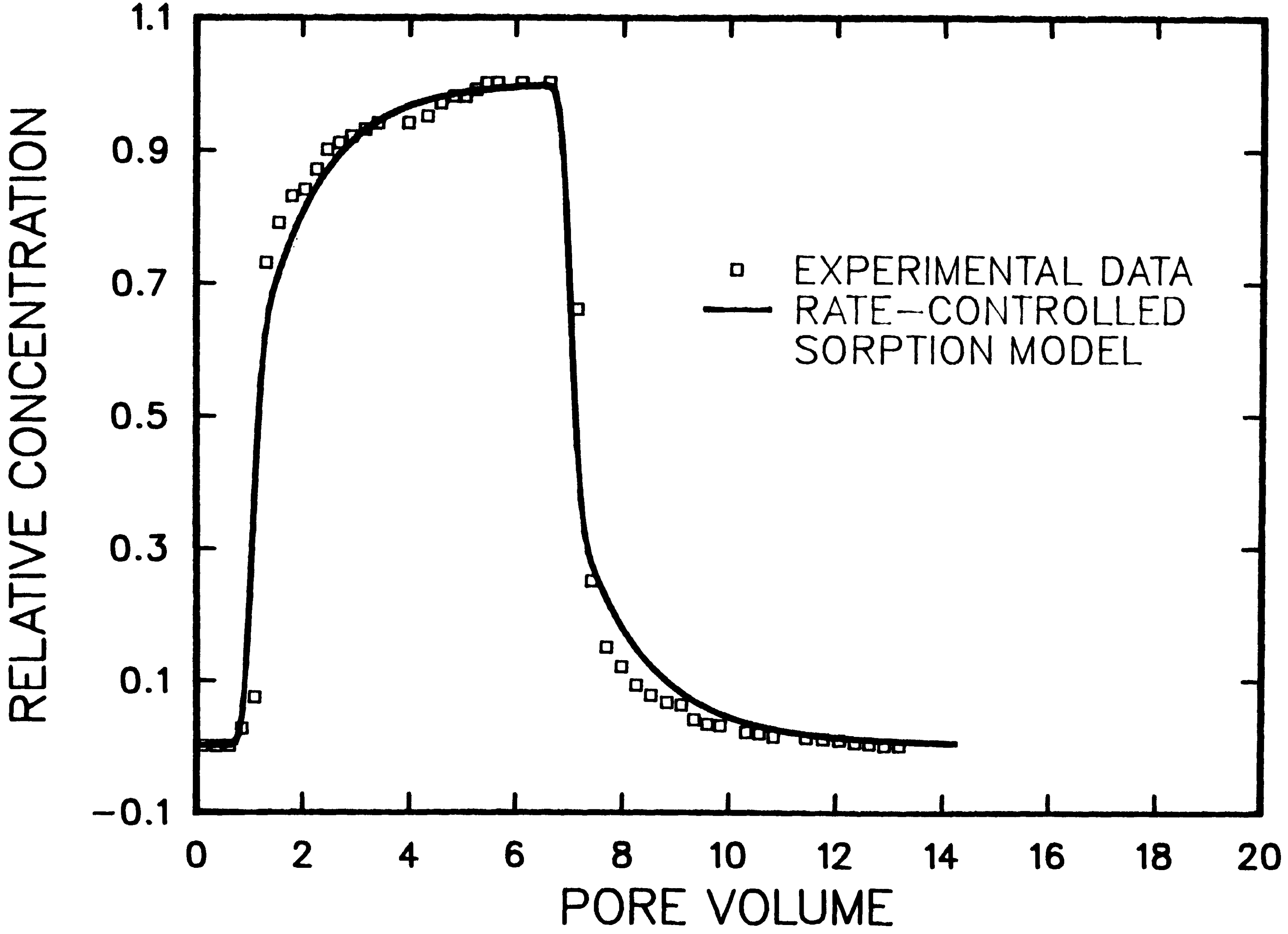

Figure C–9.—Simulation of experimental data with the rate-controlled sorption model.

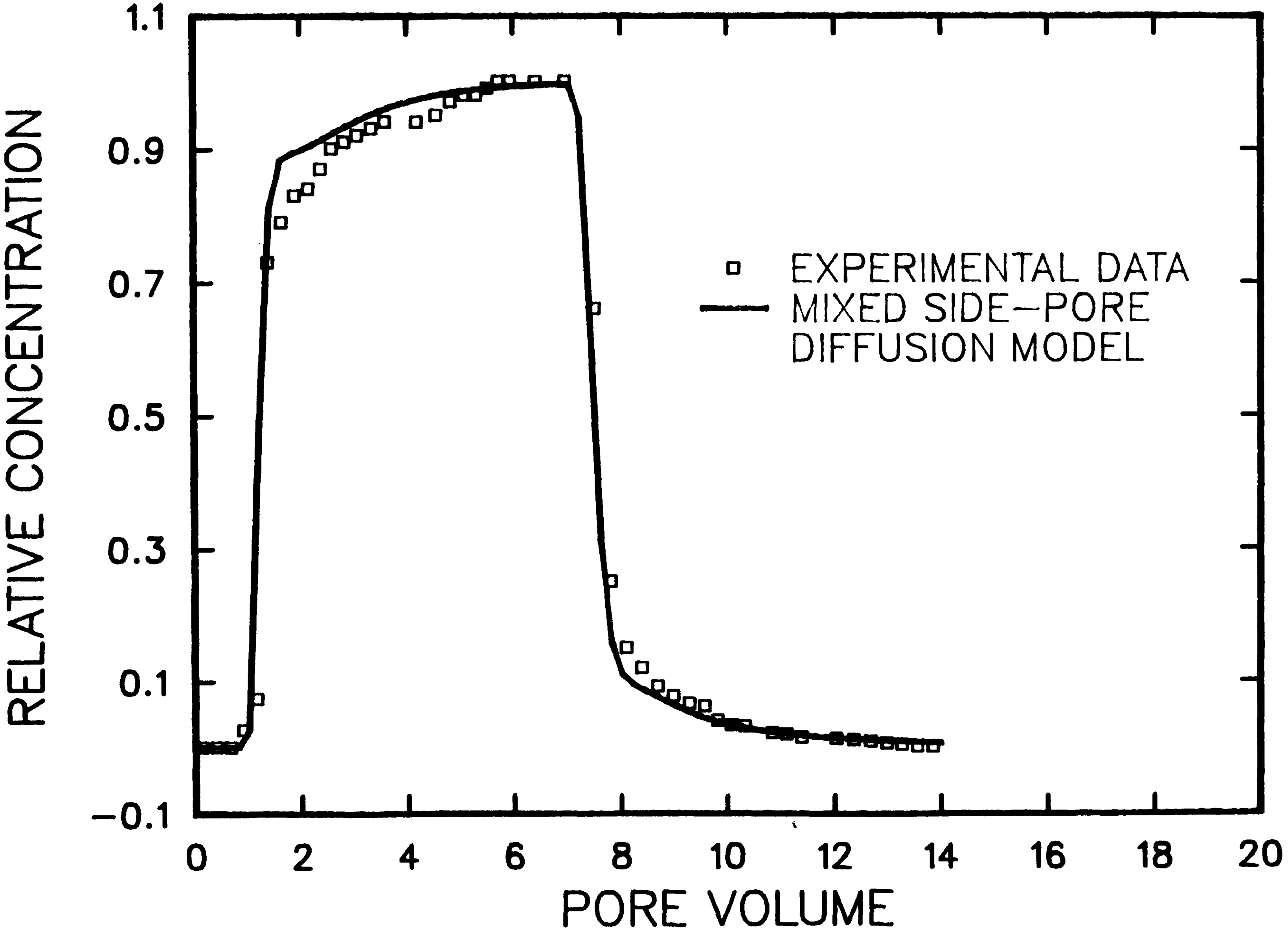

Figure C–10.—Simulation of experimental data with the mixed side-pore diffusion model.

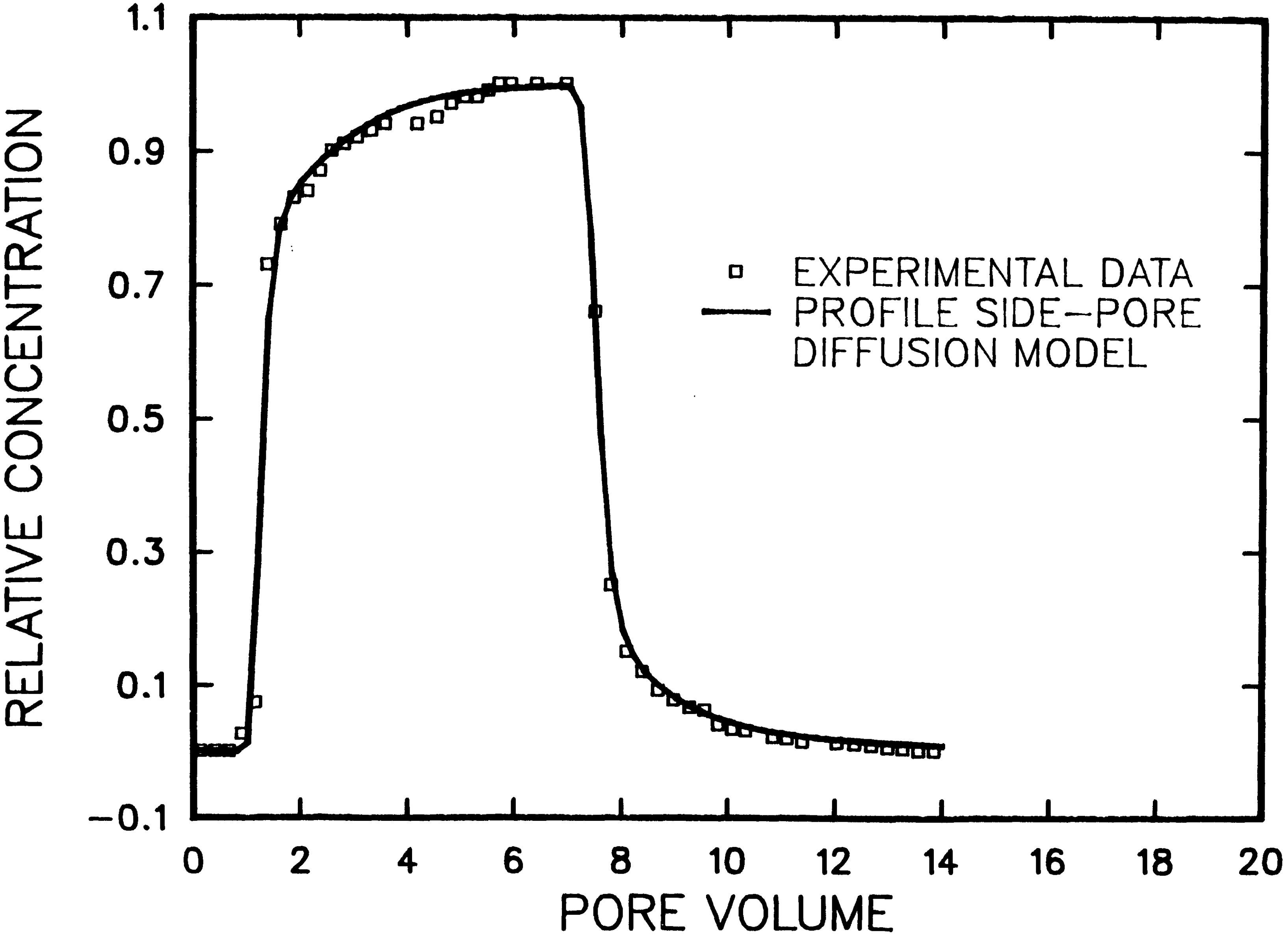

Figure C–11.—Simulation of experimental data with the profile side-pore diffusion model.

experimental breakthrough curve with approximately the same degree of accuracy as the reaction rate model; however, the mixed side-pore diffusion model was applicable over a wider range of concentrations.

Best results were achieved with the more complex and conceptually realistic profile side-pore diffusion model. Results from this model fit all of the experimental data points and could also be used over a range of concentrations.

Transferability of the results from this study to the Cape Cod natural-gradient tracer test will provide crucial information concerning the validity of laboratory experiments in providing information on field processes. Although actual values for some of the physical properties determined in the laboratory are unlikely to apply to an aquifer because of scale differences between laboratory and field, conceptually realistic models such as the profile side-pore diffusion model should be able to simulate field transport conditions more accurately than rate-controlled sorption or mixed side-pore diffusion models.

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(p. 163 follows)

SOLUTE DIFFUSION WITHIN SAND OF THE CAPE COD, MASSACHUSETTS, AQUIFER

By Warren W. Wood[1], Paul P. Hearn, Jr.[1], and Thomas F. Kraemer[1]

ABSTRACT

Laboratory experiments have suggested that matrix diffusion is a major mechanism controlling cation transport in ground water of the Cape Cod, Massachusetts, aquifer. Experiments using radioisotopes, in combination with deferential leaching and air abrasion techniques demonstrate that cations penetrate into the interior of mineral grains. Scanning-electron microscopy and X-ray analyses of material in the interiors of the feldspars and biotite confirm the presence of authogenic clays in the interior of the grains. These internal clays are believed to act as cation-exchange sites for the intruding cations. Mercury-porosimetry studies support the presence of significant internal porosity of all the mineral grains examined in this study. The demonstrations of apparent matrix diffusion in this aquifer have significant importance in solute-transport modeling.

INTRODUCTION

Knowledge of reactions between organic or inorganic solutes and solid phases in aquifers is of vital importance in evaluating the transport of toxic and radioactive wastes by ground water. Most evaluations of the rock-water interaction have implicitly assumed that the grain surfaces are the only significant chemically-active area. However, a series of laboratory investigations have suggested that the interiors of the sand grains from Cape Cod, Mass., have two to three times the sorption capacity of their surfaces.

It is of some value to note that solutes diffuse into the interior of sand grains as well as being fixed on grain surfaces. To the authors' knowledge, this phenomenon has not been previously reported although the numerical evaluation of breakthrough curves in some studies suggested that something analogous must be occurring (that is, double-porosity models and aggregate-diffusion models). The first indication of a time-dependent reaction in the Cape Cod sands came from column tests conducted as part of the tracer-selection procedure. Figure C-12 shows the results of one such test in which the shape of the lithium-breakthrough curve (initial concentration of 6.8 mg/L (milligrams per liter)) was distorted relative to that of conservative bromide (input concentration of 51 mg/L). The "tailing off " of lithium values as the volume of fluid eluted through the column increases suggests a lack of equilibrium. These results prompted a series of batch experiments in which sediment from the Cape Cod tracer site was split into twelve 150 gram samples, placed into 100 mL (milliliters) of Cape Cod ground water that had been tagged with 0.3 mg/L lithium and then sealed in flasks. Samples were shaken continuously at 22 °C (Celsius), and opened and analyzed for lithium at specific time intervals. The results from these tests clearly demonstrate that lithium concentrations decrease linearly as a function of the logarithm of time after approximately 100 minutes (fig. C-13). These results, together with the results of the column tests, strongly suggest time-dependent removal of lithium from solution. Because common lithium compounds are very soluble and lithium concentrations did not change in control samples (without sediment) over time, it was concluded that lithium was removed from solution by sorption or exchange with solid phases.

In order to identify the phases responsible for the observed sorption a fine-sand fraction (from 63 to 355 μm (micrometers)) was separated into three density fractions (1) less than 2.58 g/cm^3 (grams per cubic centimeter) (largely feldspar), (2) between 2.58 and 2.70 g/cm^3 (largely quartz), and (3) greater than 2.70 g/cm^3 (mostly biotite, with minor magnetite, amphibole, and ilmenite). The relative proportions (weight percent) of these three fractions were 5, 92, and 3 percent, respectively. Twenty-four-hour Kd (distribution coefficient) tests were run on each density fraction and on an unsplit sample of the same material. These tests showed that the Kd of the feldspar fraction was 22.2 mL/g (milliliters per gram), biotite 15.4 mL/g, quartz 1.8 mL/g, and the total sample 2.9 mL/g. Time- dependent sorption studies also were conducted on each fraction

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

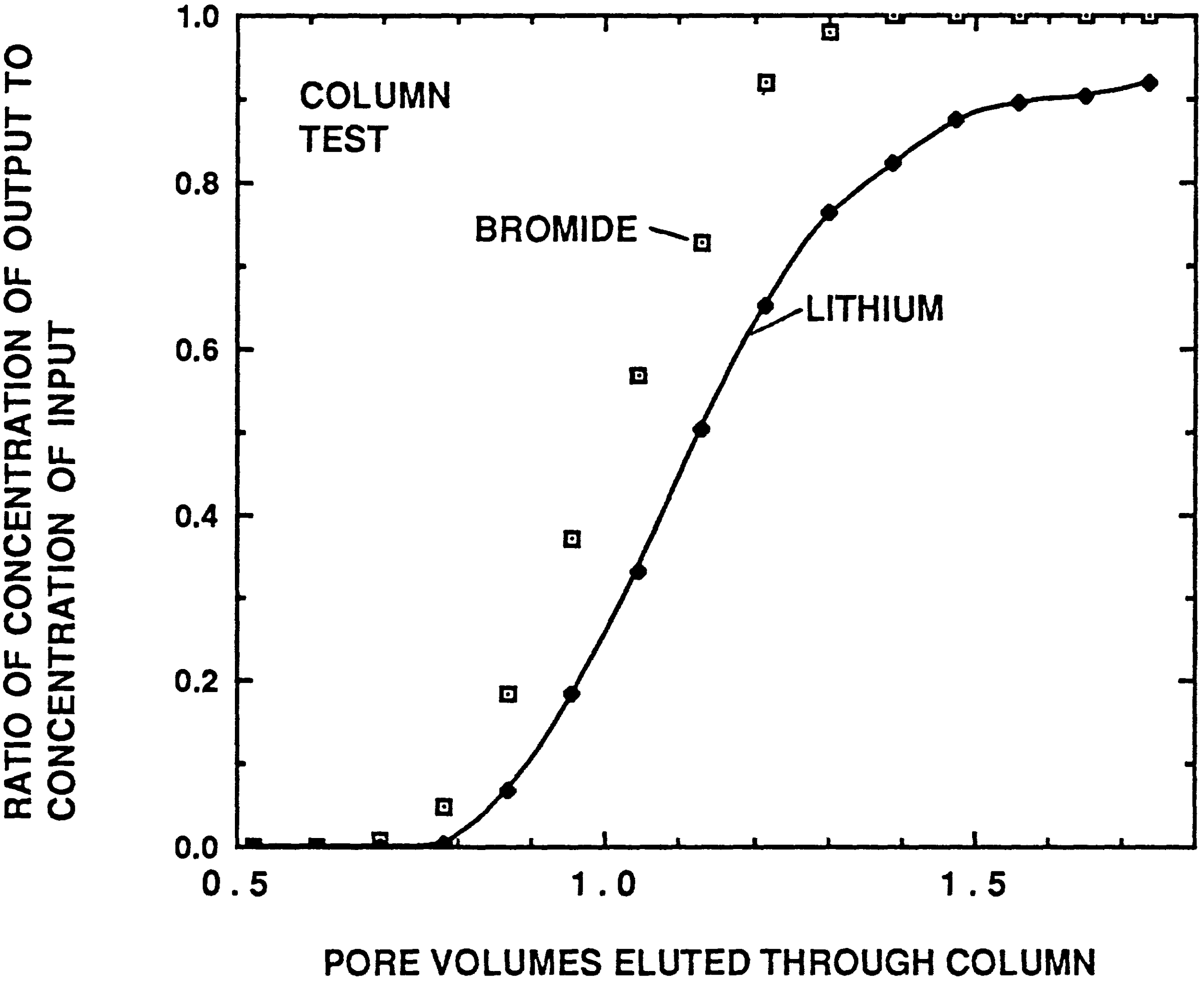

Figure C–12.—Ratio of bromide and lithium concentration in the output of a column filled with sediment from Cape Cod to the input to that column as a function of the number of pore volumes of fluid eluted from the column.

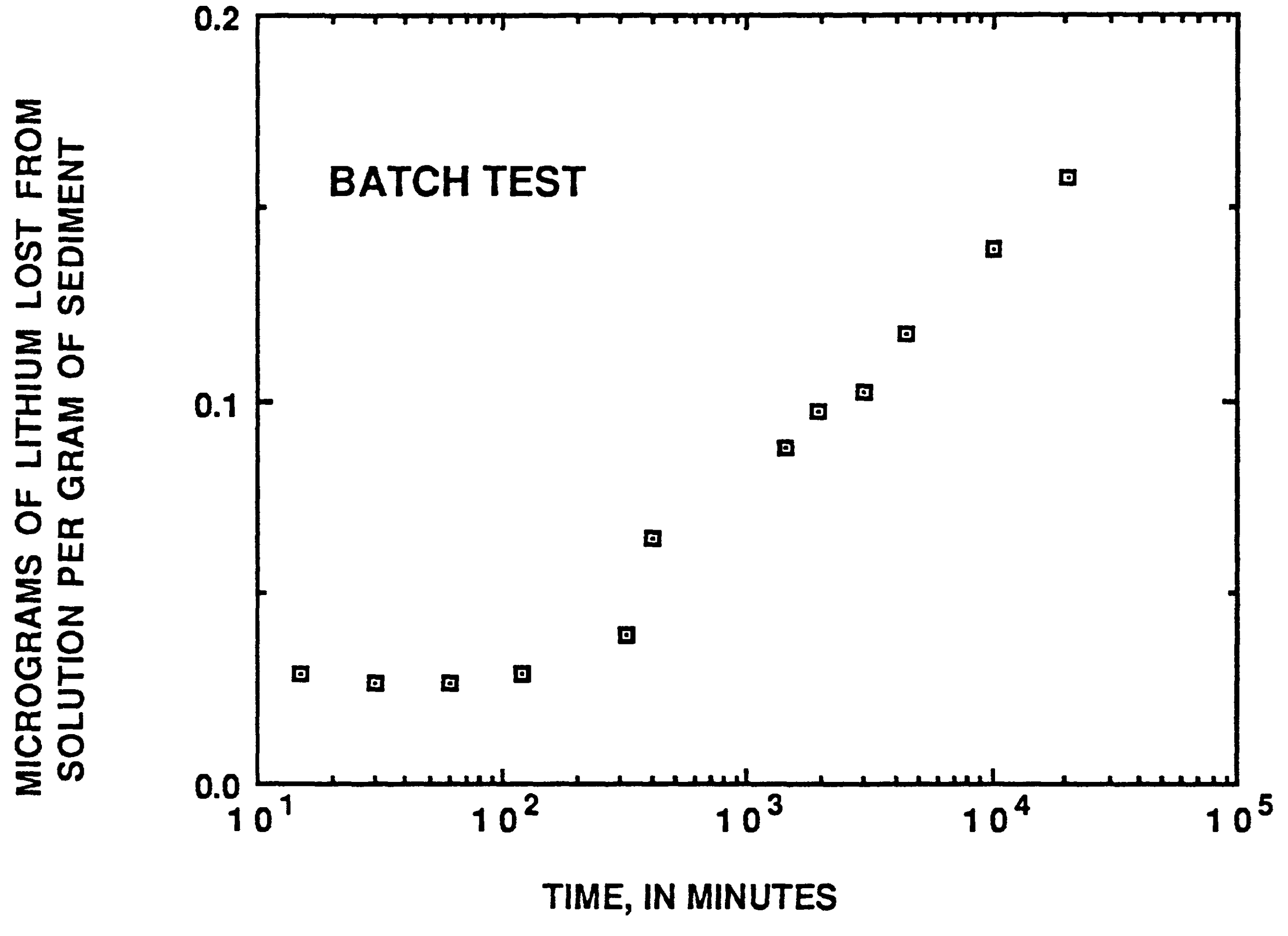

Figure C–13. – Amount of lithium lost from solution per gram of sediment as a function of the logarithm of time the sediment is in contact with the solution.

using Cape Cod ground water tagged with sodium-22 (^{22}Na). All fractions showed a rapid initial takeup of ^{22}Na from solution; however, only the feldspar and biotite fractions continued to remove significant amounts of ^{22}Na from solution with time.

The results of these experiments establish that cations are removed from solution over time and suggest the solid phases that are responsible, but do not identify the location of sorption. It could be argued that the time-dependent sorption was occurring at sites of different energy levels on grain surfaces or that cations were diffusing into the grains. To resolve this question, several additional experiments were conducted. Scanning electron microscopy (SEM) showed that plagioclase in microperthite grains in the feldspar fraction had partially weathered to clay. Cross sections of these weathered grains showed a distinct honeycomb texture where micropores were lined with clay. Samples of feldspar grains were cleaned, to remove any clays attached to the surface, by using a mild detergent in a stirring bath. These cleaned grains were disrupted with a high-power ultrasonic probe, and the silt and a fine fraction (less than 38 μm) separated for X–ray-diffraction analysis. The less-than-38 μm fraction shows the presence of smectite, kaolinite, and possibly illite, confirming the SEM observations. The presence of internal porosity was supported by mercury-porosimetry determinations that showed that the internal porosity of all the minerals was approximately 10 percent. In another test, the three mineral fractions were immersed for 14 days in a Cape Cod ground water that had been labeled with ^{22}Na washed, dried, and then subjected to an air-mill abrasion procedure. This procedure permits the removal of 1 or 2 μm of the grain surface at a time and is analogous to peeling an onion. Gamma radiation measurements of both the abraded surface material and the remaining grains confirm that more than 90 percent of the ^{22}Na was on the outer 3 or 4 μm of the quartz, whereas less than 50 percent was on the outer surface of feldspars and biotite fractions. In another experiment, the three mineral reactions were immersed in Cape Cod water that had been tagged with ^{22}Na for 14 days, and then leached by 0.25 molar $CaCl_2$ for 1 hour. Approximately 50 percent of the radioactive ^{22}Na was removed from each fraction by this procedure. A second leaching of 4 hours further reduced the radioactivity of the minerals but all retained easily detectable amounts of ^{22}Na and further supports the hypothesis that reaction sites are present in the interior of the grains.

SUMMARY

The data outlined above strongly suggests (1) that time-dependent sorption of trace quantities of inorganic cations was at least twice as great as that which occurred during a 24-hour Kd determination; (2) that diffusion into grain interiors is a major mechanism controlling the concentration of cations in this system and, therefore, must be considered in solute transport simulations in certain clastic aquifers; and (3) because of the nonequilibrium diffusion nature of transport in this system, a conservative ion may not be a good indicator of hydrodynamic dispersion exhibited by a reacting ion.

USE OF TRACER TESTS TO MEASURE THE TRANSPORT AND CONSUMPTION OF METHANE IN A CONTAMINATED AQUIFER

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

ABSTRACT

Rates of methane oxidation were measured in a nitrate-enriched zone of an unconfined sand and gravel aquifer (Cape Cod, Massachusetts) using in situ natural-gradient tracer tests. Methane oxidation was calculated from breakthrough curves of methane relative to halide and inert gas (hexafluoroethane) tracers and confirmed by the appearance of ^{13}C-enriched carbon dioxide in experiments with ^{13}C-enriched methane as the tracer. Methane oxidation predominantly occurred in a zone of denitrification; the highest rates of methane oxidation and denitrification were found at the same depth. These results indicate that nitrate may be a possible electron acceptor for methane oxidation in ground-water systems.

INTRODUCTION

Methane oxidation and denitrification are two bacterial processes considered likely to be key mechanisms for removal of contaminants from ground water – denitrification because the process reduces nitrate, a common ground-water contaminant (Robertson, 1979; Katz and others, 1980; Porter, 1980; Burden, 1982), to N_2 (Gillham and Cherry, 1978; Vogel and others, 1981; Howard, 1985; Trudell and others, 1986; and Slater and Capone, 1987), and methane oxidation because it has been suggested as a potential *in situ* treatment process for removal of halogenated aliphatic compounds (Wilson and Wilson, 1985; Semprini and others, 1988). However, these processes are rarely linked, either spatially or conceptually, in ground-water or surface-water systems. In this study, we examined these processes in a nitrate-enriched zone of an unconfined sand and gravel aquifer using *in situ* natural-gradient tracer tests. These tracer tests take advantage of natural ground-water flow to transport injected tracers through undisturbed sections of an aquifer. We found that high rates of methane oxidation occurred in the same zone that displayed relatively high rates of denitrification, high concentrations of nitrous oxide, and extremely low concentrations of dissolved oxygen. Stoichiometrically, the amount of methane consumed greatly exceeded oxygen availability, demonstrating that anoxic methane oxidation was occurring within this ground-water zone. These results suggest that nitrate may be a possible electron acceptor for methane oxidation, a microbial process which would have a high energy yield and which could have important geochemical significance.

STUDY SITE

The study site is a freshwater sand and gravel glacial outwash aquifer located on Cape Cod, Mass., which has been contaminated by land disposal of treated sewage since 1936. The resulting contaminant plume is greater than 3.5 km (kilometers) long, 0.9 km wide, and 23 meters thick (LeBlanc, 1984a). In general, the contaminant plume consists of vertical and horizontal gradients of specific conductance (50-400 uS (microsiemens)), dissolved oxygen (0-8 mg/L (milligrams per liter)), pH (5-7.1), dissolved organic carbon (1-4 mg/L, much of it refractory in nature), and inorganic compounds, such as chloride (0-28 mg/L), sulfate (4-30 mg/L), nitrate (0-16 mg N/L), and ammonium (0-10 mg N/L) (LeBlanc, 1984a, b; Thurman and others, 1986). These gradients have resulted in corresponding distribution patterns of bacterial abundance and heterotrophic uptake (Harvey and others, 1984). The chemical makeup of the plume, especially with regard to inorganic nitrogen species, is similar to that associated with more than 17 million residential septic systems across the U.S. (Canter and Knox, 1985) and, therefore, represents increasingly common conditions in regional aquifers.

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

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

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

MATERIALS AND METHODS

Ground-water samples for vertical profiles were collected from multilevel sampling devices (Garabedian, 1987) with a peristaltic pump at a site located in the center of the contaminant plume 0.25 km downgradient from the contaminant source. This distance represents 1.5 to 3.0 years travel time for regional ground-water flow. For oxygen analysis, samples were collected in 300 mL (milliliter) biochemical oxygen demand (BOD) bottles positioned in 2-liter gas-tight jars to prevent air contamination. Each jar was connected in line between the sampling well and the pump. Inflowing sample entered the BOD bottle first, then overflowed into the larger vessel; 2 to 3 liters were pumped through each BOD bottle. Oxygen was assayed by the iodometric method (American Public Health Association, 1981). Samples for nitrate determination were filtered and assayed with the cadmium reduction method (American Public Health Association, 1981), while nitrous oxide in the headspace of argon-sparged serum bottles containing 15 mL of water sample was analyzed by gas chromatography with an electron capture detector (Smith and Duff, 1988). No significant differences were found in concentrations of dissolved constituents in comparable samples collected with a down well pump. Denitrification rates in aquifer sediments were measured in intact cores. Aquifer sediments were collected in the immediate vicinity of the multilevel sampling well with a wireline piston core barrel (Zapico and others, 1987) fitted with 5-cm (centimeter) diameter by 1.5 meter-long aluminum core liners. This coring method retains the porewater, thus preventing exposure of the sediments to air and, therefore, maintaining sample integrity. The core and liner were cut into segments corresponding to the depths of the adjacent well points. Acetylene-amended ground water (from the same depth as each core segment and with the *in situ* oxygen partial pressure) was pumped through each subcore with a peristaltic pump (3-4 pore volumes). The cores were subsequently stoppered and denitrification assayed with the acetylene blockage technique (Balderston and others, 1976; Yoshinari and others, 1977; Smith and Duff, 1988).

Methane oxidation was assayed *in situ* at the same location and in an uncontaminated part of the aquifer using natural gradient tracer tests (n = 4). Ground water (100 liters) was pumped in a closed system from two ports of a multilevel injection well into a gas-impermeable bag (which had been flushed five times with nitrogen gas), amended with sodium chloride (or sodium bromide), hexafluoroethane, and methane (either unenriched or ^{13}C-enriched), and pumped back into the ground through the same two ports. Care was taken to avoid altering the *in situ* oxygen concentration of the injectant and to avoid pumping any gas bubbles into the ground. Situated 6.7 meters downgradient from the injection well were four multilevel sampling wells (1 meter apart, 15 ports apiece, each port spaced 0.6 meter vertically) located on a line perpendicular to local ground-water flow. Water samples (20 mL) were collected daily from these wells and assayed for the injection components. Halides were assayed in the field by ion-specific electrode (corroborated with ion chromatography); samples for gas analysis were collected in a gas-tight syringe, injected into a sealed serum bottle, and the gases assayed by gas chromatography with a flame ionization detector using a headspace equilibration technique (Molongoski and Klug, 1980). Dissolved inorganic carbon in 1-liter samples was precipitated as strontium carbonate, filtered, and the ^{13}C/^{12}C content determined by mass spectrometry (McCrea, 1950).

RESULTS AND DISCUSSION

The geochemical environment at the sampling site exhibited steep vertical gradients of dissolved oxygen and nitrate concentrations (fig. C–14a), and other constituents characteristic of the contaminant plume (data not shown). These gradients are common throughout the plume because the plume is overlain by uncontaminated ground water originating from areal recharge (LeBlanc, 1984a) and because vertical dispersion is quite small (Garabedian, 1987). Typically, the gradients occur over relatively narrow depth intervals. Below 8 meters, oxygen values were 2 to 3 micromoles per liter (the detection limit) and coincided with a zone of high nitrate concentration (200-1,000 micromoles per liter) which extended 6-12 meters below land surface. The plume extended to a depth of 35 meters at this location. The nitrate-containing interval also contained very high concentrations (40 nanomoles per liter) of nitrous oxide (fig. C–14b) and concentrations of nitrogen gas

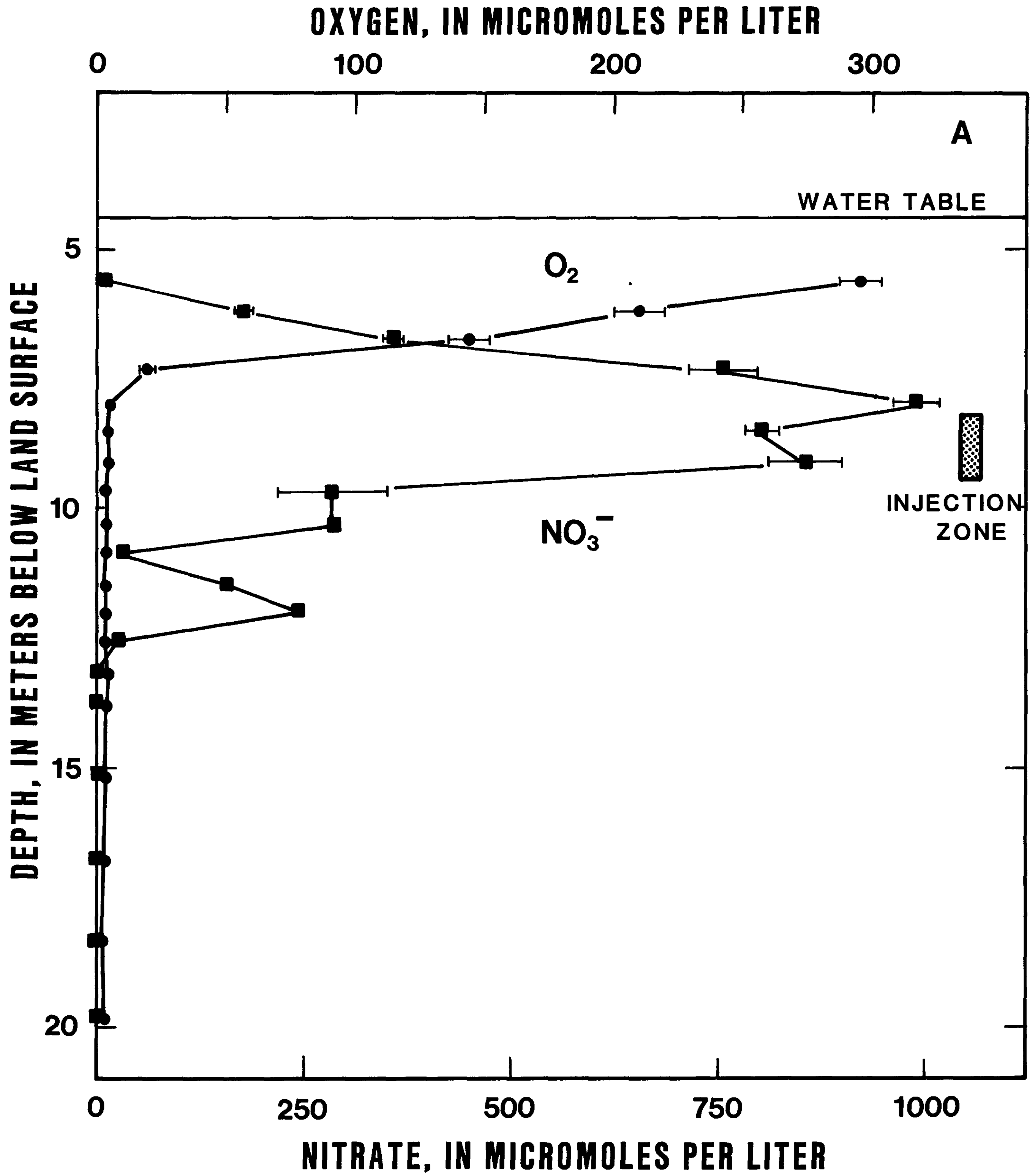

Figure C–14a.—Vertical profiles at sampling site, November 1986. Vertical bar in panel A denotes depth interval in which tracers were injected; bar graph in panel B presents denitrification rates. Error bars represent standard error of the mean.

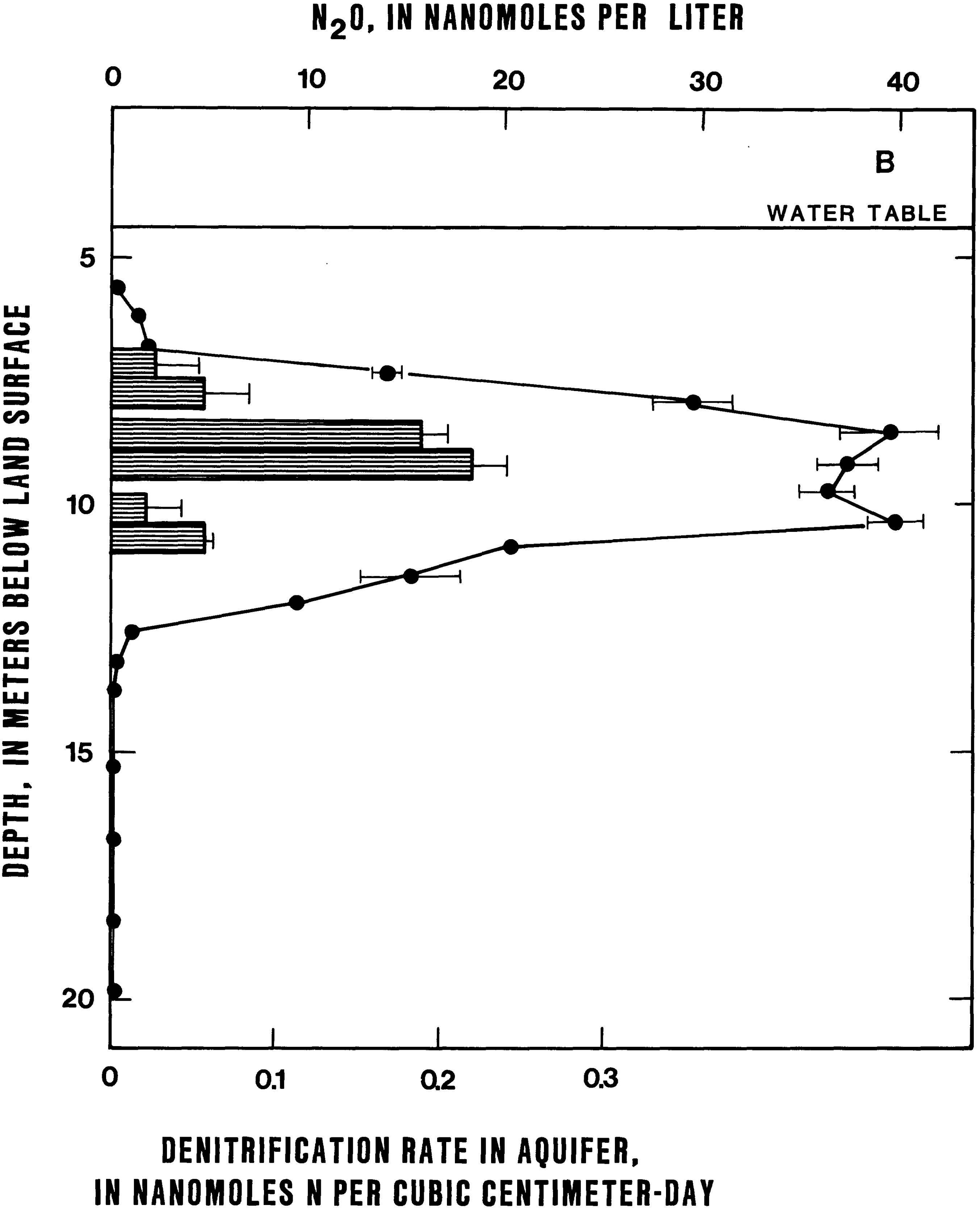

Figure C–14b.—Vertical profiles at sampling site, November 1986. Vertical bar in panel A denotes depth interval in which tracers were injected; bar graph in panel B presents denitrification rates. Error bars represent standard error of the mean.

(1–2 millimoles per liter, data not shown) that were well in excess of atmospheric equilibration. These profiles indicate that an active zone of denitrification may exist within the aquifer in this vertical interval. This was confirmed by directly assessing rates of denitrification at *in situ* nitrate and oxygen concentrations in intact cores of aquifer sediments collected from this zone (fig. C–14b). Peak activity occurred within the same interval as the peak nitrous oxide and nitrate values, but the zone of activity was only 4 to 5 meters thick. Maximum rates of nitrate reduction were an order of magnitude lower than generally found for estuarine and coastal marine sediments (Hattori, 1983). It is interesting to note that the oxygen concentration within this zone may have been optimal for nitrous oxide accumulation (Yoh and others, 1983; Jörgensen and others, 1984), resulting in the very high levels.

This same zone also possessed the capability to oxidize methane, even though ground-water methane concentrations were below atmospheric equilibrium levels. Natural-gradient tracer tests demonstrated that methane, hexafluoroethane, and chloride were transported at equivalent rates within this zone. The peak concentration of each arrived at the sampling well on the same day (fig. C–15a). However, when normalized to the injectate concentration, the hexafluoroethane and chloride breakthough curves were identical while methane was substanitally attenuated. For any given sample, the amount of methane consumed can be calculated as the difference between unattenuated transport (from hexafluoroethane, bromide, or chloride) and the measured methane concentration (see fig. C–15b). The loss of methane was not a physical process inasmuch as both an inert gas and conservative ions were transported identically. This attenuation of methane was most likely the result of methane oxidation by the resident microbial population. To test this hypothesis, another tracer test was conducted at the same site using ^{13}C-enriched methane to look for formation of ^{13}C-enriched carbon dioxide. The breakthough curves for this experiment (fig. C–15b) demonstrate that methane oxidation was occurring within this zone of denitrification. Furthermore, the maximum amount of methane consumed (7.5 μmol/L (micromoles per liter)) was greater than three times the total available oxygen concentration (2.3 micromoles per liter, standard error = 0.1). Inasmuch as the ratio of oxygen consumed to methane consumed is 1.5 to 2.0 to 1 for aerobic methane oxidation, it appears that oxygen was not the major electron acceptor for the methane oxidized within the aquifer. The symmetry of the methane breakthrough curves (figs. C–15a, b) suggests that an adaptation period for methane as a substrate was not required, even though *in situ* methane concentrations are less than 0.7 micromoles per liter. For comparison, we also conducted a tracer test in an uncontaminated, well oxygenated (greater than 250 micromoles per liter) part of the aquifer and found that this predisposition for methane oxidation occurred aerobically as well.

Anoxic methane oxidation has been the focus of several recent investigations (Reeburgh, 1980; Lidstrom, 1983; Iversen and Jörgensen, 1985; Iversen and others, 1987; Ward and others, 1987). Evidence is growing that indicates that the process occurs in surface-water systems (marine and freshwater), both in sediments and in water columns. Although it has not been directly proven, sulfate reduction is often considered to be the electron-accepting step in these habitats (Devol and Ahmed, 1981; Iversen and Jörgensen, 1985). Little attention has been given to nitrate as a potential electron acceptor for anoxic methane oxidation even though it would have more than an order of magnitude higher energy yield than sulfate reduction. There are, however, reports of methane oxidation by denitrification in the wastewater-treatment literature (Sollo and others, 1976). Although the electron acceptor could not be ascertained in this ground-water study, nitrate seems to be a likely candidate, given its availability and energy yield. The denitrifying zone also contains sulfate (40 micromolar) and soluble iron (2 micromolar) but no detectable hydrogen sulfide or ferrous sulfide and no iron oxyhydroxides (D. Lovley, U.S. Geological Survey, oral commun., 1988). Hence, sulfate reduction and iron reduction were not involved. Given the magnitude of ground-water nitrate contamination in the United States and in Europe, the potential for anoxic methane oxidation in ground-water systems may be of widespread importance in the removal of both nitrate and organic contaminants and could form the basis for *in situ* decontamination treatments. In addition, denitrification-coupled methane oxidation could be important in coastal environments where nitrate transported by ground water has been implicated in surface-water eutrophication (Capone and Bautista, 1985; Slater and Capone, 1987).

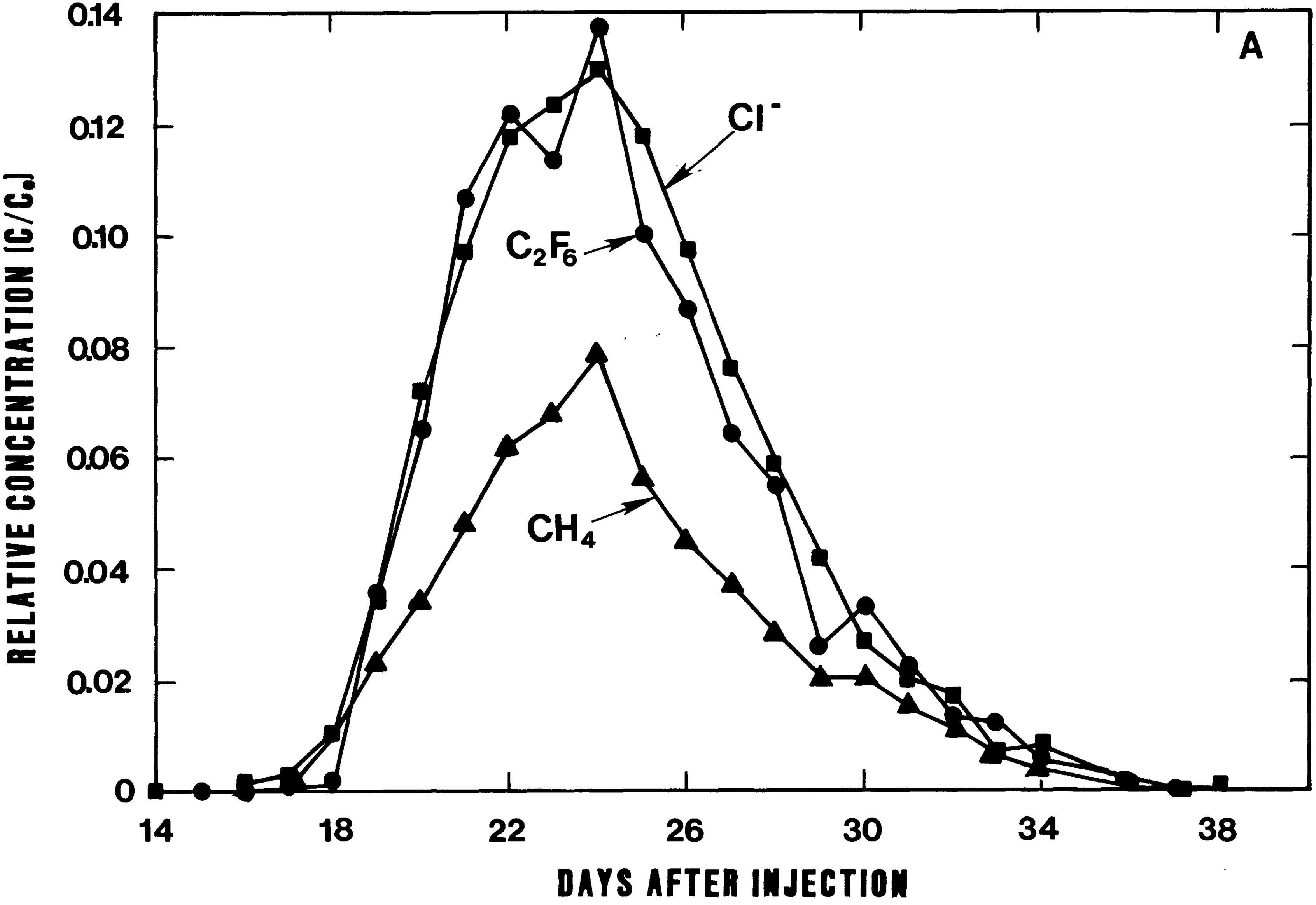

Figure C–15a.—Time course of the relative concentrations of chloride (Cl$^-$), hexafluoroethane (C_2F_6), and methane (CH_4) during a natural gradient tracer test (November 1986) from a sampling well screened at 9.7 meters beneath land surface.

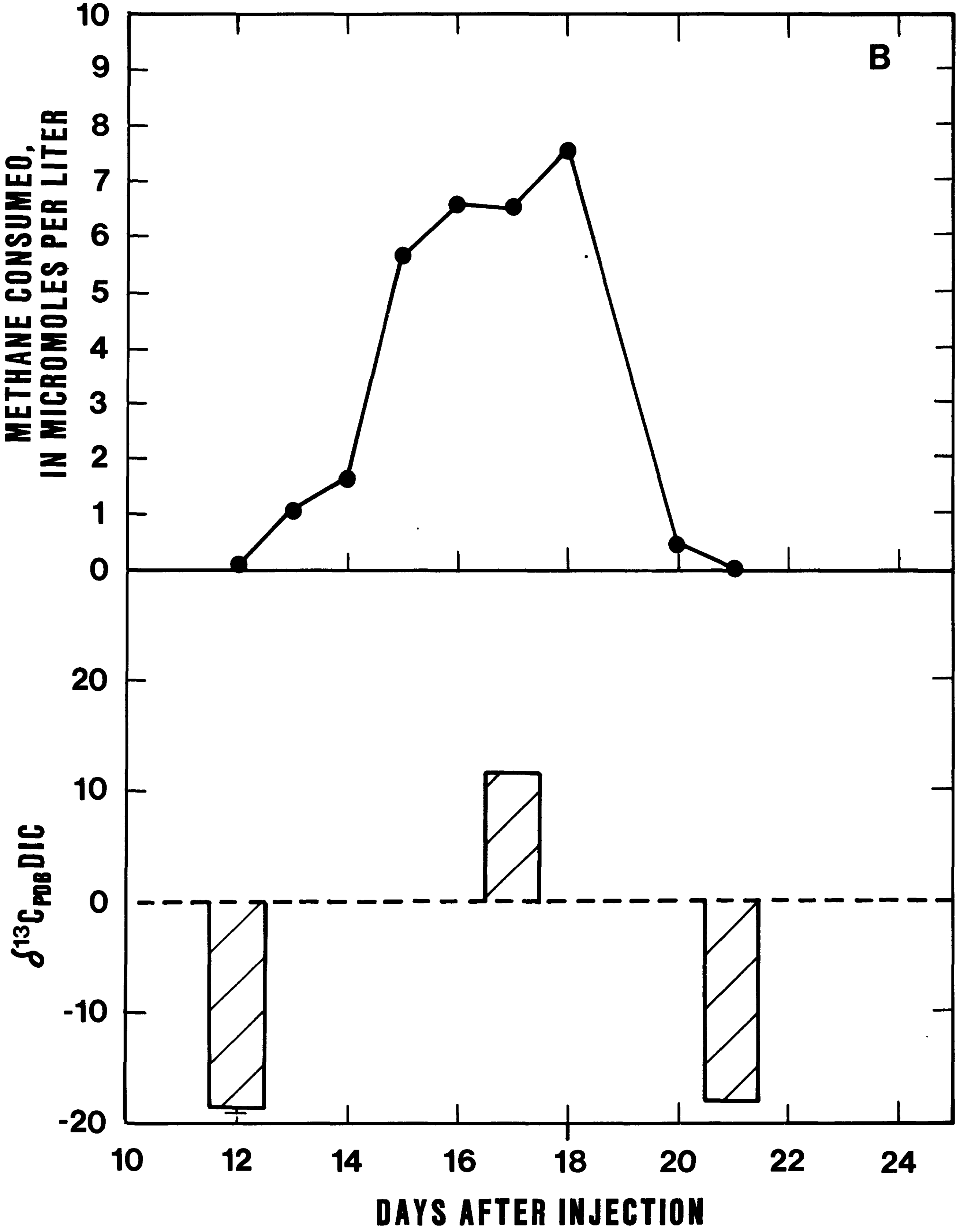

Figure C-15b.—Time course of methane consumption and $\delta^{13}C$ values of dissolved inorganic carbon from the same depth during a second tracer test with ^{13}C-enriched methane (99 percent). Error bar is standard deviation.

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INFLUENCE OF GEOCHEMICAL HETEROGENEITY IN A SAND AND GRAVEL AQUIFER ON THE SORPTION OF CHLOROBENZENES

By Larry B. Barber, II[1]

ABSTRACT

The partitioning of nonionic-organic solutes between the aqueous and sediment phases within an aquifer is a function of the organic-carbon content of the sediment. It is proposed that naturally occurring organic compounds (humic substances) preferentially associate with iron-oxide coated mineral surfaces as the result of charge interactions. The resulting carbon-enriched iron oxide surfaces should be a more effective sorbent than the bulk sediment. A numerical simulation is presented that demonstrates the potential effect of sediment-organic carbon association with a particular mineral phase. A one-dimensional solute-transport model, coupled with partition theory and the measured organic-carbon content of particle-size and mineralogical fractions from the Cape Cod (Massachusetts) Toxic Waste Research site, is used to simulate the sediment geochemical effect on the subsurface transport of a series of chlorinated benzene compounds.

INTRODUCTION

Previous articles have described the occurrence, distribution, and fate of organic contaminants in ground water at the Cape Cod (Massachusetts) Toxic Wastes Research (CCTWR) site (Thurman and others, 1986, Barber, 1988, Barber and others, 1988). These studies have shown that many recalcitrant organic compounds have persisted for long periods in the ground water with little apparent decrease in concentration because of chemical or biological processes. Many of the compounds with moderate to high aqueous solubilities (for example, surfactants and chlorinated solvents) appear to be transported at the same velocity as the ground water, suggesting little sorptive interaction with the sediments. This rapid transport is consistent with a partition-sorption model and the low-organic carbon content of the aquifer material (less than 0.1 percent). However, for compounds with low solubilities, such as alkylphenols, sorption appears to be occurring and the sequence of retardation is consistent with partitioning (the least soluble compounds have the most restricted distribution).

The focus of this study is the sorption of nonionic organic solutes on the CCTWR site aquifer sediments, and the effect of geochemical factors (mineralogy and organic grain coatings) on sorption. Specifically, this paper presents a simulation of the influence of sediment properties on the transport of a series of chlorinated benzenes, based on a one-dimensional solute transport model (Grove and Stollenwerk, 1984), and distribution coefficients (Kd's) calculated from partition theory (Chiou and others, 1983) and measured sediment-organic carbon concentrations.

THEORETICAL DEVELOPMENT

Numerous investigators have shown that the uptake of nonionic organic solutes by natural sediments is dependent on the amount of sediment-organic carbon present (Schwarzenbach and Westall, 1981; Chiou and others, 1983; Karickhoff, 1984). The uptake can be described in terms of a distribution coefficient,

$$\mathrm{Kd} = \frac{\mathrm{Cs}}{\mathrm{Cw}} \qquad (1)$$

where

Cs is the concentration of the sorbed species on the sediment phase (M/M), and

Cw is the aqueous concentration of the species of interest (M/L^3).

The Kd for a hypothetical sediment sorbent of 100 percent organic matter (Kom) can be predicted from the octanol-water partition coefficient (Kow) of the solute of interest (which is a function of aqueous solubility) by the equation of Chiou and others (1983),

$$\log \mathrm{Kom} = 0.904 \log \mathrm{Kow} - 0.779. \qquad (2)$$

The Kom (organic-matter partition coefficient) can be converted to an organic

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

carbon basis (Koc) by multiplying Kom by 1.724 (assuming organic matter is approximately 60 percent carbon). The Koc values then can be used to calculate sediment Kd values by normalizing to the fractional organic-carbon content of the sediments (foc),

$$\mathrm{Kd} = \mathrm{Koc} \times \mathrm{foc}. \qquad (3)$$

Although partitioning into sediment organic matter can be adequately described (generally within a factor of 2) by the above equations, the actual nature of the sorbent phase in aquifer systems is poorly understood. Aquifer sediments are complex chemical matrices, in which the organic-carbon fraction generally is less than 0.1 percent. At such low carbon levels, the role of the mineralogical composition of the sediments may become important (Karickhoff, 1984). A secondary mineralogical control model has been proposed (Barber, 1987a, b) that suggests the chemical composition of the aquifer sediments can influence the quantity and location of organic carbon associated with the sediment phase. It has also been proposed (Barber, 1987a), that geological processes, such as weathering and density effects on sedimentation, operate in a manner such that mineral phases containing significant sediment-organic carbon can be preferentially concentrated within certain particle-size classes and localized stratigraphic zones; thus, the spatial relation of the various mineral and particle-size components (geochemical heterogeneity) may play an important role in affecting the transport of organic contaminants.

TARGET COMPOUNDS

Chlorobenzenes were selected for investigation because of several factors: (1) They are an environmentally important class of organic contaminants, and several chlorobenzene species are present in the contamination plume at the CCTWR site; (2) they are nonionic and nonpolar in character; (3) they exhibit a systematic increase in Kow (decrease in aqueous solubility) with increased chlorination; (4) their physicochemical properties are well known; and (5) they are readily available in pure form. Table C-4 lists the aqueous solubility, Kow, and Koc data for the compounds evaluated in this study. Only one isomer was selected (with an increment in Kow as uniform as possible) for each level of chlorination.

Table C–4. – Summary of Kow, Kom, Koc, and solubility data for chlorobenzene compounds considered in this study [Mg/L, milligrams per liter]

Compound	log[1] Kow	log[2] Kom	log[3] Koc	Solubility[4] (mg/L)
Chlorobenzene	2.84	1.79	2.03	502.8
1,4-Dichlorobenzene	3.47	2.36	2.59	90.6
1,2,3-Trichlorobenzene	4.14	2.96	3.20	31.5
1,2,3,4-Tetrachlorobenzene	4.60	3.38	3.62	4.3
Pentachlorobenzene	5.20	3.92	4.16	.56
Hexachlorobenzene	5.50	4.19	4.43	.005

[1] Values from Pereira and others, 1988.

[2] Calculated from equation 2

[3] Koc = 1.724 Kom.

[4] Data from Yalkowsky and others, 1979.

SIMULATIONS

The transport of chlorobenzenes was simulated using the one-dimensional, equilibrium-controlled sorption model of Grove and Stollenwerk (1984). The model was used to predict the relative transport velocities of the solutes on the basis of calculated Kd values using the sediment organic-carbon content of the various size and mineralogy classes (Barber, 1987a).

The transport model is based on the following one-dimensional differential equation (Grove and Stollenwerk, 1984),

$$e\frac{dCw}{dt} + e\,V\frac{dCw}{dx} - e\,D\frac{d^2Cw}{dx^2} = \mathrm{CHEM} \qquad (4)$$

and

$$\mathrm{CHEM} = -\,pb\frac{dCs}{dt}, \qquad (5)$$

where

e is effective porosity, (dimensionless)

t is time (T),

V is interstitial fluid velocity (L/T),

x is distance (L),

D is the hydrodynamic dispersion coefficient (L^2/T), and

pb is bulk density of the porous medium (M/L^3).

The aquifer properties and other input data used in the model are listed in table C-5. Table C-6 lists the measured organic-carbon contents of the sediment and mineralogical fractions, and the calculated Kd values.

Table C-5. – Summary of input data for one-dimensional equilibrium controlled flow model
[Grove and Stollenwerk, 1984]

Input variable	Input variable[1]
Calculation variables:	
Type of sorption	0
Concentration boundary condition	1
Number of nodes	101
Time increment	14.48
Pore volumes in simulation	2
Printout increment	1
Fractional cell distance of transport	0.2
Nodes for calculation	101
Aquifer data:	
Time of pulse	111 days
Column length	100 meters
Fluid velocity[2]	0.30 meter per day
Molecular diffusion constant	0
Dispersivity[2]	0.97 meter
Bulk density	1.64 kilograms per cubic meter
Effective porosity	0.38
Sorption variables:	
Linear isotherm slope (Kd)	See table C-6
Input solute concentration	20 percent water solubility

[1] All input values not listed here are assumed to be default values.

[2] From Garabedian and others, 1987.

Several assumptions were made in the application of this model: (1) Partitioning can be described by a linear isotherm; (2) fluid velocity is sufficiently low relative to the reaction kinetics so that equilibrium is attained; (3) molecular diffusion is negligible relative to mechanical dispersion; and (4) linear-flow velocity within the aquifer is constant and does not vary as a function of time or space.

RESULTS

The results of the numerical simulations are summarized in table C-7. The effect of particle size and mineralogy on the relative transport of the various solutes is shown in figure C-16. These data were calculated assuming a uniform flow velocity, which is valid for the different mineralogical components of a given particle size. However, the flow velocity will differ depending on particle size; thus, the data that show the effect of particle size on retardation are presented in this manner solely to illustrate the influence of sediment carbon on sorption and are not intended to represent actual flow relations in the aquifer system.

Table C-6. – Summary of data on sediment organic carbon and calculated chlorobenzene distribution coefficients as a function of particle size and mineralogy

foc = fraction organic carbon
CB = chlorobenzene
DCB = 1,4-dichlorobenzene
TriCB = 1,2,3-trichlorobenzene
Tet CB = 1,2,3,4-tetrachlorobenzene
PCB = pentachlorobenzene
HCB = hexachlorobenzene

nd = not determined
B = bulk sediment sample
M = magnetic mineralogical fraction
NM = nonmagnetic mineralogical fraction

Particle size[1] and mineralogic Fraction	foc	Kd[2] CB	Kd[2] DCB	Kd[2] TriCB	Kd[2] TetCB	Kd[2] PCB	Kd[2] HCB
<63 B	0.00054	0.06	0.21	0.86	2.23	7.79	14.54
<63 M	nd	nd	nd	nd	nd	nd	nd
<63 NM	nd	nd	nd	nd	nd	nd	nd
63-125 B	.00022	.02	.09	.35	.91	3.17	5.93
63-125 M	.00064	.07	.25	1.02	2.65	9.23	17.24
63-125 NM	.00016	.02	.06	.25	.66	2.31	4.31
125-250 B	.00012	.01	.05	.19	.50	1.73	3.23
125-250 M	.00064	.07	.24	.98	2.56	8.94	16.70
125-250 NM	.00010	.01	.04	.16	.41	1.44	2.69
250-500 B	.00008	.01	.03	.13	.33	1.15	2.15
250-500 M	.00065	.07	.26	1.03	2.69	9.37	17.51
250-500 NM	.00002	<.01	.01	.03	.08	.29	.54

[1] Particle size given in micrometers.

[2] Distributuion coefficient (Kd = Koc x foc).

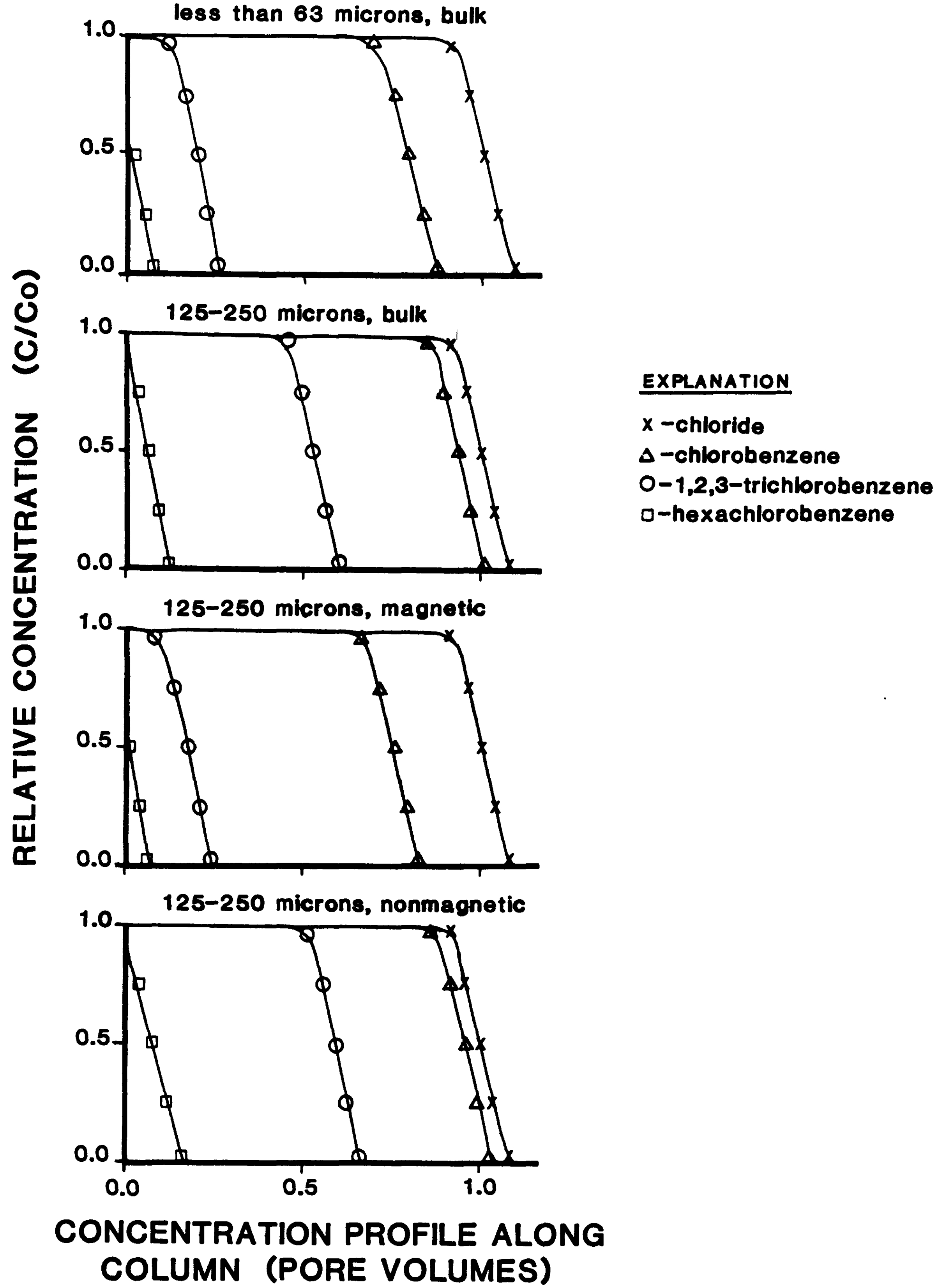

Figure C–16. – Effect of particle size and mineralogy on the relative rates of transport for a conservative tracer (chloride) and three chlorobenzene isomers (calculations based on Kd values given in table C–6 and a uniform flow velocity of 0.3 meters per day).

Table C–7. —Summary of predicted retardation factors and ground-water flow velocities for chlorobenzenes as a function of mineralogy and particle size

V = Velocity = 0.30 meter per day

Rf = Relative retardation factor = 1+(pb*kd/e)
where
pb (bulk density) = 1.64 grams per cubic centimeter,
e (porosity) = 0.38, and
Kd = (distribution coefficient) = values given in table C-6

CB = chlorobenzene
DCB = dichlorobenzene
TriCB = trichlorobenzene
TetCB = tetrachlorobenzene
PCB = pentachlorobenzene
HCB = hexachlorobenzene

nd = not determined
B = bulk sediment sample
M = magnetic mineralogical fraction
NM = nonmagnetic mineralogical fraction

Particle size[1] and mineralogic fraction	Rf CB	V CB	Rf DCB	V DCB	Rf TriCB	V TriCB	Rf TetCB	V TetCB	Rf PCB	V PCB	Rf HCB	V HCB
<63 B	1.25	0.24	1.92	0.16	4.70	0.06	10.64	0.03	34.61	0.01	63.77	0.005
<63 M	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
<63 NM	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
63-125 B	1.10	.27	1.37	.22	2.51	.12	4.93	.06	14.96	.02	26.57	.011
63-125 M	1.29	.23	2.09	.14	5.38	.06	12.42	.02	40.84	.01	75.39	.004
63-125 NM	1.07	.28	1.27	.24	2.10	.14	3.86	.08	10.96	.03	19.60	.015
125-250 B	1.05	.28	1.20	.25	1.82	.16	3.14	.10	8.47	.04	14.95	.020
125-250 M	1.28	.23	2.05	.15	5.25	.06	12.07	.02	39.59	.01	73.07	.004
125-250 NM	1.05	.29	1.17	.26	1.69	.18	2.78	.11	7.22	.04	12.62	.024
250-500 B	1.04	.29	1.14	.26	1.55	.19	2.43	.12	5.98	.05	10.30	.029
250-500 M	1.30	.23	2.10	.14	5.45	.06	12.60	.02	41.46	.01	76.56	.004
250-500 NM	1.01	.30	1.03	.29	1.14	.26	1.36	.22	2.24	.13	3.32	.090

[1] Particle size given in micrometers.

As shown by the data in table C-7, the effect of variations in carbon content as a function of mineralogy and particle size potentially can influence the rates of transport for nonionic solutes. This model predicts that, with decreasing particle size (increasing organic-carbon content), the relative retardation (sorption) increases and the flow velocity decreases. Simultaneously, a decrease in flow velocity will occur as the result of the lower hydraulic conductivity for the smaller particle size. The net result is that the fine-grained material potentially has a greater capacity for solute interactions than the coarser material. For a given particle size, the retardation effect increases with decreasing solubility of the solute.

The effect of mineralogy is of the same order of magnitude as that of particle size. For a given particle size, the bulk of the organic matter appears to be concentrated in the magnetic-mineral fraction, probably as the result of interaction between negatively charged natural organic matter and positively charged surfaces of iron oxides (Barber, 1987a). As a result, the magnetic fraction will have a greater retarding effect on transport velocities than the bulk material and the nonmagnetic fraction.

SUMMARY AND CONCLUSION

This paper presents theoretical evidence showing the potential effect of geochemical heterogeneity on transport of nonionic organic solutes in ground water. The sediment-organic carbon content increases with the fine-grained particle-size fractions, and with magnetic minerals within a given particle size. As a result, sorption affinity is greater in these sediment fractions than in the bulk aquifer material. These results suggest that further study of the spatial distribution and sorptive characteristics of the various mineral substrates within an aquifer, will improve understanding of chemical interactions and transport processes in ground-water systems.

FUTURE RESEARCH

The predicted effect of mineralogy and particle size on sorption of nonionic organic solutes is presently being evaluated by laboratory batch and column experiments. Geochemical heterogeneity at the CCTWR site is also under investigation. The spatial relations among the various chemical substrates are being evaluated by field coring efforts in which detailed stratigraphic logs of the mineralogical and particle-size distributions are being developed.

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TRANSPORT OF BACTERIA IN A CONTAMINATED AQUIFER

By Ronald W. Harvey[1]

ABSTRACT

The transport of bacteria through contaminated aquifers is becoming an increasingly important issue in public health and waste management. Many factors involved in the transport of bacteria through ground water are poorly understood and there is a scarcity of field data. This paper evaluates two factors: (1) the importance of colloid filtration theory as a determinant of the extent of transport and the size distribution of transported bacteria and (2) the role of secondary pore structure in observed transport characteristics. Experiments were conducted at a small-scale, natural-gradient ground water injection site in an area of organically contaminated ground water (Cape Cod, Massachusetts) and in the laboratory by use of flow-through columns packed with aquifer sediments. Results from these experiments indicate that secondary pore structure relating to the manner in which the aquifer sediment particles are spatially arranged has a substantial effect on transport characteristics of bacteria-sized particles. Also, a modified dispersion-corrected, colloid-filtration model may be used to predict bacterial immobilization at particle surfaces and changes in bacterial size distribution that occurs with transport downgradient through aquifer sediments of Cape Cod.

INTRODUCTION

Migration of indigenous bacteria through contaminated aquifers is becoming an increasingly important issue in waste management. Degradation of highly mobile and persistent ground-water contaminants may be enhanced by cotransport of bacteria that have become acclimated to their degradation. Transport of nonindigenous bacteria in ground water also is of environmental concern, inasmuch as the appearance of microbial pathogens in water-supply wells has contributed significantly to the number of waterborne disease outbreaks (Keswick, 1984). Also, recent advances in the field of molecular genetics have enhanced the feasibility of using genetically engineered microorganisms in aquifer-restoration experiments. Critical to the success of many schemes that employ genetic technology in *in-situ* treatment of organically contaminated aquifers is the ability of the engineered organism to reach the contaminant-affected area in the aquifer. Some models can predict the extent of transport of bacteria through porous media (Corapcioglu and Haridas, 1984, 1985); however, these models can substantially underestimate bacterial transport that is observed in the field (Germann and Douglas, 1987), and corroborative experimental data on bacterial transport are scarce. It is clear that improvements to models and additional experimental data on bacterial transport are needed to predict the movement of indigenous and nonindigenous bacteria through porous-media aquifers.

This paper describes a natural-gradient, ground-water tracer experiment in which indigenous, ground-water bacteria were stained, injected into an organically contaminated part of the Cape Cod (Mass.) aquifer, and recovered downgradient. Results of a transport experiment performed with a flow-through column packed with aquifer sediment are also described. Two factors are evaluated here: (1) the importance of colloid filtration theory as a major determinant of the extent of transport and the size distribution of transported bacteria in the contaminant plume, and (2) the importance of secondary pore structure (macropores) to the transport of bacteria through sandy aquifer sediments.

MATERIALS AND METHODS

A stainless-steel submersible pump was used to collect bacteria-laden ground water (Harvey and others, 1984) from a screened, PVC observation well (5.0-cm (centimeters) diameter, 250-μm (micrometers) slot width) located 100 meters downgradient from an on-land, treated-sewage infiltration bed. A morphologically diverse population of bacteria was concentrated onsite from 600 liters of contaminated ground water to 8 liters (final volume) by using a hollow-fiber, tangential-flow filtration device (Kuwabara and Robinson, 1987), which was operated at a processing rate of

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

2 L/min (liters per minute). Recovery of bacteria in the 8 liters of retentate was about 33 percent. Because bacterial recovery was sufficient for the injection experiment, no attempt was made to resuspend and recover bacteria that had become immobilized within the hollow-fiber filters. Recovered bacteria (0.2–1.6 μm long) were stained with the fluorochrome DAPI (4′,6-diamidino-2-phenylindole) at 5 μM (micromolar) final concentration for 24 hours at 4 ° C (degrees Celsius). The stained bacteria were diluted with ground water collected from the area of injection test (500 meters downgradient from the treated-sewage infiltration bed and 9 meters below land surface (BLS)) and concentrated to a final volume of 90 liters. This was done to dilute the DAPI below its staining threshold. Bromide was added to the injectate (150 mg/L (milligrams per liter) final concentration) as a conservative tracer.

The bacteria and bromide were added slowly to the aquifer at 8.5 and 9.1 meters BLS and monitored as they moved with the natural ground-water flow past a row of multilevel samplers (6.9 meters downgradient) set perpendicular to the direction of ground-water flow. Ground water was collected on a daily basis from sampling ports located in the path of injectate travel. Bromide was measured with a specific-ion electrode and confirmed by ion chromatography. Preparations for enumeration of DAPI-stained bacteria and fluorescent microspheres were made with 100 to 200 mL (milliliters) of sample to obtain accurate counting statistics. The DAPI-stained bacteria in these samples fluoresced under incident UV light (340-380 nm (nanometers) excitation) and were enumerated on black polycarbonate membrane filters (0.2-μm pore size, 25-mm (millimeter) diameter) using a microscope that was fitted for epifluorescence, as described by Harvey and others (1984).

The applicability of a colloid-filtration theory to bacterial transport was examined by applying a colloid-transport model to observed transport characteristics of bacteria in the small-scale injection test and to observed changes in bacterial abundance and size distributions along the longitudinal axis of the contaminant plume.

Aquifer sediments were collected from the site, sterilized, and repacked into glass columns (0.6 meters long, 5.0 cm inside diameter) to examine the effect of secondary pore structure upon transport characteristics of bacteria-sized particles. This procedure yielded a porosity similar to that observed in the field tests (0.35). The columns were packed as uniformly as possible using a mechanical packer (Soil Physics Laboratory, U.S. Geological Survey, Menlo Park, Calif.). The objective was to alter the secondary pore structure of the aquifer sediments dramatically from what is observed at the field site. Columns were initially eluted with filter-sterilized, degassed 0.005 molar $CaSO_4$ solution until permeability stabilized. Flow-through column experiments were then conducted in the upflow mode at 20 °C and 40 mL/h (milliliters per hour) (1.4 m/d (meters per day) linear velocity) through the column using an 0.5-liter syringe pump that delivers accurately at low flow rates. Well-characterized, bacteria-sized microspheres (carboxylated latex; 0.2, 0.7, and 1.35 μm diameter) and bromide (Br^-) (20 mg/L (milligrams per liter)) were added as injectate to the columns. Data on breakthrough of the different sizes of carboxylated microspheres were compared to data generated in a small-scale forced-gradient field test reported earlier (Harvey and others, 1989).

RESULTS AND DISCUSSION

Pore Structure

Retardation factors for DAPI-stained bacteria in the natural-gradient tracer test are listed in table C–8. These values are compared to the results of other ground-water tracer experiments in which transport of microorganisms relative to bromide were examined. For both the faster (8.5 meters BLS) and slower zones (9.1 meters BLS) at the small-scale test site, the arrival time downgradient of the stained bacteria was nearly coincident with that of Br^-. In contrast, calculated retardation factors (ratio of time required to reach peak abundance for the microorganisms to time to peak concentration for Br^-) for all of the other injection tests employing microorganisms were substantially less than 1.0. However, a retardation factor just slightly less than 1.0 at a point 1.7 meters downgradient was obtained in a previous forced-gradient experiment with stained indigenous bacteria that was done at another site in the Cape Cod aquifer.

Retardation factors substantially less than 1.0 indicate that transport of microorganisms not attenuated by the medium is, on the average,

Table C–8.—Differences in transport velocity of microorganisms and bromide in small-scale ground-water tracer experiments

[Distance is between points of injection and recovery. Retardation factor (dimensionless) calculated as the ratio of time required to reach peak abundance for microorganism to time to peak concentration for bromide]

Reference	Microbe	Aquifer	Type of test	Distance (meters)	Retardation factor
Champ and Schroeter, 1988	*Escherichia coli*	Fractured crystalline rock	Forced-gradient	12.7	0.13
Wood and Ehrlich, 1978	*Saccharomyces cerevisiae* (yeast)	Sand and gravel (with clay and carbonate	Forced-gradient	1.5	.71
Harvey and others, 1989	Indigenous bacterial	Well-sorted sand and gravel	Forced-gradient	1.7 3.2	.95 .56
This experiment	Indigenous bacterial	Well-sorted sand and gravel	Natural-gradient	6.7 6.7	.97 none

significantly faster than that of Br$^-$ and, presumably, mean ground-water flow. The apparent enhancement in transport velocity of the unattenuated microorganisms was greatest in the experiment that involved a fractured crystalline-rock aquifer. It is hypothesized that this phenomenon is caused by preferential transport of the microbes along preferred flow paths (large pores and channels), because they may be excluded from the smaller pores on the basis of size. The near absence of rapid transport of the indigenous bacteria relative to bromide at the small-scale, natural-gradient tests may be caused by the absence of much secondary pore structure; this is consistent with the tightly packed, well-sorted nature of the aquifer sediments.

The importance of secondary pore structure to the transport characteristics of bacteria-sized particles in the Cape Cod aquifer may be examined by employing repacked aquifer sediments in flow-through column experiments. Results of a transport experiment using three size classes of bacteria-sized, carboxylated microspheres and a column repacked with aquifer sediments from the Cape Cod site are listed in table C–9. Also listed in table C–9 are results of microsphere transport in an earlier small-scale, natural-gradient ground water tracer test (values calculated from Harvey and others, 1989). Immobilization of microspheres in the column was inversely related to size, that is, the smaller microspheres were attenuated by the media to a lesser degree than the larger microspheres. It is not clear why the smaller microspheres are preferentially transported relative to larger microspheres through the column, although straining may be a possibility. This was in direct contrast to their transport characteristics in the aquifer, where the smaller microspheres were immobilized in aquifer sediments to a greater degree than were the larger microspheres. This observation is consistent with colloid-filtration theory, which predicts that smaller bacteria-sized particles being transported through porous media should become immobilised at stationary solid surfaces faster than larger bacteria-sized particles. The reason for this is that small-scale particle movement, and the likelihood that particles will encounter a solid surface, are governed largely by diffusion or Brownian motion, which increases with decreasing particle size.

Table C–9.—Retardation factors and maximum dimensionless concentrations for breakthrough of selected carboxylated microspheres in column and field experiments

[(C/Co) max is the maximum dimensionless concentration at the downgradient sampling point. Retardation factor (dimensionless) is the time to peak breakthrough for the microspheres normalized to time to peak breakthrough for bromide]

Microsphere diameter (micrometers)	(C/Co) max X 10^{-6}		Retardation factor	
	Field	Column	Field	Column
0.2	6.0	303.0	1.4	0.53
0.5	44.0	[1]29.0	1.4	[1].57
1.3	65.0	18.0	1.1	.63

[1] Size class for column was 0.7 micrometers.

In the aquifer material of Cape Cod, the carboxylated microspheres are retarded somewhat relative to bromide, apparently because of their surface characteristics (Harvey and others, 1989). The more rapid transport of the microspheres relative to bromide in the column experiment suggests that substantial secondary pore structure was created when the column was packed with aquifer material or resaturated with water. It has been observed, from previous flow-through column experiments (R.W. Harvey, U.S. Geological Survey, unpublished data on file, Menlo Park, Calif.) that transport characteristics of both bacteria and microspheres is partially dependent on the manner in which the columns are packed. Therefore, transport characteristics of bacteria and bacteria-sized particles through columns that have been repacked with subsurface sediments can be quite complex and it appears that a great deal of caution must be exercised when extrapolating results of particle transport studies performed with columns to the ground water environments.

Filtration Theory

A colloid filtration model (Yao and others, 1971) was applied to the breakthrough data for DAPI-stained bacteria in the small-scale injection test. An important factor in the application of this model is the efficiency with which collisions between bacteria and stationary solid surfaces result in the immobilization or sorption of the bacteria. This dimensionless factor (α) was estimated from measured aquifer properties and observed transport characteristics of the stained bacteria. Two methods were used to correct for macroscopic (nonchemical dispersion). The first was to normalize the integral of the dimensionless concentration history for the bacteria appearing at the downgradient samplers to that of bromide. The second method involved inclusion of a one-dimensional solution of the advection-dispersion equation (Freeze and Cherry, 1979) and a longitudinal dispersivity calculated from observed transport characteristics of bromide (S.P. Garabedian, U.S. Geological Survey, written commun., 1988). Both methods yielded similar estimates for α. Estimates of α using the first method were 8.1×10^{-3} and 9.7×10^{-3} for the faster and slower layers, respectively. Estimates of α using the second method were 6.6×10^{-3} and 9.5×10^{-3}. These calculated values are likely to be underestimates. Although the DAPI-stained bacteria did not appear to be reproducing within the timeframe of the injection experiment, they likely were subject to predation by protozoa. Significant predation would cause an overestimation of the rate at which the bacteria were being sorbed by particle surfaces.

An estimate of α also was obtained from reported (Harvey and George, 1987) distributions of free-living bacteria within the contaminant plume along a longitudinal transect from 0.26 to 1.0 km (kilometers) downgradient from the on-land, treated-sewage disposal beds. The alpha value calculated from these data (4.3×10^{-5}) likely represents an upper estimate, because it is assumed in the model that there was no net bacterial productivity; that is, that total gain in biomass resulting from growth is completely offset by losses from predation and lysis. Because the zero net growth assumption is not consistent with estimated *in-situ* growth rates reported for the contaminant plume (Harvey and George, 1987), it would appear that the magnitude of alpha may lie between 7×10^{-3} and 4×10^{-5}. However, because α depends, in part, on aquifer properties, its value may have substantial spatial variability.

Inasmuch as the colloid-filtration model predicts differential transport on the basis of particle size, a dispersion-corrected colloid filtration model was applied to observed size distributions of the free-living bacterial population in contaminated ground water adjacent to the sewage-infiltration beds. The objective was to compare predicted size distributions with observed values at various distances downgradient. Because α may differ spatially, a range of estimates were used in this model. The results are summarized in table C–10. An alpha value of 10^{-4}, which falls within the range of estimates calculated in this study, resulted in predicted size distributions for unattached bacteria that were quite similar to those that were observed, particularly in ground water 0.65 km downgradient.

The observed and predicted decreases in average cell size with increasing distance downgradient from the source of contamination is not what would be predicted on the basis of nutrient availability. This is because average cell size commonly is directly related to nutrient content of the environment. Therefore, free-living bacteria in high-nutrient ground water close to

Table C–10.—Observed average cell sizes for free-living bacteria transported downgradient through the contaminant plume and predicted values using a colloid filtration model and several estimates of the coefficient

[Distances are downgradient from well F314; NC, cannot be calculated because rate of attenuation would preclude population from reaching the downgradient observation wells; km, kilometer; µm, micrometer]

Distance	Average cell size for free-living bacteria		
	0 km	0.38 km	0.65 km
Observed:	0.46µm	0.55µm	0.71µm
Predicted:[1]			
Alpha = 4.3×10^{-5}		0.53µm	0.57µm
Alpha = 8.5×10^{-3}		NC	NC
Alpha = 1.0×10^{-4}		0.61µm	0.71µm

[1] Using dispersion-corrected, colloid-filtration model.

the sewage loading beds may be expected to have a larger average cell size than bacteria in nutrient-depleted ground water further downgradient. It is possible that the observed changes in cell-size distribution is a result of a shift in the makeup of the bacterial population with increasing distance downgradient. However, substantial increases in average diameter of polydispersed populations of bacteria-sized microspheres have been observed during transport in ground-water injection experiments. Therefore, it seems reasonable to invoke an abiotic mechanism, at least in part, to explain observed increases in bacterial size during transport through the aquifer. Because the transport process may depend on the bacterial size class, bacterial size may be a factor to consider in aquifer-restoration experiments in which selected or genetically engineered bacteria are injected into organic-contaminated ground water.

In summary, there are many factors, both biotic and abiotic, that can affect transport of bacteria through contaminated aquifers. The importance of secondary pore structure and colloid filtration cannot be ignored. Additional data on bacterial transport are needed, preferably from a variety of aquifers and hydrologic conditions.

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FIELD AND LABORATORY STUDIES OF COUPLED FLOW AND CHEMICAL REACTIONS IN THE GROUND-WATER ENVIRONMENT

By James A. Davis[1], Douglas B. Kent[1], and Brigid A. Rea[1]

ABSTRACT

A new research effort is described that emphasizes the use of laboratory and field approaches to understand the principal processes governing the transport of metals that undergo significant chemical reactions in the ground-water environment. The research approach will stimulate the development of transport models that couple the mathematical description of advection and hydrodynamic dispersion with relevant chemical relations for reactive metal ions in ground waters. Primary objectives include an improved understanding of (1) the rates of sorption processes and their inclusion in coupled transport models and (2) the importance of complexation and oxidation-reduction reactions in the transport of solutes. The research will make significant contributions toward assessing risks arising from industrial, nuclear, and municipal contamination of aquifers.

INTRODUCTION

The developed nations of the world continue to experience an ever-increasing need to predict the movement and fate of chemical substances in the ground-water environment. This need is being driven today largely by problems in assessing the suitability of sites for nuclear-waste disposal and problems in industrial and municipal pollution. Reliable assessment of hazards or risks arising from ground-water contamination in these environments and the design of efficient and effective means of dealing with contaminated sites require a capability to predict the behavior of dissolved solutes in flowing ground water. Reliable and quantitative predictions of contaminant movement require an integration of the processes controlling transport, hydrodynamic dispersion, and chemical and biological reactions affecting soluble species in ground water. In the general case, represented by most field settings, these processes are coupled—that is, they are not independent of each other.

Through use of the convection-dispersion solute-transport equation, considerable advances have been made over the past 20 years in the ability to model the transport of dissolved constituents that neither undergo reactions in the aqueous phase nor interact with the solids (Freeze and Cherry, 1979). Other advances have been made in modeling solute transport coupled with a few relatively simple reactions, such as first-order decay, ion exchange, and simple sorption reactions, using the assumption of local chemical equilibrium (Rubin and James, 1973; Valocchi and others, 1981; Reynolds and others, 1982). The problem of fully coupled transport with multiple reactions has only been addressed in a general mathematical framework (Rubin, 1983), and considerable work is still needed that use a variety of approaches, including laboratory studies, field studies, and the development of more general and computationally efficient solute-transport models. A new research effort is underway to address some of these needs, with an emphasis on transport coupled with sorption processes.

The purpose of this paper is to review some of the important literature relevant to the topic of transport coupled with sorption reactions and to provide a detailed overview of research objectives in new investigations at the Otis Air Force Base field site. Specific chemical reactions will be studied in this new effort, but the findings are expected to be of general significance.

The results of this research, if successful, will provide guidance to modelers working on the general problem of transport of reactive solutes.

BACKGROUND

Chemical Reactions on Mineral Surfaces

The concentrations of many elements in ground waters commonly reflect undersaturation with respect to pure solid phases of known composition and structure, and aqueous concentrations of these elements are often thought to be controlled by sorption reactions (Davis and Hayes, 1986).

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

The most common inorganic adsorbents in geological materials are hydrous metal oxides (as discrete minerals or as coatings), carbonates, clays, and other aluminosilicates, whereas the most common organic adsorbents consist of detrital plant material and humic coatings on mineral surfaces. Many studies of transition-metal sorption onto geological materials have concluded that the iron and manganese hydrous oxides and organic matter are the predominant adsorbents (Jenne, 1968, 1977; Lion and others, 1982; Davis, 1984; and Tessier and others, 1985), although Fuller and Davis (1987) have recently shown that calcite dominated the sorption of Cd on an aquifer sand. Among the inorganic adsorbents, hydrous metal oxides may have the greatest affinity for ions because of their charged, reactive hydroxyl surface groups, and their large specific surface area. The oxides of iron, manganese, aluminum, and silicon are of major importance in ground waters.

Assessment of the long-term fate of toxic substances that enter ground water requires the identification and understanding of processes controlling the release, movement, and retention of individual solutes within the range of possible geochemical settings. Processes involving reactions on mineral surfaces—for example, adsorption and surface precipitation—are likely to occur and need to be understood in order to model transport properly. A variety of empirical approaches have frequently been used to model solute binding by mineral surfaces, including use of partition coefficients, isotherm equations (such as those of Freundlich and Langmuir) and Kurbatov plots (Honeyman and Leckie, 1986), but these empirical fitting parameters have little transfer value for describing sorption processes. For example, values for radionuclide retardation factors used in radiological risk-assessment models are almost always conservative (small) because the processes causing retardation are poorly understood and few field data are available (Kent and others, 1986). Many assessment models in current use rely on distribution coefficients (K_d) or sorption ratios (R_d) and do not explicitly incorporate the physical-chemical characteristics of the systems being studied (Cranwell and others, 1982; Till and Meyer, 1983). K_d and R_d are defined as the amount of solute taken up per gram of adsorbent divided by the amount of solute per cubic centimeter of water. Distribution coefficients evaluated for site-specific materials are observed to vary over several orders of magnitude without providing any insight as to why such variability might be expected and, thus, predicted (Daniels and others, 1982). Such coefficients are necessarily limited to particular conditions and are not easily extrapolated to other conditions of reactant concentration, pH, or ionic strength.

A more fundamental, mechanistic approach that uses the surface-ionization and complexation concept in conjunction with classical Gouy-Chapman double-layer theory and its extensions (Stern-Grahame) is now widely accepted in modeling the interactions of solute ions with mineral surfaces (Davis and others, 1978; Schindler, 1981; James and Parks, 1982; Langmuir, 1987). For example, this model has been successfully used to (1) explain the adsorption of uranium(VI) by ferrihydrite, of thorium and radium by quartz and kaolinite, and of lead by birnessite (Catts and Langmuir, 1986; Hsi and Langmuir, 1985), (2) interpret the effect of carbonate alkalinity on thorium speciation in the presence of goethite (LaFlamme and Murray, 1987), and (3) rationalize the effects of ionic-strength variations on the adsorption of cadmium and lead by goethite (Hayes and Leckie, 1987).

Current experimental procedures for collecting partitioning and retardation data for toxic compounds and site-specific geological materials usually involve studies with short contact times (reaction period between the geological material and the solutes), small samples (less than 1 kg (kilogram)) and, for column studies, short path lengths (1 meter or less), as compared to the time and space dimensions of real-world applications. Questions remain concerning the applicability of batch studies of adsorption to transport parameters in column studies and the scale-up from laboratory column experiments to field applications.

Field Studies

Although laboratory column and batch studies can be used to test the coupling of physical and chemical processes in the transport of reactive solutes, the difficulties in extrapolating to multidimensional problems of much greater scale are severe. The apparent dispersivity of solutes transported in aquifers has been found from field tests to be much larger than that expected from laboratory column tests. Although this discrepancy can, to some degree, be explained by the scale of the investigation, it appears that enhanced mixing is occurring in many aquifers compared to that observed in laboratory column experiments. The enhanced mixing of conservative solutes in aquifers has been attributed to fluid-velocity variations induced by the heterogeneity of hydraulic conductivity in the aquifer (Gelhar and Axness, 1983). An even greater degree of dispersion is observed for reactive solutes, which can be explained by either a state of disequilibrium of sorption-desorption processes during transport, or if the local equilibrium assumption is believed to be applicable, the enhanced dispersion can still be explained by the physical heterogenity of the system's adsorptive properties (Garabedian, 1987).

A limited number of field tests of sufficient detail and reliability have been performed that enable satisfactory examination of the factors mentioned previously. Of these, only the tracer studies at Borden Air Force Base in Canada (Criddle and others, 1986; Curtis and others, 1986; Freyberg, 1986; Mackay, Ball, and Durant, 1986; Mackay, Freyberg, Roberts, and Cherry, 1986; Roberts and others, 1986; Sudicky, 1986) and Otis Air Force Base (Garabedian, 1987; Stollenwerk and Grove, 1987) have been particularly comprehensive. The tracer test at Otis Air Force Base was designed to test the relation between field-scale dispersion and aquifer heterogenity developed by Gelhar and Axness (1983). Injected tracers were bromide, lithium, and molybdenum ions. Major conclusions of the study were that (1) longitudinal mixing was the dominant dispersion process, which reached a Fickian limit after 40 meters of travel; (2) transverse horizontal and vertical dispersion were relatively small; and (3) horizontal displacement of the injected solute cloud was accurately predicted using estimates of the hydraulic conductivity, porosity, and measured hydraulic gradient (Garabedian, 1987). Solute concentrations were highly variable and difficult to predict on a small scale but the average characteristics (the spatial moments) could be predicted. Lithium transport was retarded relative to bromide by a factor of approximately 1.6, but batch sorption studies showed a very slow rate of equilibration with the aquifer material (a medium to coarse sand), indicating the need for a nonequilibrium modeling approach. Molybdenum transport depended on many factors, including pH and the concentration of other anions – for example, phosphate and sulfate – and the sorption isotherm was nonlinear (Stollenwerk and Grove, 1987), indicating the need for a multispecies modeling approach to account for the effects of competitive adsorption.

Solute Transport Modeling

The mathematical formulation and solution of coupled transport equations depends considerably upon whether the chemical processes can be described by kinetic or equilibrium approaches (Rubin, 1983). The appropriate choice depends on the rates of chemical and physical processes relative to the bulk fluid flow rate and a subjective assessment of the permissible level of error for the model (Jennings and Kirkner, 1984; Valocchi, 1985; Bahr and Rubin, 1987). Because an equilibrium approach greatly simplifies the mathematical and conceptual framework of the solute-transport problem, and there is evidence that microscopic adsorption reactions of many solutes are rapid (Hayes and Leckie, 1986), the local-equilibrium assumption commonly has been used in both field and laboratory models of solute transport. However, numerous studies have shown that the local equilibrium approach does not always provide an adequate model for solute transport through porous media (James and Rubin, 1979; Reynolds and others, 1982; Valocchi, 1985). Interest in nonequilibrium transport models has been growing as a result (van Eijkeren and Loch, 1984; Kirkner and others, 1985), but few data are available that demonstrate whether the rates or solute sorption on geological materials are controlled by diffusive transport or by rates of chemical reactions (Fuller and Davis, 1987). Although significant advances are being made in the ability to model coupled reaction and flow (Narasimhan and others, 1986; Lewis and others, 1987), this approach is still limited by a lack of relevant kinetic and thermodynamic data for appropriate interactions in the environment. Further advances in this field will require the combination of detailed laboratory and field investigations with additional refinement of mathematical modeling approaches.

RESEARCH APPROACH

Laboratory Studies

The purpose of these studies is to assess the primary mineral phases that contribute to sorption of the trace elements zinc (Zn), chromium

(Cr), and selenium (Se) onto Otis sand. A preliminary study with a simple mineral assemblage of quartz and iron oxyhydroxides will be conducted because these minerals are believed to be the most important adsorbent phases in the sand. The simple mineral assemblage approach also will allow modeling of transport in laboratory column experiments using material that can be well characterized in terms of its physical and chemical properties. Both equilibrium and kinetic aspects of the sorption processes will be investigated. Equilibrium aspects that will be studied include (1) a characterization of the adsorption properties in single mineral systems and mixtures of the minerals; (2) the effect of a wide range of solution conditions on the extent of adsorption (for example, pH, ionic strength, concentration of a complexing ligand (EDTA), concentration of a competing ions (Ca and PO_4), and solute concentration); and (3) the effect of water: solid ratio on adsorption. Rate studies in stirred suspensions will be performed to constrain the rate expressions that describe the sorption processes. Transport of the adsorbing solutes through columns packed with the same adsorbents (simple mineral assemblages or natural materials) will be studied over a wide range of solution compositions and fluid flow rates. The primary objective is to gain an improved understanding of the rates of sorption processes in porous media and their importance in transport modeling. Additionally, methods for characterizing the adsorption properties of the natural materials will be developed. The chemical composition of the surficial material of Otis sand will be determined by surface spectroscopy, and the sorption behavior of Zn and Cr(VI) on the sand will be compared to that predicted from a model of their sorption on pure mineral phases.

Field Investigation

The previous injection experiment at Otis Air Force Base (Garabedian, 1987; Stollenwerk and Grove, 1987) has characterized the hydrologic properties of the site in great detail, which allows an opportunity to explore more complex geochemical transport experiments with other reactive tracers. The approach at this site will be to inject bromide as a conservative tracer in addition to three reactive tracers (Zn, Cr, Se), whose transport is expected to be considerably influenced by chemical reactions. Three small-scale experiments (observation of tracer movement for approximately 13 meters) were begun in July 1988 to test the rates of transport of these tracers.

The reactive tracers (Zn, Cr, Se) were injected as single pulses into the sand and gravel aquifer and are being monitored as the tracer clouds move downgradient. The Cr and Se were injected as dissolved salts (K_2CrO_4, Na_2SeO_4), whereas the Zn was injected as the EDTA chelate. A major objective in using the EDTA chelate of Zn in the experiment is to test the ability of a complexing agent to increase the mobility and transport of heavy metal ions, such as Zn. The distribution coefficient (K_d value) for Zn sorption on the sand is expected to be quite large, implying a low mobility for Zn in the aquifer (Freeze and Cherry, 1979). Without chelation, an ion such as Zn could move through the aquifer at a velocity several orders of magnitude slower than the conservative tracer, bromide (Br), because of strong adsorption onto sand and gravel surfaces in the aquifer. However, in the presence of strong complexing agents, the velocity of the metal chelate may be as great as that of the conservative tracer, Br. Transport models need to be capable of describing these competitive chemical processes because the measurement of large distribution coefficients for solutes is sometimes used to argue that many radionuclides in radioactive wastes would be greatly retarded by geochemical "barriers," and, hence, these radionuclides can be considered to be effectively immobile. But field studies have shown that radionuclides may be quite mobile in ground waters when complexed with organic ligands (Means and others, 1978; Cleveland and Rees, 1981; Killey and others, 1984). In fact, the movement and redistribution of many trace metals in low-temperature aqueous environments may be controlled by the formation of non-adsorbing complexes (Davis and Leckie, 1978; Vuceta and Morgan, 1978). Thus, the injection of ZnEDTA in the aquifer is meant to serve as a general model for chelate-facilitated transport of metal ions in ground waters. Because of the pronounced nonlinear relation between EDTA concentration and Zn adsorption onto the aquifer minerals, transport modeling of Zn will require a coupled model that considers aqueous speciation of Zn, such as those presented by Cederberg and others (1985) and Lewis and others (1987).

A second major objective of the field experiments is to evaluate the importance of redox gradients and changing chemical conditions on transport of the reactive tracers. The sand and gravel aquifer is characterized by a gradual change in the redox state as a function of depth--varying from oxygenated, uncontaminated water near the water table to reducing water in the center of the sewage plume. The uncontaminated water contains dissolved oxygen and very low concentrations of dissolved iron (Fe) and manganese (Mn). At the center of the sewage plume, there is virtually no dissolved oxygen and high concentrations of dissolved Fe(II) and Mn(II) (Thurman and others, 1984). The Cr and Se tracers may exist in more than one oxidation state, and the mobilities of the different oxidation states of these elements may differ by orders of magnitude. The injections will contain the most oxidized forms of these elements, Cr(VI) and Se(VI). These species of the elements are weakly reacting anions whose transport will be slightly retarded by sorption reactions with the aquifer minerals. As the Cr and Se tracers encounter more reducing conditions, they may be reduced to Cr(III) and Se(IV) or Se(O). These forms of the elements, in contrast to the more oxidized forms, are highly retarded by interactions with the aquifer sediments, and should be transported at a velocity considerably slower than the conservative tracer, Br. Of the three injections made in July 1988, two were made into intervals of the aquifer characterized by reducing conditions and one into oxic conditions. One of the injections into an anoxic interval was made with the tracers dissolved in oxic ground water, whereas the other was made with the tracers dissolved in anoxic ground water. A comparison of the results of these experiments will allow an assessment of the importance of the redox environment on the mobilities of the tracers.

The proposed research addresses several fundamental problems in applying coupled transport models to ground-water environments: (1) The limited availability of kinetic and thermodynamic data for sorption processes; (2) laboratory approaches that characterize the important physical and chemical parameters are needed to describe earth materials in terms of simple adsorption models previously developed for simple mineral assemblages; (3) the local equilibrium assumption for reactive solutes and real-world geological materials may not be universally applicable; (4) the relation between column-scale and adsorption parameters determined in batch- and column-transport experiments requires additional testing; (5) the importance of complexation and oxidation-reduction reactions (and the redox environment) in controlling the migration of some elements may be important; (6) few detailed field-scale tests of reactive tracer transport are available; and (7) there is a need for long-term research studies of coupled transport with chemical reactions in which detailed laboratory, field, and modeling approaches are used in a comprehensive manner. Thus, this new research effort addresses important needs for future solute-transport modeling.

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CHAPTER D – ARSENIC CONTAMINATION IN THE WHITEWOOD CREEK-BELLE FOURCHE RIVER-CHEYENNE RIVER SYSTEM, WESTERN SOUTH DAKOTA

(p. 199 follows)

OVERVIEW OF RESEARCH ACTIVITIES ON THE CHEYENNE RIVER SYSTEM, WESTERN SOUTH DAKOTA

By Kimball E. Goddard[1]

ABSTRACT

In April 1985, the Whitewood Creek-Belle Fourche River-Cheyenne River-Lake Oahe surface-water system in western South Dakota was selected for investigation as part of the U.S. Geological Survey Toxic Substances in Surface-Water and Sediments Thrust program. Alluvial flood-plain sediments in this system contain arsenic and other trace metals derived from the 100 million metric tons of gold-mill tailings that were discharged into Whitewood Creek between 1876 and 1977.

Research activities include (1) sediment studies of the distribution, transport rate, and ultimate fate of arsenic and other trace metals sediments; (2) geochemical studies of trace metal partitioning between various solid phases and between solid and dissolved phases; and (3) biologic investigations of the effect of arsenic and other trace metals on the stream ecosystem. Preliminary findings indicate that arsenic is widely distributed in alluvial sediments and is being actively transported on suspended sediment. Total arsenic concentrations range from 300 to 5,000 micrograms per gram in flood-plain sediment, 20 to 960 micrograms per gram in suspended-sediment, and 20 to 260 micrograms per gram in Lake Oahe sediments. Although as much as 50 percent of the total arsenic mass is in the form of arsenopyrite, adsorption-desorption of arsenic from ferric oxyhydroxides is the dominant process controlling dissolved-phase concentration.

INTRODUCTION

About 100 million Mg (megagrams) of finely-ground mill tailings were discharged into Whitewood Creek near Lead, S. Dak., between 1876 and 1977 (Marron, 1987). The tailings contained substantial concentrations of arsenic (As) and other trace elements resulting in widespread contamination of the alluvial sediments along Whitewood Creek and the Belle Fourche and Cheyenne Rivers (fig. D-1). The primary contaminant is As derived from, or still present as, FeAsS, a gangue mineral common to the gold-bearing deposits at Lead. The trace elements antimony (Sb), cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), mercury (Hg), and silver (Ag) also are associated with the mill tailings and are present in the contaminated alluvial sediments. This paper briefly describes the physical and hydrologic conditions at the site and discusses active research studies. A short summary of important conclusions also is included.

The presence of As and other trace metals in Whitewood Creek and the downstream rivers was alleviated by the discontinuance of tailings discharge in December 1977. However, the large deposits of As-bearing sediments present along Whitewood Creek and the Belle Fourche and Cheyenne Rivers continues to adversely affect the quality of surface water and ground water in the affected parts of the Cheyenne River basin. Because the sediment was deposited by natural surface flow, the sediments are very susceptible to resuspension and downstream movement during periods of high discharge when sediment enters the flow from streambed scouring, bank collapse, or by input from overland runoff. Dissolved As, derived from seepage of ground water from the alluvium and desorbed from streambed material, is present in concentrations as large as 130 μg/L (micrograms per liter) (Goddard, in press) in Whitewood Creek. Water in parts of the alluvial aquifers along Whitewood Creek and the Belle Fourche River also receive As and other trace metals through leachate derived from overlying sediment deposits.

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[1] U.S. Geological Survey, Rapid City, S. Dak.

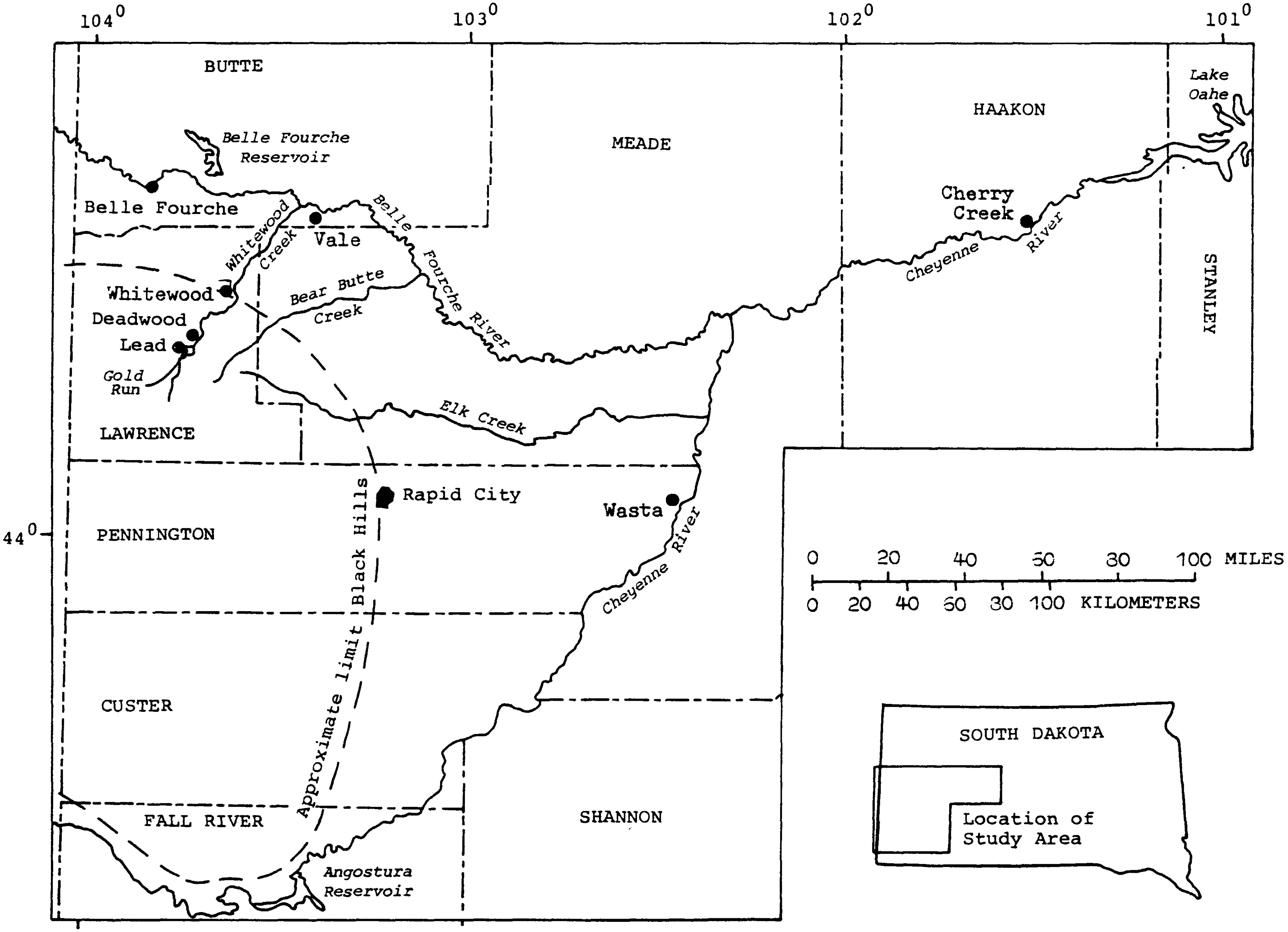

Figure D-1.–Location and components of the Cheyenne River System in western South Dakota.

RESEARCH ACTIVITIES

Although the magnitude of As and other trace element concentrations in the Cheyenne River basin have been documented by previous investigations (Cherry and others, 1986; Goddard, in press), many questions remain about the processes that affect the contaminated sediments. Although the original source of As was FeAsS present in the tailings discharge at Lead, the present-day (1987) source of As and other trace metals is much less obvious because of the dispersed nature of the sediments. How much of the originally discharged material remains in the basin? How much of the As mass still exists as FeAsS? What mechanisms are responsible for As transport? What are the annual rates of downstream transport? What processes are acting on the As mass as it is deposited in Lake Oahe? These questions are the focus of research now in progress.

Research activities on the Cheyenne River System can be roughly divided into three groups. First are studies of the distribution, transport rate, and ultimate fate of the As and trace metal-bearing sediments. Second are geochemical studies of the physical and chemical processes that govern the partitioning of As and other trace metals between various solid phases and between solid and dissolved phases. Third are biologic investigations of how the stream ecosystem interacts with the large concentrations of As and other trace constituents present in the bottom sediments and water.

Sedimentological studies include (1) estimation of the mass and determination of the physical and chemical properties of sediment deposits along Whitewood Creek and the Belle Fourche and Cheyenne Rivers, (2) determination of the annual transport rates for As and selected trace metals for sites on Whitewood Creek and the Belle Fourche and Cheyenne Rivers, and (3) characterization of sediments deposited in the Cheyenne River arm of lake Oahe.

Preliminary results indicate that As concentrations in flood-plain sediments range from 300 to 5,000 ug/g (micrograms per gram) and are related to grain-size distribution (Marron, 1987). The As concentrations in actively transported suspended-sediments are about an order of magnitude smaller, 20 to 960 ug/g, (W.R. Roddy, U.S. Geological Survey, written commun., 1988) because of dilution by sediment entering the stream system from unaffected basins. Sediments in the Cheyenne River arm of Lake Oahe have strata that are enriched in As, 30 to 260 ug/g (Horowitz and others, 1988), and the concentrations generally increase with depth, indicating that As transport rates are decreasing over time.

Geochemical studies include (1) partitioning between FeAsS and Fe oxyhydroxide-bound As in flood plain, channel, and suspended sediments; (2) adsorption-desorption of As from Fe oxyhydroxides under laboratory and field conditions; (3) identification and composition of colloids present at alluvial seeps along Whitewood Creek; and (4) concentration controls for dissolved-phase As in Whitewood Creek.

The FeAsS continues to be a primary contaminant and contains as much as 50 percent of the total As mass in contaminated flood-plain sediments (McKallip and others, 1989, this Proceedings).

However, As adsorption to and desorption from Fe oxyhydroxides is a more dominant process than FeAsS oxidation in controlling dissolved-phase As connections in ground and surface waters (Fuller and others, 1988; Goddard and Wuolo, 1988; Goddard and others, 1988).

Biological studies are (1) determination of the effects of periphyton and algae on As partitioning and transport, and (2) bioaccumulation of As by selected benthic invertebrates in Whitewood Creek and the Belle Fourche River.

Uptake of As by periphyton and algae during growth cycles and subsequent As release during decay may be an important factor in As transport (Kuwabara and others, 1989, this Proceedings). The As appears to be accumulating in some benthic invertebrates; however, adsorption onto the surfaces of the organism rather than incorporation into biologic material, may be the dominant process (Cain and others, 1989, this Proceedings).

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ARSENIC IN THE ALLUVIAL SEDIMENTS OF WHITEWOOD CREEK AND THE BELLE FOURCHE AND CHEYENNE RIVERS IN WESTERN SOUTH DAKOTA

By Thomas E. McKallip[1], Kimball E. Goddard[1], and Arthur J. Horowitz[2]

ABSTRACT

Large volumes of arsenopyrite-bearing tailings discharged over a 100-year period from gold mines near Lead, South Dakota, have accumulated as arsenic-rich contaminated sediment in the flood plains and channels of Whitewood Creek and the Belle Fourche and Cheyenne Rivers in western South Dakota. Extensive oxidation of arsenic-rich contaminated sediments is visually evident. The heavy-mineral fractions of contaminated sediments were isolated by using a bromoform flotation coupled with centrifugation. Percentages of heavy minerals ranged from 0.8 to 6.9 in channel sediments and from 14 to 56 in flood-plain sediments. Concentrations of arsenic ranged from 25 to 990 micrograms per gram in suspended and bottom sediments and from 830 to 5,000 micrograms per gram in flood-plain sediments.

Percentages of heavy minerals and concentrations of arsenic and iron are smaller in suspended and bottom-sediment samples than in flood-plain samples. This indicates a recent change in the source of part of the sediment for the Cheyenne River system.

INTRODUCTION

From 1878 to 1977, about 90 million (Mg) (megagrams) of milled gold-mine tailings were discharged into the Cheyenne River system at Whitewood Creek downstream from Lead, S. Dak. In December 1977, the discharge of tailings was diverted away from Whitewood Creek and dammed at Grizzley Gulch near Lead (fig. D-2). It is estimated that 18,000,000 Mg of sediment, originating from tailings discharge, are stored in the flood plains of Whitewood Creek and the Belle Fourche and Cheyenne Rivers downstream from Lead (Marron, 1987).

Reported percentages of arsenopyrite in the gold ore mined at Homestake[3] (the largest gold-mining company in the area) range from 0.25 percent (South Dakota Department of Health, Division of Sanitary Engineering, 1960) to 0.75 percent (Noble, 1950). Undoubtedly, the amount of arsenopyrite discharged to the river system varied with time as the location of mining in the ore body changed. It is probable that several hundred thousand megagrams of arsenopyrite were discharged to the river system.

Total arsenic (As) concentrations in samples of contaminated sediments from the flood plains of Whitewood Creek and the Belle Fourche and Cheyenne Rivers have been determined in studies by Goddard (in press) and Marron (1987). Total As concentrations in the suspended and bottom sediments of the Cheyenne River system are being investigated as part of the ongoing U.S. Geological Survey applied research studies of the Cheyenne River system, South Dakota.

The partitioning of As in the alluvial sediments of the Cheyenne River system has not been quantified. The processes of As-mineral oxidation and the adsorption and coprecipitation of As are active in the alluvial sediments (Fuller and others, 1988; Goddard, in press). It is the purpose of this paper to quantify the partitioning of As into light- and heavy-mineral fractions in the alluvial settings of the Whitewood Creek and the Belle Fourche and Cheyenne Rivers.

In this study, sediment samples collected from the channels and flood plains of Whitewood Creek and the Belle Fourche and Cheyenne

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[1] U.S. Geological Survey, Rapid City, S. Dak.

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

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

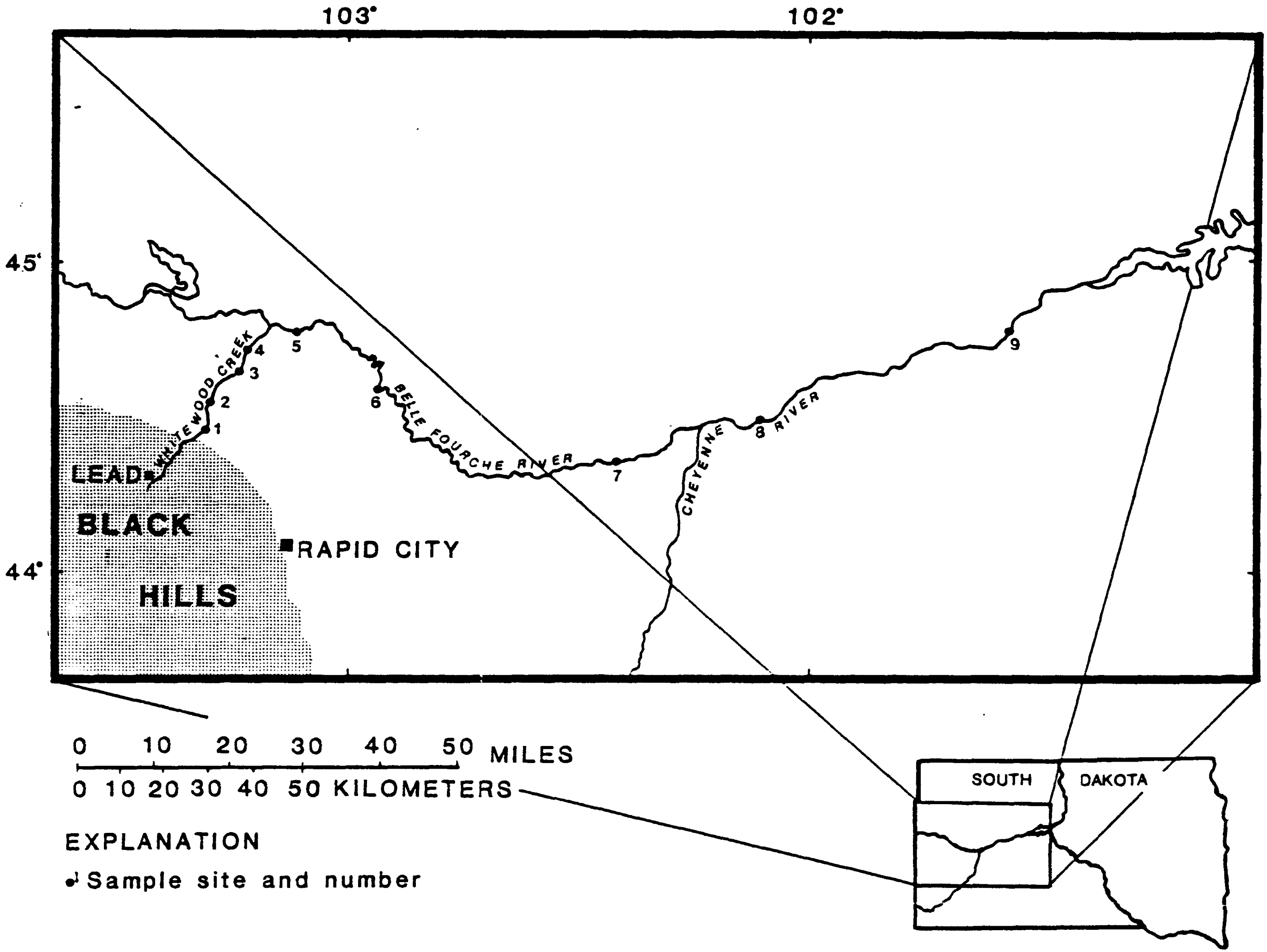

Figure D-2. –Location of study area and sampling sites.

In this study, sediment samples collected from the channels and flood plains of Whitewood Creek and the Belle Fourche and Cheyenne Rivers were separated into density fractions using a bromoform flotation. The samples and their light- and heavy-mineral fractions were analyzed chemically and the partitioning of As and iron (Fe) into light- and heavy-mineral fractions was determined.

SELECTION OF SEDIMENT SAMPLES

Samples selected for this study are splits of contaminated sediment samples collected for the U.S. Geological Survey applied research studies of the Cheyenne River system, South Dakota, and splits of samples collected for studies by Marron (1987) and Dorfschmidt (South Dakota School of Mines and Technology, oral commun., 1988). Collection sites for the selected samples are shown in figure D-2.

Samples of channel sediments consist of suspended and bottom sediments. Depth-integrated suspended sediments were collected during periods of high flow in water years 1986-87, concentrated by centrifugation, and freeze-dried. Bottom sediments were skimmed from the top 50 mm (millimeters) of the streambed at several regularly spaced points on cross sections, and sieved through a 63-μm (micrometer) nylon screen. The less-than-63-μm fraction was freeze-dried.

Samples of visibly oxidized (red) flood-plain sediment were collected at five locations in soil pits dug along transects perpendicular to Whitewood Creek and the Belle Fourche and Cheyenne Rivers (Marron, 1987), and samples of visibly unoxidized (gray) sediment were collected from cut banks on Whitewood Creek and the Belle Fourche River (Goddard, in press). Oxidized flood-plain sediment samples were collected at five sites by Marron (1987). One oxidized flood-plain sediment sample was selected from the four to eight samples collected at each site. The selected samples had As concentrations larger than the mean of the samples collected at each respective site.

ANALYSES OF SEDIMENT SAMPLES

A quantitative heavy-mineral separation was performed on all of the sediment samples analyzed. The procedure consisted of weighing about 2 grams of sediment with a precision of 0.001 gram into a 50-mL (milliliter) plastic centrifuge tube containing 20 mL of bromoform. The sample was then dispersed for 1 hour in an ultrasonic bath. The samples were then centrifuged for 10 minutes using a centrifuge with a fixed angle rotor at 8,000 r/min (revolutions per minute), after which the fractionated sample was frozen. The small mass of heavy minerals in the samples was collected without remixing by cutting the centrifuge tube and splitting the frozen bromoform. Heavy- and light-mineral fractions were recovered by melting the bromoform pellets, drawing off the bromoform with a pipet, and rinsing the fractions with ethanol before oven-drying at 40 °C (degrees Celsius) for 4 hours. The heavy-mineral fraction was weighed with a precision of 0.0001 gram and recorded as a percentage of the total sample. In order to recover as much of the heavy-mineral fraction as possible, the resulting light-mineral fraction was subjected to the above procedure two to five times. The heavy minerals which were separated by repetitions of this procedure were aggregated. A heavy-mineral separation was considered complete when the mass of heavy minerals recovered in the last repetition was less than 10 percent of the total mass of heavy minerals collected. Precision of the method of heavy-mineral separations was monitored by the determination of percentage of the heavy minerals in replicate samples.

Chemical analyses were performed on splits of the samples before fractionation and also on the heavy- and light-mineral fractions of eight samples. Flood-plain samples and a bottom-sediment sample from site 6 (fig. D-2) were analyzed by the U.S. Geological Survey laboratories in Lakewood, Colo. Total digestion was by $HF/HClO_4/HNO_3$ acid, and quantification was by inductively coupled plasma atomic-emission spectroscopy. Splits of all other samples, including eight heavy- and light-mineral fractions, were analyzed by the U.S. Geological Survey in Doraville, Ga. The procedures of Horowitz and Elrick (1985) and Elrick and Horowitz (1985) were used. Sample digestion was with HF/HClO4/HNO3 at 200 °C. Quantification was by hydride-generation atomic-absorption spectrophotometry. Precision was monitored by replicate analyses and generally was better than ±10 percent. Laboratories at both locations monitor bias by means of rock standards.

Heavy-Mineral Separations

The calculated percentages of heavy minerals in samples from suspended and bottom sediments and from the flood plain of Whitewood Creek and the Belle Fourche and Cheyenne Rivers range from 0.5 to 56 percent (table D-1). The largest difference between replicate samples in percentages of heavy minerals is 40 percent in a suspended-sediment sample from site 6 with less than 1 percent heavy minerals. The difference in percentages of heavy minerals is 14 percent in replicates of a bottom-sediment sample from site 1 with at least 6 percent heavy minerals. The difference in percentages of heavy minerals among replicates of two oxidized flood-plain sediment samples from sites 5 and 6 are 10 and 8 percent, respectively. Percentages of heavy minerals at sites 5 and 6 are at least 20 and 36 percent respectively.

Percentages of heavy minerals were small in suspended- and bottom-sediment samples (less than 7 percent) and generally large in oxidized and unoxidized flood-plain sediment samples (14-56 percent). The two samples that were visually identified as unoxidized flood-plain sediments have the largest percentages of heavy minerals.

Chemical Determinations

Chemical determinations of As and Fe concentrations in the whole-sediment samples

Table D-1.—*Percentages of heavy minerals and chemical determinations of arsenic and iron in unfractionated sediment samples*

[Replicate values determined for percentages of heavy minerals are shown adjacent to one another; –, not analyzed]

Sediment type	Location	Percentage of heavy minerals	Arsenic (micrograms per gram)	Iron (weight percent)
Suspended	1	2.2	570	7.0
Suspended	4	2.7	770	5.6
Suspended	6	.6, .9	188	4.2
Suspended	7	1.1	[1]220	[1]5.0
Suspended	9	.5	25	3.9
Bottom	1	6.9, 6.0	[1]990	[1]7.8
Bottom	4	1.7	660	4.7
Bottom	6	2.1	180	4.4
Bottom	7	2.1	600	4.7
Bottom	9	.8	40	3.2
Oxidized flood plain	2	32	2,100	17.0
Oxidized flood plain	4	27	4,600	15.0
Oxidized flood plain	5	20, 22	1,400	10.0
Oxidized flood plain	6	39, 36	5,000	16.0
Oxidized flood plain	8	14	830	7.8
Unoxidized flood plain	3	56	4,500	–
Unoxidized flood plain	5	48	2,700	–

[1] Average of replicate chemical analyses.

also are given in table D – 1. Concentrations of As range from 25 to 5,000 μ g/g (micrograms per gram) and concentrations of Fe range from 3.2 to 17 weight percent.

The results of total chemical analyses for As and Fe in the heavy- and light-mineral fractions of eight samples are given in table D-2. Calculated total concentrations of As and Fe in unfractionated samples were determined using the following equation:

$$CTC = [CL \cdot (100 - H) + CH \cdot H]/100 \qquad (1)$$

where:

CTC = calculated total concentrations

CL = total concentration in light-mineral fraction

CH = total concentrations in heavy-mineral fraction

H = percentage of heavy minerals in the sample

Table D-2.—*Selected constituents from chemical analyses of heavy-mineral fractions*

Sediment type	Location	Mineral fraction	Percent of mineral fraction	Total arsenic (micrograms per gram)	Calculated total arsenic (micrograms per gram)	Arsenic percent of calculated total arsenic	Total iron (weight percent)	Calculated total iron (weight percent)	Iron percent o calculatec total iron
Suspended	6	Heavy	[1]0.75	3,700		8	35.0		6
		Light	99	300			4.0		
		Whole		188	325		4.2	4.2	
Bottom	1	Heavy	[1]6.5	6,000		37	30.0		27
		Light	93	700			5.8		
		Whole		[1]990	1,000		[1]7.8	7.3	
Bottom	6	Heavy	1.7	9,900		22	31.0		11
		Light	98	[1]600			[1]4.2		
		Whole		660	760		4.7	4.7	
Oxidized flood plain	4	Heavy	27	7,700		43	28.0		56
		Light	73	3,800			8.0		
		Whole		4,600	4,800		15	13	
Oxidized flood plain	6	Heavy	37	7,500		56	28.0		68
		Light	63	3,500			7.8		
		Whole		5,000	5,000		16	15	
Oxidized flood plain	8	Heavy	14	3,100		53	29.0		55
		Light	85.9	[1]450			[1]3.8		
		Whole		830	830		7.8	7.4	
Unoxidized flood plain	3	Heavy	55.7	8,500		95	25.0		88
		Light	44.3	520			4.2		
		Whole		4,500	5,000		--	15.8	
Unoxidized flood plain	5	Heavy	48.1	5,200		99	22.0		90
		Light	51.9	69			2.3		
		Whole		2,700	2,500		--	11.8	

[1] Average of replicate analyses.

Calculated total concentrations of As range from 325 to 5,000 μg/g and Fe 4.2 to 15.8 weight percent (table D-2). In the unfractionated samples, chemically determined As ranges from 188 to 5,000 μg/g, and Fe ranges from 4.2 to 16 weight percent. With the exception of the As concentration of the suspended-sediment sample collected at site 6, the calculated total concentrations agree favorably with concentrations determined in unfractionated samples by chemical analysis; differences are 14 percent or less.

Percentages of the calculated total concentrations of As in heavy-mineral fractions range from 8 to 99, and percentages of Fe range from 6 to 90 percent. Percentages of total calculated As in the heavy-mineral fractions of the three oxidized flood-plain samples are all close to 50 percent. More than 95 percent of the As in the two visually identified unoxidized flood-plain samples is in the heavy-mineral fraction.

Discussion

Percentages of heavy minerals were small in suspended- and bottom-sediment samples (less than 7 percent) and generally large in oxidized and unoxidized flood-plain sediment samples (14-56 percent). The flood-plain sediment samples were deposited during a period of tailing discharge and the percentages of heavy minerals in these samples are related to the extent of mixing of the tailings system with uncontaminated sediments. Suspended- and bottom-sediment samples were collected in the 1986 and 1987 water years after the cessation of tailings discharge.

Concentrations of As and Fe (table D-1) tend to be smaller in suspended- and bottom-sediment samples than in flood-plain samples. Concentrations of As range from 25 to 990 μg/g in suspended and bottom samples and range from 830 to 5,000 μg/g in flood-plain samples. Similarly, concentrations of iron range from 3.2 to 7.8 weight percent in suspended and bottom sediments and 7.8 to 17 weight percent in flood-plain sediment samples. The mean concentrations of As and Fe in suspended- and bottom-sediment samples differ from the respective mean of As and Fe concentrations in flood-plain sediment samples at a 99-percent confidence level. The smaller percentages of heavy minerals and smaller concentrations of As and Fe in suspended- and bottom-sediment samples is consistent with the discontinuance of a significant source of sediment (tailings discharge) in the upper part of the basin.

A substantial part of As in oxidized flood-plain and bottom- and suspended-sediment samples is in their light-mineral fractions. This is probably the result of the oxidation of As minerals and then absorption and coprecipitation of As in the light-mineral fractions of the sediments.

CONCLUSIONS

Differences in percentages of heavy minerals among sediment samples appear to be large in samples with small percentages of heavy minerals (less than 1 percent). Precision improved with increasing percentages of heavy minerals. Percentages of heavy minerals in the suspended- and bottom-sediment samples are nearly an order of magnitude lower than the percentages of heavy minerals in flood-plain samples. Arsenic in unoxidized flood-plain sediment samples has largely been restricted to the heavy-mineral fractions; more than 95 percent of the As in two unoxidized flood-plain samples was in their heavy-mineral fractions. A substantial part of As in oxidized flood-plain and bottom- and suspended-sediment samples is in their light-mineral fractions. This is probably the result of the remobilization of As by As-mineral oxidation and adsorption and coprecipitation of As in the alluvial sediments.

Percentages of heavy minerals and concentrations of As and Fe are smaller in active channel sediments than in flood-plain samples. This is consistent with the discontinuance of a significant source of sediment (tailings discharge) to the Cheyenne River system.

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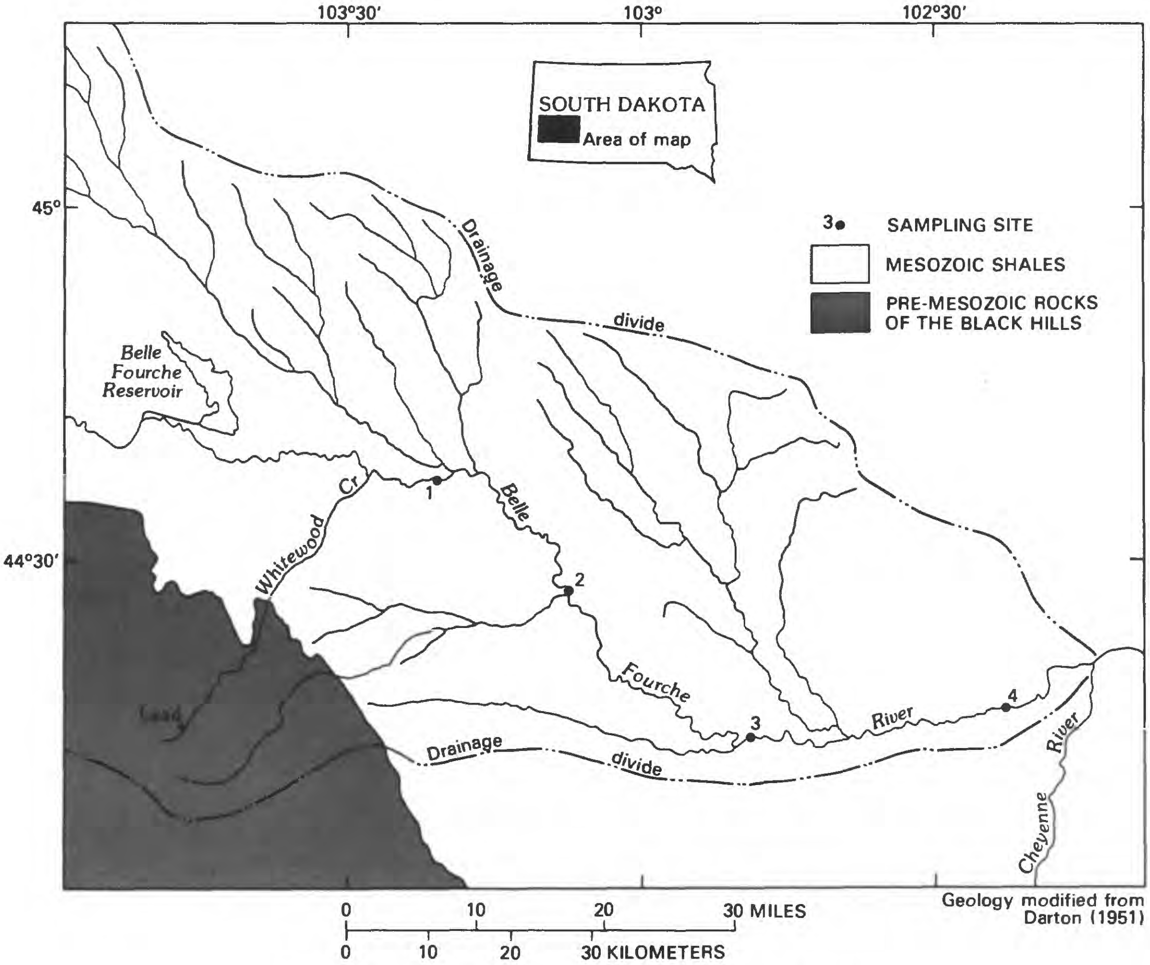

Figure D-3.—Location and geology of the study area.

crush ore at Lead. By 1976, after 100 years of production, the major mining company in the Lead area had milled more than 100,000,000 Mg (megagrams) of ore (Homestake Gold Mine, 1976).

The milled tailings were discharged into Whitewood Creek (fig. D-3) by a small tributary until 1977. Whitewood Creek was an efficient conduit of tailings into the Belle Fourche River, which is a meandering stream with an alluvial flood plain. The Belle Fourche River is underlain by Mesozoic shales in the study area (fig. D-3). The Mesozoic shales are more important than other bedrock units in the study area as sources of sediment to streams (Hadley and Schumm, 1961). An irrigation system that was built in 1910 diverts most of the water and sediment at all levels of flow from the Belle Fourche River at a point that is about 30 km (kilometers) upstream from the mouth of Whitewood Creek (fig. D-3). The Belle Fourche River is flanked by multiple terraces.

METHODS

Four sampling sites (fig. D-3) were located along reaches of the Belle Fourche River where lateral migration was minimal during the period of airphoto coverage (1939-81). A total of 125 sediment samples were collected from auger holes that were dug into overbank sediments along transects that were perpendicular to the river at these sites. Three transects extended away from the channel on the insides of meander bends at each site. Stainless-steel implements were used to scrape samples from the sides of the auger holes at depth intervals of 0.4 meter or less. Samples

TRENDS IN ARSENIC CONCENTRATION AND GRAIN-SIZE DISTRIBUTION OF METAL-CONTAMINATED OVERBANK SEDIMENTS ALONG THE BELLE FOURCHE RIVER DOWNSTREAM FROM WHITEWOOD CREEK, SOUTH DAKOTA

By Donna C. Marron[1]

ABSTRACT

Arsenic-contaminated overbank deposits along the Belle Fourche River in west-central South Dakota resulted from the discharge of a large volume of mine tailings into Whitewood Creek between the late 1800's and 1977. The arsenic-contaminated overbank deposits are typically less than 2 meters thick and extend about 90 meters away from the channel along the insides of meander bends. Carbonate minerals in the contaminated sediments limit desorption of arsenic by preventing acid formation.

Within the contaminated overbank deposits along the Belle Fourche River, average arsenic concentrations decrease by a factor of three, and grain-size distributions become finer in a downstream direction. These changes only occur along channel reaches that receive significant inflow from tributaries draining shale-bedrock watersheds and appear to be caused by the dilution of mine tailings by uncontaminated sediment with a relatively finer grain-size distribution. An influx at high flow of uncontaminated sediment from terraces and the premining flood plain as well as from tributaries causes arsenic concentrations in parts of the contaminated deposit that are farthest away from the channel to be two to three times less than arsenic concentrations in overbank sediment that is immediately adjacent to the channel.

INTRODUCTION

The discharge of mine tailings into Whitewood Creek at Lead, S. Dak. (fig. D-3), between the late 1800's and 1977 resulted in the deposition of millions of megagrams of arsenic-contaminated sediment on flood plains downstream from the mining area (Marron, 1987). The arsenic-contaminated flood-plain deposits consist of overbank sediments, point-bar deposits, and filled abandoned meanders along Whitewood Creek, the Belle Fourche River, and the Cheyenne River (fig. D-3). The contaminated deposits along the Belle Fourche River are more voluminous than those along Whitewood Creek and contain greater concentrations of arsenic than do the deposits along the Cheyenne River. At least half of the mine wastes that were deposited along the Belle Fourche River flood plain are contained in overbank deposits (Marron, 1987). Arsenic concentrations as high as 5,000 μg/g (micrograms per gram) in the contaminated deposits have caused environmental controversy and concern (Goddard, in press).

The objective of this paper is to define and explain spatial trends in arsenic concentration and grain-size distribution in contaminated overbank sediments along the Belle Fourche River. The definition of such trends provides practical information on the extent of the present arsenic-contamination hazard downstream from Lead. An understanding of the causes of these trends provides insights that are useful in the prediction of the nature and extent of contaminant deposition downstream from point sources of contamination. These insights also lead to an improved understanding of the workings of fluvial systems at high flow.

STUDY AREA

The mine tailings discussed in this paper resulted from gold mining in and around Lead, S. Dak. (fig. D-3). The ore mined and milled at Lead consists mostly of silicates, iron and magnesium carbonates, and metallic sulfides (Noble, 1950). Gold is associated with arsenopyrite (FeAsS) in the ore body. Stamp mills that yield sand-size and finer particles, and rod-and-ball mills that yield silt-size and finer particles have been used to

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[1] U.S. Geological Survey, Indianapolis, Ind.

were stored in plastic bags and were air dried. Arsenic concentrations were obtained by use of a semiquantitative colorimetric method (O'Leary and Meier, 1986). Grain-size information was obtained by using wet sieving (greater than 64-μm (micrometers) fraction), and pipettes (less than 64 μm fraction). Arsenic concentrations, grain-size distributions, and surveyed flood plain positions of the samples have been published by Marron (1988).

CHARACTERISTICS OF CONTAMINATED OVERBANK SEDIMENTS

The arsenic-contaminated overbank deposits along the Belle Fourche River have a distinctive orange-brown color that facilitates their identification in the field. The contaminated overbank deposits along the Belle Fourche River are typically up to 2 meters thick and extend about 90 meters away from the channel (fig. D-4). The deposits are most common along the insides of meander bends because the river terraces and shale bluffs that are common along the outsides of meander bends generally were too high to receive overbank deposition during the period of mine-tailings discharge. Two levels of contamination within the contaminated overbank deposits were defined in the field based on the intensity of the orange-brown color. A zone of highly contaminated sediment typically is present between the channel and a zone of moderately contaminated sediment.

Distinctions between different levels of contamination were quantified using arsenic concentrations of samples collected at depths of 0.4 meter or greater from auger holes. Auger holes that yielded one or more samples with more than 600 μg/g of arsenic at sites 1, 2, and 3, and more than 400 μg/g of arsenic at site 4, were considered to be in highly contaminated sediment. The remaining auger holes that yielded one or more samples with arsenic concentrations of 200 to 600 μg/g at sites 1, 2, and 3, and 200 to 400 μg/g at site 4, were considered to be in moderately contaminated sediment. Samples with less than 200 μg/g of arsenic were considered uncontaminated. The transition from highly to

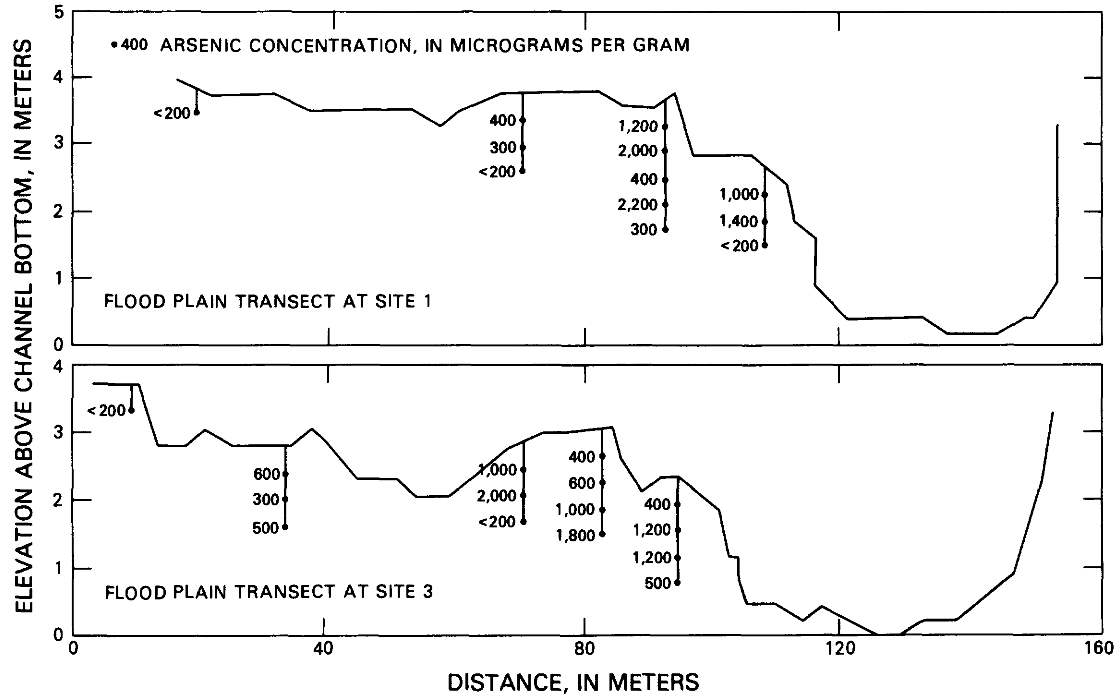

Figure D-4.—Examples of flood-plain cross sections with auger holes. (Arsenic concentrations of samples collected from the auger holes are in μg/g. <, less than.)

moderately contaminated sediment commonly occurs between 40 and 60 meters away from the Belle Fourche River channel along flood-plain cross sections (fig. D-4).

Trends in Arsenic Concentration and Grain-Size Distribution

Average arsenic concentrations of highly contaminated sediments decrease between sites 1 and 2 and between sites 3 and 4 (table D-3). The decreases are significant at the 90-percent level of confidence, using a t-test. Average arsenic concentrations of highly contaminated samples decrease along flood-plain segnents that contain the mouths of major tributaries that drain shale-bedrock watersheds and remain consistent along the flood-plain segment that does not receive significant tributary inflow from the north (table D-3, fig. D-3). Geochemical conditions in and around the contaminated flood-plain deposits favor dilution with uncontaminated sediment over desorption of arsenic into the alluvial aquifer as the dominant mechanism for decreasing arsenic concentrations of sediments. Carbonate minerals in the ore body and in nearby rock units, plus the lime that is added to the mine tailings during milling, limit the desorption of arsenic from sediments by preventing acid formation. The decreases in arsenic concentrations of the highly contaminated sediments are best explained by dilution of the mine tailings with uncontaminated sediments that were transported into the Belle Fourche River channel by tributaries draining shale-bedrock watersheds.

The decreases in average arsenic concentrations of highly contaminated sediments coincide with fining trends in grain-size distribution of those sediments (table D-3). Increases in average weight percentages finer than 16 µm and decreases in average weight percentages coarser than 64 µm from sites 1 to 2 and from sites 3 to 4 are significant at a 90-percent level of confidence using a t-test. The average grain-size distribution of highly contaminated sediment does not change significantly between sites 2 and 3. The uncontaminated sediment that is brought into the Belle Fourche River by tributaries that drain shale-bedrock watersheds is finer-grained than the milled mine-tailings that were discharged at Lead during the period of mine-tailings discharge. Dilution of the mine

Table D-3.—*Average values of grain-size distribution and arsenic concentration of samples*

[<, less than; wt. %, weight percent; µm, micrometer; µg/g, micrograms per gram]

Site	Contamination level	Wt. % <16µm (mean ± standard deviation)	Wt. % <16-64µm (mean ± standard deviation)	Wt. % <64 µm (mean ± standard deviation)	Arsenic concentration (µg/g) (mean ± standard deviation)	Number of samples
1	High	20 ± 4	27 ± 12	53 ± 14	1,722 ± 673	18
1	Moderate	27 ± 7	28 ± 11	46 ± 16	350 ± 100	11
1	None	26 ± 12	21 ± 9	52 ± 16	<200	10
2	High	31 ± 13	27 ± 9	42 ± 17	1,427 ± 408	13
2	Moderate	32 ± 12	21 ± 15	42 ± 21	372 ± 125	9
2	None	30 ± 15	11 ± 13	59 ± 27	<200	6
3	High	32 ± 9	28 ± 11	41 ± 16	1,355 ± 780	22
3	Moderate	22 ± 4	25 ± 12	53 ± 11	400 ± 0	3
3	None	29 ± 10	7 ± 8	64 ± 11	<200	3

tailings in transport in the Belle Fourche River during the period of mine-tailings discharge, by the fine-grained, uncontaminated sediment brought into the Belle Fourche River by tributaries draining shale-bedrock watersheds, appears to have caused the parallel decreases in arsenic concentrations and fining trends in grain-size distribution of the highly contaminated overbank sediments along the Belle Fourche River downstream from Whitewood Creek.

Within flood-plain cross sections, arsenic concentrations of arsenic-contaminated sediments are lowest in the auger holes that are farthest from the Belle Fourche River channel (fig. D-4). This contrast between highly and moderately contaminated sediment appears to reflect an extra influx of uncontaminated sediment into the Belle Fourche River at the very high levels of flow required to deposit the moderately contaminated sediments in the position that they occupy relative to the Belle Fourche River channel. The contrast differs from the downstream decreases in arsenic concentration in an important way. Moderately contaminated samples have similar or coarser grain-size distributions than highly contaminated sediments within flood-plain cross sections (table D-3), whereas downstream decreases in arsenic concentrations coincide with fining trends in grain-size distribution. The uncontaminated sediments that diluted the mine tailings and caused the cross-flood-plain pattern of arsenic concentration had grain-size distributions that were similar to or coarser than those of the contaminated sediment. Grain-size distributions of uncontaminated samples (table D-3) and field observations of the texture of alluvium in terraces along the Belle Fourche River indicate that terraces and the premining flood plain are likely sources for relatively coarse-grained uncontaminated sediment. The undercutting of streambanks and terraces is likely to be initiated at very high levels of discharge.

CONCLUSIONS

Arsenic-contaminated overbank sediments that were deposited along the Belle Fourche River during the period of mine-tailings discharge into Whitewood Creek have physical and chemical characteristics that reflect conditions of sediment transport during that period. The contaminated sediments are typically as much as 2 meters thick and extend about 90 meters away from the channel along the insides of meander bends. The intensity of the orange-brown color of the arsenic-contaminated sediments roughly corresponds to their level of arsenic contamination. A zone of highly contaminated sediment typically occurs between the channel and a zone of moderately contaminated sediment. Carbonate minerals in the mine tailings and associated alluvium prevent acid formation; this condition lends stability to the association between arsenic and sediment in the study area.

The highly contaminated overbank sediments along the Belle Fourche River show marked downstream changes in grain-size distribution and arsenic concentration. The sediments get finer and arsenic concentrations decrease along channel segments that contain the mouths of major tributaries draining shale-bedrock watersheds. Grain-size distributions and arsenic concentrations remain consistent along a channel reach that does not receive significant tributary inflow from the north. The downstream changes in arsenic concentrations and grain-size distribution appear to result from the dilution of contaminated sediment by uncontaminated fine sediment that is brought into the Belle Fourche River by major tributaries draining shale-bedrock watersheds. Downstream changes in arsenic concentrations indicate that the highly contaminated overbank sediments were diluted by a factor of about three along the Belle Fourche River downstream from Whitewood Creek. Decreases in arsenic concentration across the flood plain appear to reflect an extra influx of uncontaminated sediment into the Belle Fourche River at very high levels of flow. Terraces and premining flood plain sediments are likely sources of uncontaminated sediments that could have diluted contaminated sediments, at very high flow, without systematically changing their grain-size distribution.

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ARSENIC GEOCHEMISTRY OF RAPIDLY ACCUMULATING SEDIMENTS, LAKE OAHE, SOUTH DAKOTA

By Walter H. Ficklin[1] and Edward Callender[2]

ABSTRACT

Three sediment cores, collected from rapidly accumulating sediments in the Cheyenne River area of Lake Oahe, were analyzed for arsenic species from interstitial water and solid-sediment. In general, arsenic (V) was the predominant species in the surficial, oxidized sediments. In deeper, more reducing sediments, interstitial arsenic (III) is the dominant species. Solid-phase arsenic species distributions show approximately equal amounts of arsenic (III) and arsenic (V). In those sediment sections that exhibit a dark gray to black color, the solid-phase arsenic distribution is dominated by arsenic (III) and a residual arsenic phase that probably contains sulfide. Interstitial-water chemistry and solid-phase sulfur data indicate that these sediment intervals contain iron-and arsenic-sulfur phases that probably formed authigenically in response to the production of sulfide by microbial sulfate reduction.

INTRODUCTION

Mine-tailing wastes from a large gold mine in the Black Hills of South Dakota reside in the flood plain of the Belle Fourche River. The Cheyenne River Arm of Lake Oahe is the receiving water for the Cheyenne River system and its sediment load (fig. D-5). The arsenic (As) has been entering the reservoir as arsenate (As(V)) sorbed on ferric oxyhydroxides and possibly as unoxidized arsenopyrite associated with suspended sediment. The U.S. Geological Survey has been conducting detailed studies of the movement of the As wastes throughout the Whitewood Creek, Belle Fourche, and Cheyenne River systems (Marron, 1986; Goddard, in press). Because the reservoir sediments are the permanent resting place for the As and because of the possibility that the reservoir ecosystem could be adversely affected by the As, an understanding of the chemical reactions that control the mobility and solubility of As in the surficial sediment is of major importance.

This paper describes the analytical results for three sediment cores collected from the Cheyenne River Arm. A discussion of results of partial extraction of As with subsequent speciation relates the geochemistry of As with changes in oxidizing-reducing conditions in the sediment.

METHODS

Interstitial water was extracted from the sediment by the centrifugation method of Goodwin and others (1984). The As speciation of the interstitial water was done by the ion-exchange method of Ficklin (1983). Separation of As(III) and As(V) in the water samples was initiated within 2 to 3 hours following separation of the interstitial water from the sediment. Speciation of the As in the solid phase was done by an adaptation of the ion-exchange method for aqueous species, which consists of extraction of about 0.5 gram of wet sample with 5.0 ml (milliliters) of hot 4.ON HCl. A small volume (0.3 mL) of the HCl solution was used for speciation, based on the ion-exchange method. The acid-insoluble As residue was put into solution by the method of Olade and Fletcher (1973). The strongly acidic and strong oxidizing conditions of this reagent solubilize the remaining As, which may consist of sulfides of As and other As compounds that are not soluble in 4.0N HCl. Ferrous iron (Fe(II)) in the interstitial water was determined by the bypridine colorimetric method of Skougstad and others (1979). The Fe(II) determinations were made at the field laboratory within 2 to 3 hours after extraction of the interstitial water. The samples were stabilized with addition of enough HCl to make the solution approximately 0.12N. Redox measurements were

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[1] U.S. Geological Survey, Denver, Colo.
[2] U.S. Geological Survey, Reston, Va.

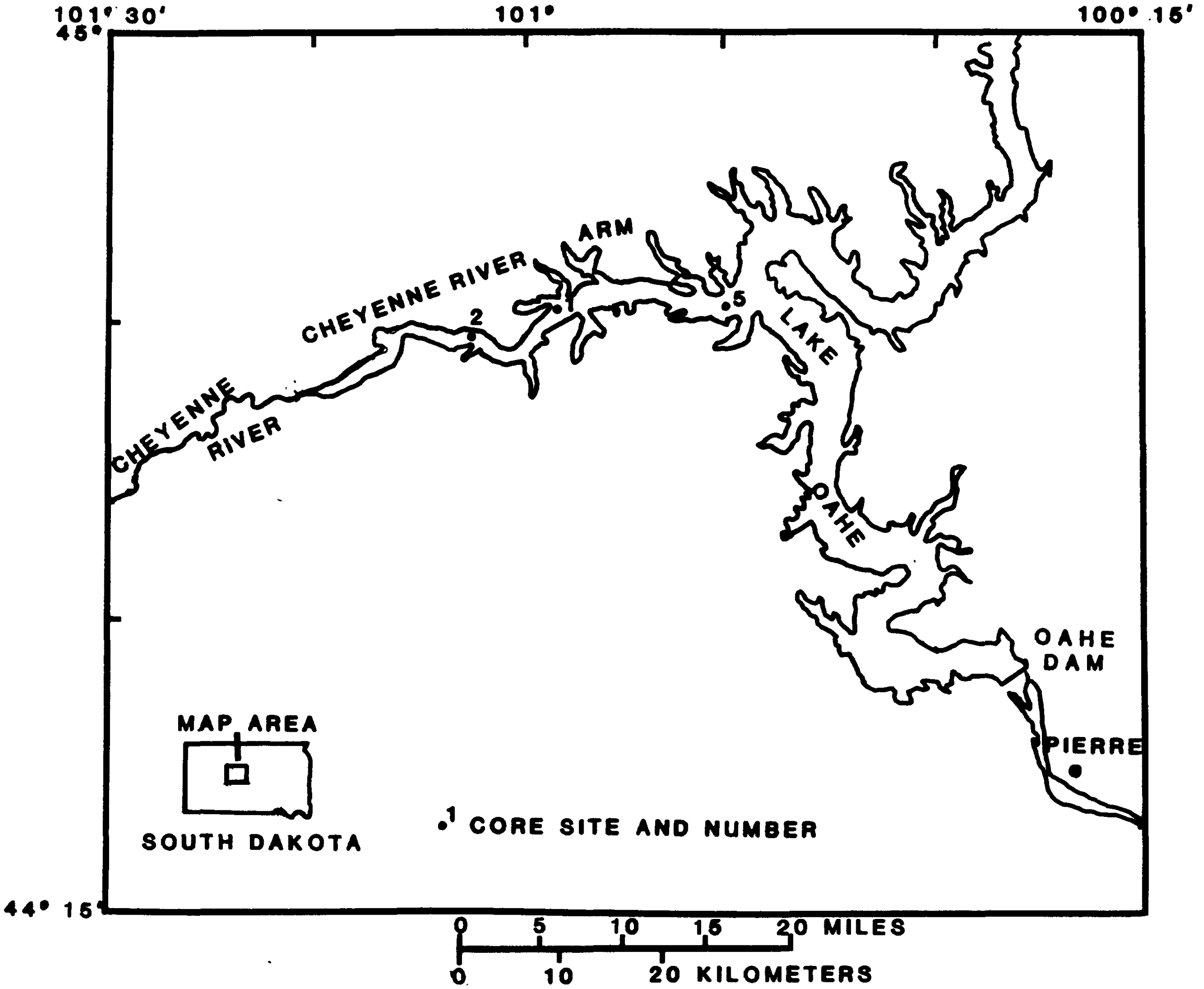

Figure D-5.—Location of cores taken in the Cheyenne River arm of Lake Oahe.

made with a platinum electrode inside a nitrogen-filled glove box. Total sulfur was determined by use of an infrared sulfur analyzer.

RESULTS

The distribution of interstitial As species (As(III), As(V)) in three cores from the Cheyenne River arm of Lake Oahe is presented in figure D-6. The sedimentation rate at site 2 is estimated to be 130 mm/yr (millimeters per year), at site 1 the rate is 80 mm/yr, and, at a point about midway between 1 and 5, the rate is 60 mm/yr. Site 2 is located approximately 12 km (kilometers) from the mouth of the Cheyenne River (fig. D-5); site 5 is located near the mouth of the Cheyenne River arm; and site 1 is located approximately midway between these two sites. The upper 80 to 100 mm (millimeters) of sediment from sites 2 and 1 exhibit oxidizing conditions as shown by the strongly positive redox potential (fig. D-7). By contrast, only the upper 40 mm of sediment at site 5 exhibits mildly oxidizing conditions. The distribution of (Fe(II) (fig. D-7) supports the redox data in that concentrations are high in underlying, less oxidizing to reducing sediments.

At site 2, which exhibits the highest overall redox potential and the lowest Fe(II) concentrations, the distribution of interstitial As species (fig. D-6) shows approximately equal amounts of As(V) and As(III) below the surficial oxidized sediment. In the surficial oxidized sediment, the As(V) species is the predominant form of As. At site 1, there is somewhat more As(III) than As(V) in the upper sediment column (fig. D-6) and the Fe(II) and As data indicate that the sediments at this site are mildly oxidizing to mildly reducing. At site 5, beneath the surficial oxidized sediment, the concentration of interstitial As(III) is approximately 10 times that of As(V). The

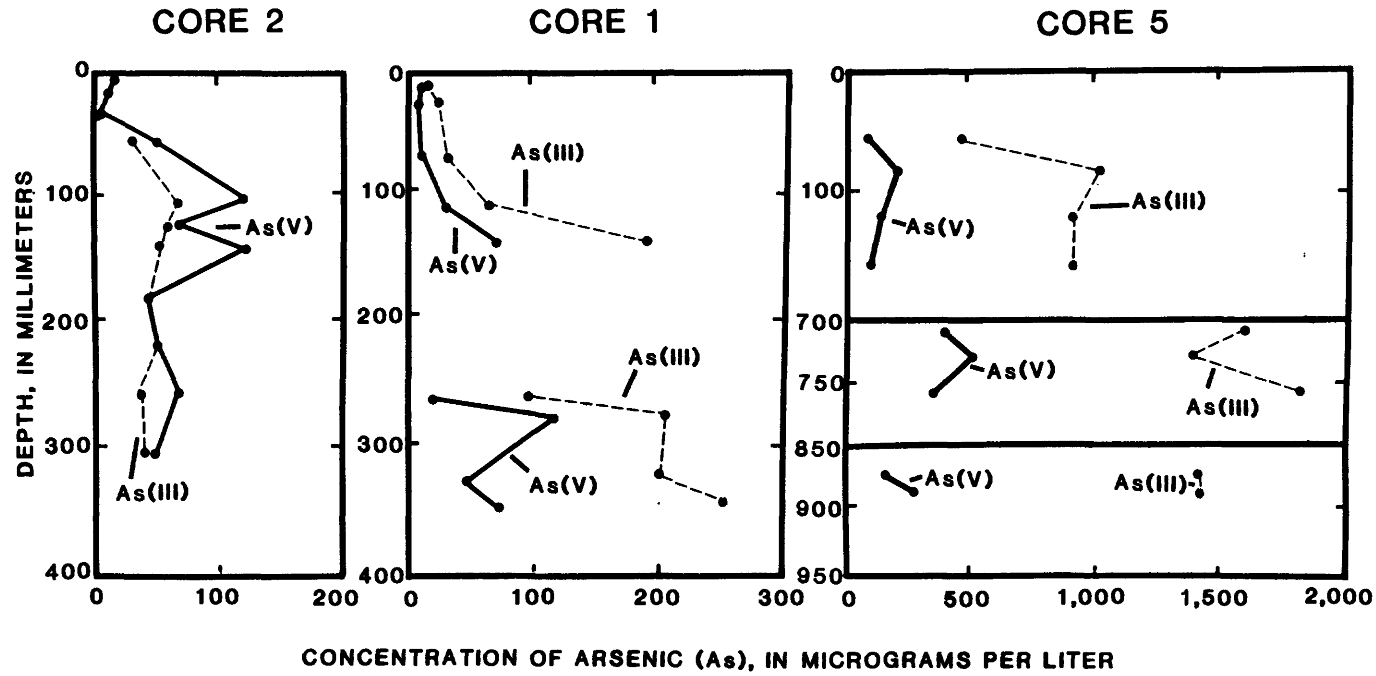

Figure D-6.—Vertical profiles of arsenic (As)(III) and As(V) concentration in interstitial water from cores 2, 1, and 5. In the intervals 0 to 100 millimeters where there are no points, the arsenic concentration was less than the detection limit (5 micrograms per liter).

concentrations of Fe(II) and As(III) are highest at site 5 (fig. D-6) relative to the other sites nearer the mouth of the Cheyenne River.

The distribution of solid-phase As species (figs. D-8 and D-9) follows the trend of redox potential and interstitial Fe(II), As(III), and As(V). At site 2, As(V) is predominant in the upper 80 mm where oxidizing conditions prevail. Below this depth, solid-phase As(V) and As(III) are present in approximately equal concentrations. The concentration of residual As (perhaps an indication of sulfide As or arsenopyrite) is about the same as As(III). Total-sulfur analyses of sediments from this site (fig. D-8) show a twofold increase in concentration below the surficial (0-80 mm) oxidized zone. It appears that the residual As extraction may include some of the sulfur phases.

At site 1, the solid-phase As(V) concentration is somewhat higher than the As(III) concentration in the upper 150 mm of the sediment column (fig. D-8). The residual As concentrations are virtually zero in these sediments and total sulfur concentrations reflect background levels. In the deeper sediment from this site, As(V), As(III), and residual As are present in approximately equal concentrations. The dark black color, low redox potential, and low Fe(II) concentrations in some of these deeper intervals suggest that iron monosulfide may be precipitating. This possibility is reinforced by the total-sulfur data which show a threefold increase for the deeper intervals (fig. D-8).

At site 5, the upper oxidized zone contains predominantly As(V) with no As(III) or residual As. The underlying sediment contains more As(III) than As(V), and more As(V) than residual As (fig. D-9). Total sulfur contents are near background levels. Deeper in the sediment column at site 5, the concentration of As(III) is approximately four times that of As(V). However, residual As concentrations are greater than the

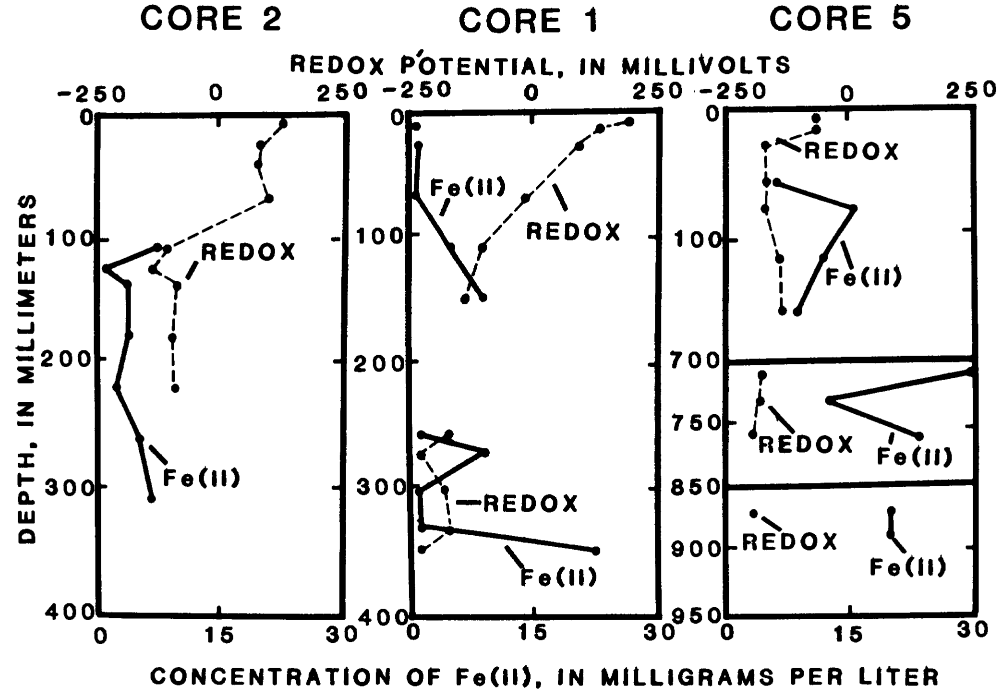

Figure D-7.—Vertical profiles of iron (Fe)(II) concentrations and redox potential measurements in cores 2, 1, and 5.

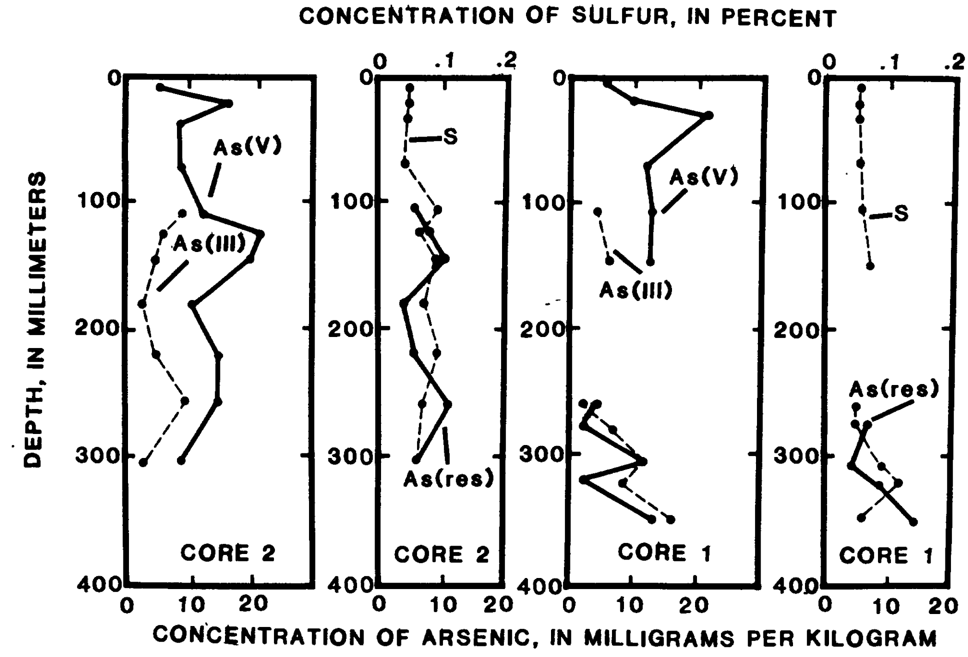

Figure D-8.—Vertical profiles of arsenic (III), arsenic (V), arsenic (residual), and sulfur (S) concentrations in cores 2 and 1.

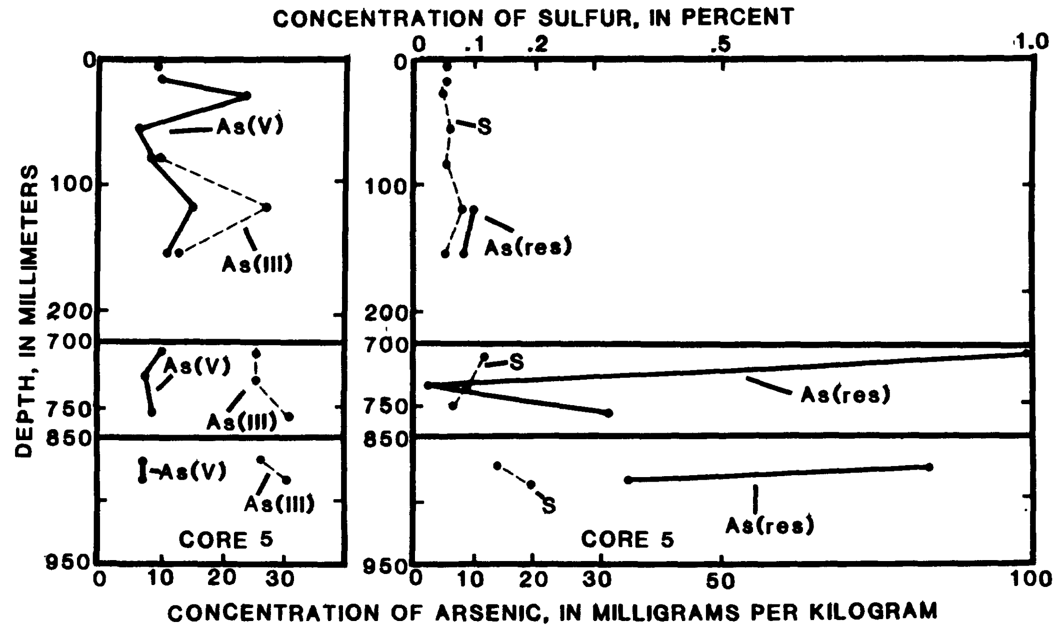

Figure D-9.—Vertical profile of arsenic (III), arsenic (V), arsenic (residual), and sulfur concentrations in core 5.

sum of As(III) and As(V) in four of the five intervals sampled. Total sulfur concentrations are three times the background concentration (fig. D-9). This suggests that the residual-As phase may contain sulfide.

DISCUSSION

The vertical distribution of redox potential, (Fe(II)), As(III) and As(V), and solid-phase As species in sediments from the Cheyenne River arm of Lake Oahe suggest the following hypothesis for the sedimentary geochemistry of As in rapidly accumulating sediments. The As is transported in the suspended load of the Cheyenne River as suspended particulate phases. Some of the As may be transported as a sulfide derived from the tailings that reside in the flood plain and some may be transported as oxidized As sorbed onto amorphous iron and manganese-oxyhydroxides. This sedimentary As is deposited in the reservoir bottom sediments that are in contact with the oxygenated water column. Continual deposition of sedimentary particulate matter, including organic matter, results in the transition from oxidizing to reducing conditions with depth in the sediment column. On occasion, the influx of labile organic matter (for example, phytoplankton, detritus) results in microbially mediated sulfate reduction. This reaction produces reduced sulfur species which combine with reduced iron and As species to precipitate insoluble sulfide phases.

From the As speciation data presented, it is clear that As(V) is the predominant species in the surficial oxidized sediments. Although the exact nature of the oxidized phase is unknown, it seems reasonable to assume that amorphous iron oxyhydroxide is a major phase. As(III) is present as well as As(V) in the underlying sediment. At site 5, the sediment contains more solid-phase As(III) than As(V). Some of the deeper sediment at sites 1 and 5 may contain authigenic sulfide phases. The dark gray to black color, the low Fe(II) concentrations, the high residual As concentrations, and the high total sulfur concentrations in these intervals suggest that sulfide phases are present. Generally, the deeper sediment at these sites show a depletion of interstitial sulfate relative to chloride. The production of sulfide, as a consequence of bacterial sulfate reduction, may be an important process in the formation and preservation of reduced As phases in the rapidly accumulating sediments of Lake Oahe.

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SOURCE AND TRANSPORT OF ARSENIC IN THE WHITEWOOD CREEK-BELLE FOURCHE-CHEYENNE RIVER-LAKE OAHE SYSTEM, SOUTH DAKOTA

By Arthur J. Horowitz[1], Kent A. Elrick[1], and Robert B. Cook[2]

ABSTRACT

From 1875 through 1977, mining, milling, and processing wastes containing quantities of arsenopyrite were produced around Lead, South Dakota. Much of this material was discharged into Whitewood Creek. From there, parts of the waste were transported to the Belle Fourche River, thence to the Cheyenne River, and finally to the Missouri River. In 1958, the Missouri River was dammed at Pierre, forming Lake Oahe. Cores collected in the lake bottom show the presence of arsenic-rich layers in the bed sediments; the arsenic was attributed to arsenopyrite in the 8-to-16 and 16-to-32-micrometer size fractions of the sediments.

Suspended-sediment samples collected in the Cheyenne River above Lake Oahe contained detectable quantities of both arsenopyrite and octahedral pyrite in the 8-to-16 and 16-to32-micrometer fractions. The arsenic concentrations found in the suspended sediment probably result from the mixing of arsenic-poor sediments from the Cheyenne River (8.5 to 10 milligrams per kilogram with arsenic-rich sediments from the Belle Fourche River (100 to 150 milligrams per kilogram in a volumetric ratio of 3 to 1.

Solid material collected from the banks and flood plains of the Belle Fourche River and Whitewood Creek contain reduced and oxidized phases. The reduced phases have an arsenic maxima in the 16-to-32 and the 32-to-63-micrometer size ranges. These fractions also contribute the most arsenic to the samples; the major source of arsenic seems to be arsenopyrite. The oxidized segments have an arsenic maxima in the less-than 2-micrometer size range. The less-than 2-micrometer maxima is associated with widely disseminated arsenic-bearing iron oxide coatings. The greater-than 63-micrometer fractions contribute the most arsenic to the oxidized samples; this arsenic, as in the reduced samples, is associated with arsenopyrite. These deposits probably are the source for the arsenic-rich suspended sediments from the Belle Fourche River and for the arsenopyrite found in the bed sediments of Lake Oahe.

INTRODUCTION

From 1875 to late 1977, significant quantities of mining, milling, and processing wastes were discharged directly into Whitewood Creek and its tributaries as a result of mining operations around Lead, S. Dak. (fig. D-10). Although the discharge of solid waste ceased in 1977 with the construction of the Grizzly Gulch containment dam, large amounts of oxidized and unoxidized waste remain in storage on and in the banks and flood plains of Whitewood Creek and the Belle Fourche River (Goddard, in press). It has been estimated that the bank and flood-plain deposits contain from 50 to 60 percent of all the material discharged from the mining and processing operations (Marron, 1986). Based on estimates from the U.S. Environmental Protection Agency (1973), there may be as much as 1.9 to 2.3 x 10^6 Mg (megagrams) of arsenic (As) in storage along these rivers (Horowitz and others, 1988).

Until 1958, unrestricted flow permitted the transport of material not retained in storage, plus any additional material eroded from the banks and flood plains of Whitewood Creek and the Belle Fourche River, to the Cheyenne River, and thence into the Missouri River. However, in 1958, the Missouri River was dammed at Pierre, forming Lake Oahe. Studies on a series of cores from Lake Oahe indicate the presence of high As-bearing layers in the bottom sediments of the lake (Horowitz and others, 1988). The highest As

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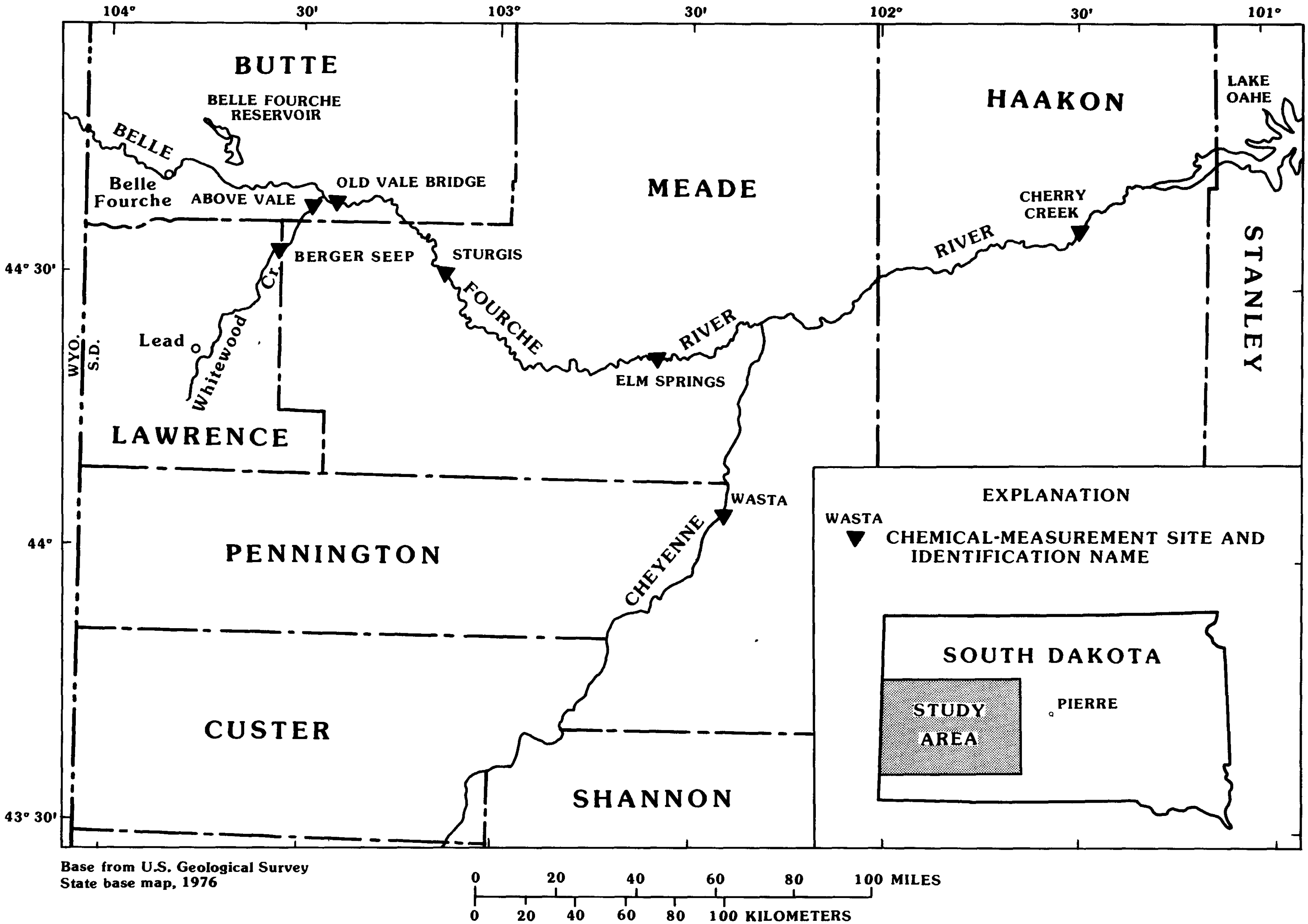
[1] U.S. Geological Survey, Doraville, Ga.

[2] Auburn University, Auburn, Ala.



Base from U.S. Geological Survey
State base map, 1976

Figure D-10.–Location of chemical measurement sites in the study area. (Modified from Goddard, in press.)

levels in these sediments were found in the 8-to-16 and 16-to-32-μm (micrometer) size fractions. Scanning electron micrsocopy (SEM) of these fractions revealed the presence of well crystallized arsenopyrite (Horowitz and others, 1988). Only relatively minor concentrations of arsenopyrite would be sufficient to account for the observed high As levels (about 150 to 250 mg/kg (milligrams per kilogram)) found in the lake sediments (about 300 to 450 mg (milligrams) of arsenopyrite per kilogram of non-As-bearing sediment).

Suspended-sediment samples collected at Cherry Creek, about 16 km (kilometers) from the mouth of the Cheyenne River Arm of Lake Oahe, showed As concentrations ranging from 12 to 36 mg/kg. The highest As-bearing sample (36 mg/kg) was size-fractioned in the same way as the core samples. The highest As levels were found in the 8-to-16 and 16-to-32-μm fractions; the same fractions that contained the highest As levels in the lake sediments. Subsequent SEM inspection of these fractions revealed the presence of both arsenopyrite and octahedral pyrite (Horowitz and others, 1988). Some As (at concentrations nearly an order of magnitude lower) also was associated with iron-oxide coatings. Octahedral pyrite normally is associated with hydrothermal deposits and is not likely to be authigenic (Barton, 1974). The sharp cleavage planes and the well-preserved nature of the pyrite would indicate rapid transport from its proposed source, the banks and flood plains of Whitewood Creek or the Belle Fourche River (Horowitz and others, 1988).

Additional suspended-sediment samples were collected from the Cheyenne River at Wasta. This site is above the confluence of the Belle Fourche and Cheyenne Rivers. The As concentrations ranged from 8.5 to 10 mg/kg. Additional samples collected at Elm Springs on the Belle Fourche, near its confluence with the Cheyenne River, contained As concentrations that ranged from 100 to 140 mg/kg. It has been estimated that suspended sediments from the Belle Fourche constitute about 25 percent, by volume, of the suspended sediments in the Cheyenne River during the period of sampling (K.E. Goddard, U.S. Geological Survey, oral commun., 1986). If that is the case, then the Belle Fourche would contribute from 25 to 35 mg/kg As, whereas the Cheyenne would contribute from 6 to 7 mg/kg As. The total calculated As concentration would then range from 31 to 42 mg/kg. This calculated value compares reasonably well with the 12 to 36 mg/kg concentration range measured at the Cherry Creek site (Horowitz and others, 1988).

Elevated As levels have been identified in Lake Oahe and attributed to the presence of arsenopyrite. Arsenopyrite and octahedral pyrite were identified in suspended sediments entering the lake. Further, it was postulated that the present-day origin of the arsenopyrite and the octahedral pyrite were the banks and flood plains of Whitewood Creek and the Belle Fourche River. This paper presents results of a study to determine if, in fact, arsenopyrite and octahedral pyrite could be isolated, identified, and chemically analyzed in material collected from the banks or flood plains of Whitewood Creek and the Belle Fourche River.

SAMPLING, SAMPLE HANDLING, AND ANALYTICAL PROCEDURES

Bank deposits were sampled at three sites along Whitewood Creek (the Berger Seep) and the Belle Fourche River (below Vale, at Old Vale Bridge). At each site, two separate samples were obtained, an "oxidized" phase and a "reduced" phase. Differentiation between oxidized and reduced segments was made on a subjective visual assessment. Material that was red-tinged was identified as oxidized whereas material that was gray was identified as reduced. After collection, the samples were shipped to Atlanta, Ga., for further processing and analysis.

Upon arrival, the oxidized and reduced samples were freeze-dried. An aliquot of each bulk sample was retained for As analysis while the remainder was wet-sieved at 63 μm to separate the material into two size ranges. Aliquots of both the less-than and the greater-than 63-μm fractions were analyzed for As. As noted in the previous section, the arsenopyrite and octahedral pyrite from the Lake Oahe sediments and from the suspended sediments, were found in material finer than 63 μm, therefore, the less-than 63-μm material was further sized into less-than 2, 2-to-4, 4-to-8, 8-to-16, 16-to-32, and 32-to-63-μm fractions. These size fractions were subsequently analyzed for As.

The size fractionation of the less than 63-μm material was carried out using air elutriation following the procedures of Horowitz and Elrick (1986). Analyses for As were performed using the procedures of Elrick and Horowitz (1986). Briefly, 0.5000 gram of solid material was digested with a combination of HNO_3, HF, and $HClO_4$, in open Teflon[3] beakers. The digested salts were solubilized in 50 percent HCl, reduced in a drybath at 90 °C with KI, and analyzed by hydride generation atomic absorption spectroscopy. Precision and bias were monitored by using a combination of National Bureau of Standards sediments and U. S. Geological Survey rock-standards. Precision was better than ±10 percent and no significant bias was detected.

RESULTS AND DISCUSSION

The analytical data for the six samples (an oxidized and reduced segment from each of the three sites) are presented in table D-4 and in figure D-11. Both the oxidized and the reduced segments display a unimodal grain-size distribution, with the greater-than 63-μm fraction usually representing the single largest fraction. The As distributions differ significantly from the grain-size distributions. The oxidized phases show a steady decrease in As concentration with an increase in grain size whereas the reduced phases tend to show an increase in As concentration with an increase in grain size up to 63 μm; the As levels then drop off sharply. Despite the high As concentrations found in the very fine-grained size fractions, the major grain-size fractional-As contributor for the oxidized phases is the greater than 63 μm fraction. This fraction's contribution is on the order of 5 to 10 times higher than from the other fractions. On the other hand, the major grain-size fractional-As contributor for the reduced phases is the less-than 63-μm fraction, with the largest contributions coming from the 16-to-32 and/or the 32-to-63-μm fractions.

In order to determine the form in which the As is held in both the oxidized and the reduced phases, and to determine if differences exist in As partitioning with grain size, selected size fractions from both phases were subjected to both optical microscopy (reflected light) and SEM/EDAX (energy dispersive X-ray analysis). Optical microscopy indicated that the coarser grain-size fractions (16-to-32 and 32-to-63-μm) of both the oxidized and reduced fractions contained substantial quantities of sulfide minerals--predominantly pyrite (both crystalline and framboidal), pyrrhotite, arsenopyrite, and some marcasite. The oxidized fractions also contained some magnetite. A number of the sulfide minerals in the oxidized samples displayed iron-oxide rinds of variable thickness, and some of the pyrrhotite grains showed signs of oxidation.

SEM/EDAX indicated the presence of substantial quantities of arsenic-bearing minerals in the reducing segments. Analyses of 15 separate grains from the three reduced samples indicated an average chemical composition (iron (Fe), 31.3±1.5 percent; arsenic (As), 47.0±28 percent; sulfur (S), 21.4±2.2 percent) very close to that reported for arsenopyrites identified and analyzed from other locations (Henry and others, 1979; Stanley and Vaughn, 1982). Further, optical microscopy indicated the presence of arsenopyrite. It would seem that the majority of the As in the reduced segments is associated with arsenopyrite.

SEM/EDAX examination of the less-than 2-μm fractions of the oxidized samples indicate that As is associated with widely disseminated iron oxide coatings. The As concentrations are on the order of 2 to 8 percent by weight The number of coated grains decreases with increasing grain size. In addition to the As-bearing iron-oxide coatings, As also is associated with iron sulfide minerals in the coarser, oxidized size fractions; however, the Fe, As, and S concentrations vary substantially. Some of the grains display typical arsenopyrite compositions, whereas others diverge (for example, Stanley and Vaughn, 1982). Further, detailed examination of individual grains indicates that chemical composition could vary, even within a grain. Although Fe, As, and S vary in these cases, S shows the greatest variation (for example, 2 to 15 percent by weight).

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

Table D-4.—*Grain-size analyses and arsenic concentrations for bank\flood-plain deposits from Whitewood Creek and the Belle Fourche River*

[<, less than; >, greater than; As, arsenic; μm, micrometer; mg/kg, milligrams per kilogram]

	Oxidized segment			Reduced segment		
Sample	Percent of sample	As - concentration (mg/kg)	As contribution (percent)	Percent of sample	As - concentration (mg/kg)	As contribution (percent)
			Whitewood Creek at Berger Seep			
Bulk		4,100			4,200	
<63 μm	32.3	6,000	47.1	95.9	4,400	99.7
<2 μm	2.9	14,000	9.1	8.6	3,500	6.3
2 - 4 μm	3.5	13,000	10.5	7.7	4,000	6.3
4 - 8 μm	3.8	10,000	8.6	11.5	4,000	10.6
8 - 16 μm	7.0	6,000	9.6	24.0	5,000	27.7
6 - 32 μm	5.8	3,500	4.3	25.9	5,500	31.9
32 - 63 μm	9.3	2,500	5.0	18.2	4,000	16.9
>63 μm	67.7	3,200	52.9	4.1	310	0.3
			Belle Fourche at Old Vale Bridge			
Bulk		5,500			2,700	
<63 μm	21.0	11,000	42.5	55.1	4,800	91.1
<2 μm	.8	22,000	3.4	1.7	2,000	1.1
2 - 4 μm	.8	21,000	3.0	2.2	1,500	1.1
4 - 8 μm	1.3	20,000	4.5	2.8	1,500	1.4
8 - 16 μm	2.3	15,000	6.4	8.3	2,000	6.1
16 - 32 μm	13.7	8,500	21.4	30.2	6,500	71.4
>63 μm	79.0	4,100	57.5	44.9	300	9.9
			Belle Fourche below Vale			
Bulk		3,200			2,400	
<63 μm	17.0	5,200	28.2	45.2	4,700	84.7
<2 μm	1.1	12,000	4.5	1.4	800	0.4
2 - 4 μm	1.4	11,000	4.8	1.8	750	.5
4 - 8 μm	1.7	10,000	5.5	2.3	850	.8
8 - 16 μm	2.4	7,000	5.5	5.0	1,700	3.8
16 - 32 μm	1.9	4,000	2.4	4.1	2,500	4.2
32 - 63 μm	8.5	2,000	5.5	30.6	6,000	75.0
>63 μm	83.0	2,700	71.8	54.8	600	15.3

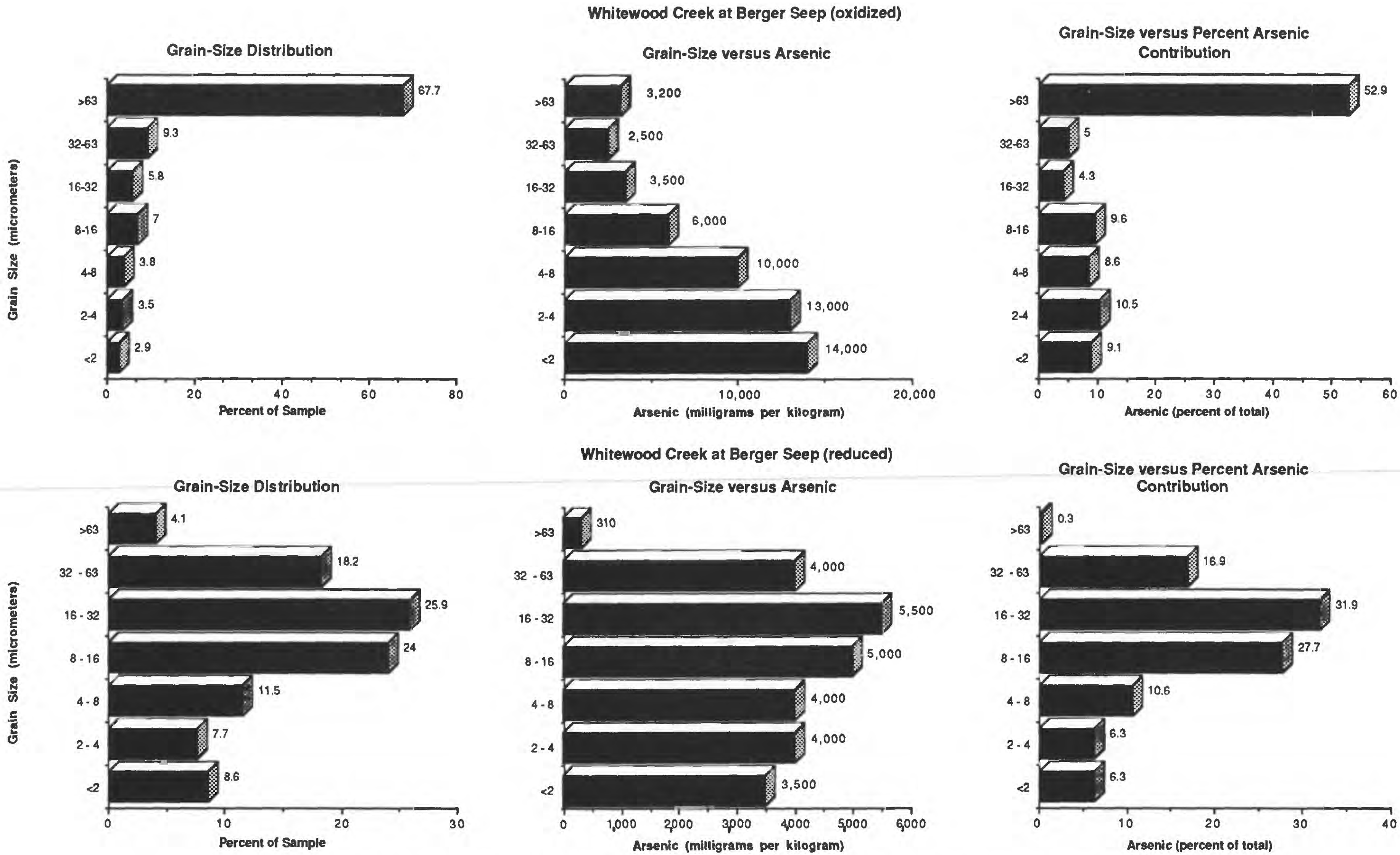


Figure D-11. –Grain size and arsenic associations in the samples from Whitewood Creek and the Bell Fourche River.

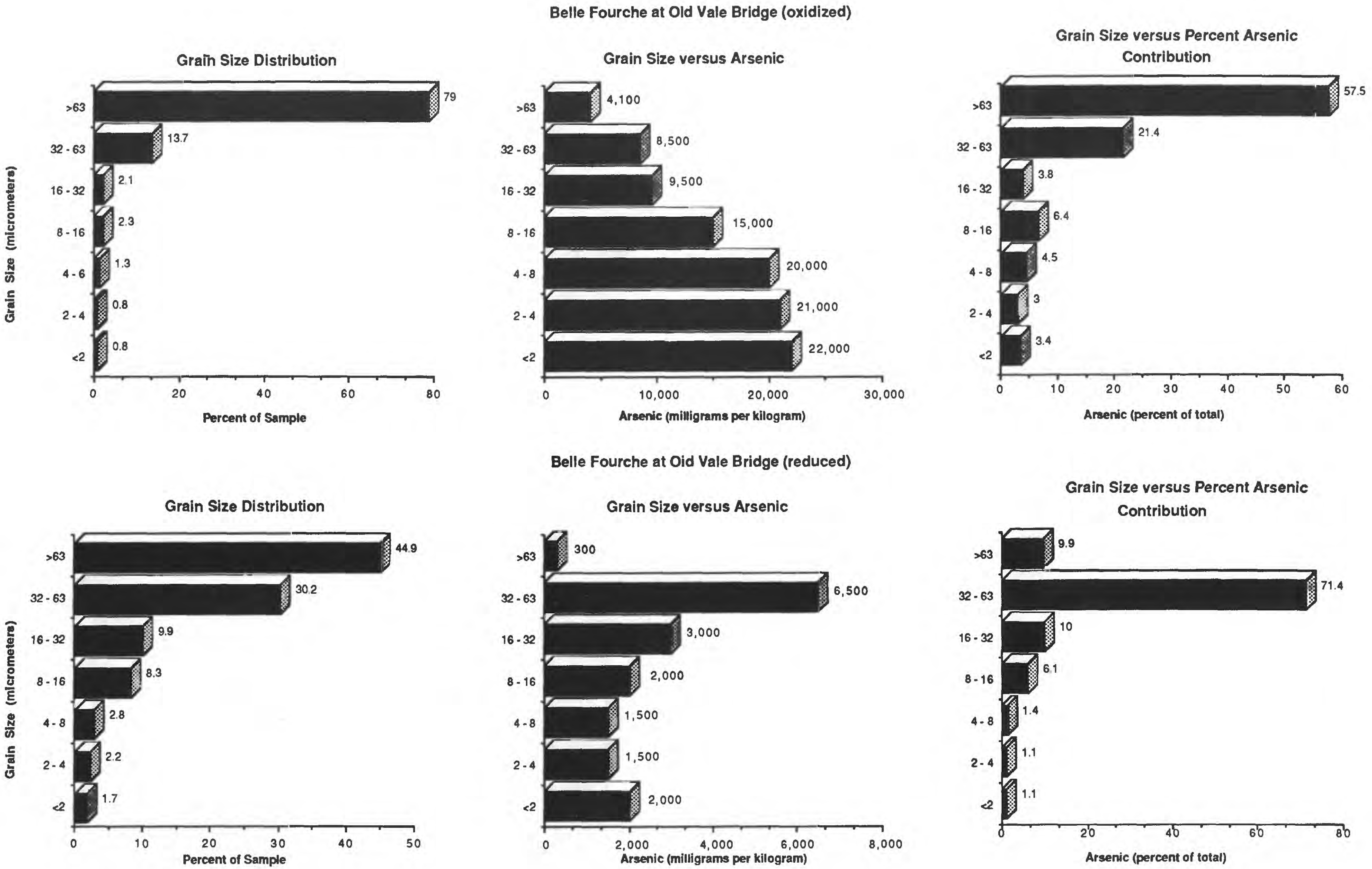


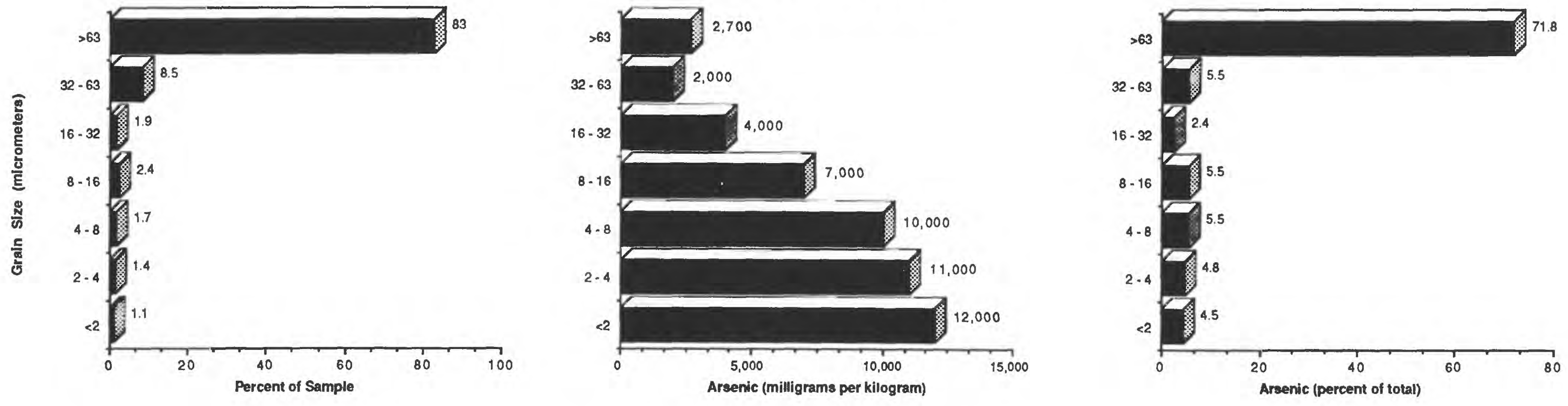
Figure D-11. --Grain size and arsenic associations in the samples from Whitewood Creek and the Bell Fourche River--Continued.

Belle Fourche below Vale (oxidized)

Grain Size Distribution

Grain Size versus Arsenic

Grain Size versus Percent Arsenic Contribution



Belle Fourche below Vale (reduced)

Grain Size Distribution

Grain Size versus Arsenic

Grain Size versus Percent Arsenic Contribution

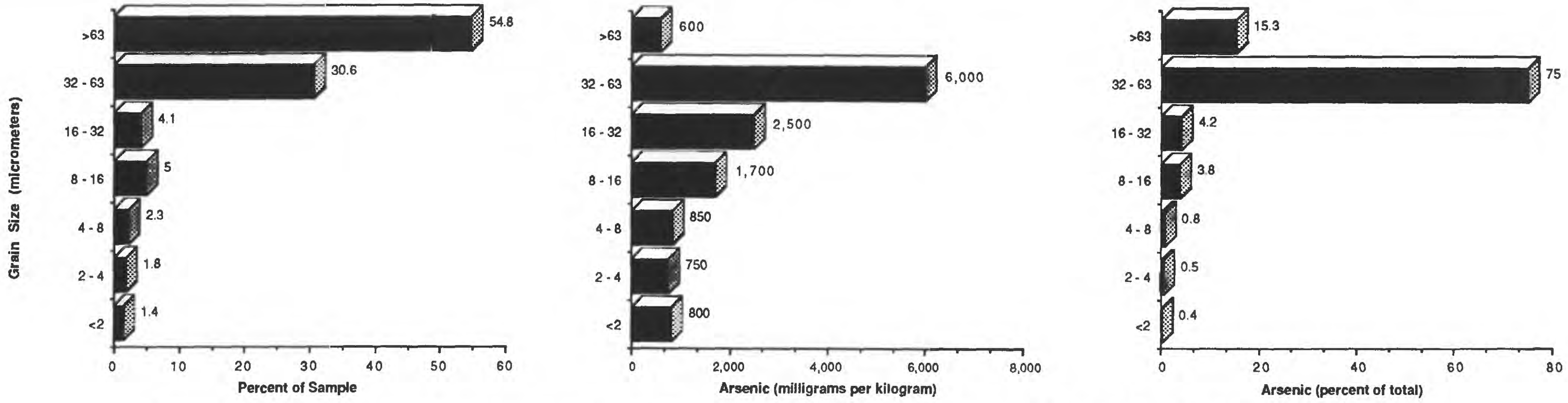


Figure D-11. –Grain size and arsenic associations in the samples from Whitewood Creek and the Bell Fourche River--Continued.

The high degree of chemical variability in the oxidized As-bearing grains could be due to differential chemical weathering, with S being the most strongly affected element. The variability also might be due to the presence of relatively thin iron-oxide coatings of varying thickness; this would affect the degree of penetration by the X-rays used in the EDAX analyses which, in turn, would affect the chemical concentrations determined. Finally, the coatings might contain finely divided grains of other minerals that also would affect the composition. Based on the microscopic examination of the grains in polished thin sections, the most likely explanation for the chemical variability is the presence of thin iron-oxide coatings of varying thickness surrounding arsenopyrite. This was confirmed by examining the polished sections with SEM/EDAX, which also indicated the presence of finely divided mineral grains cemented within the iron-oxide coatings (fig. D-12).

Chemical analyses of the underlying As-bearing sulfide minerals indicate compositions (for example, Fe, 30.6±10.5 percent ; As, 47.0±10.7 percent; S, 22.3±0.4 percent) similar to those found in the reduced samples and reported for arsenopyrites from other locations (Henry and others, 1979; Stanley and Vaughn, 1982). Thus, the oxidized segments contain As in two forms: one associated with iron-oxide coatings, and one

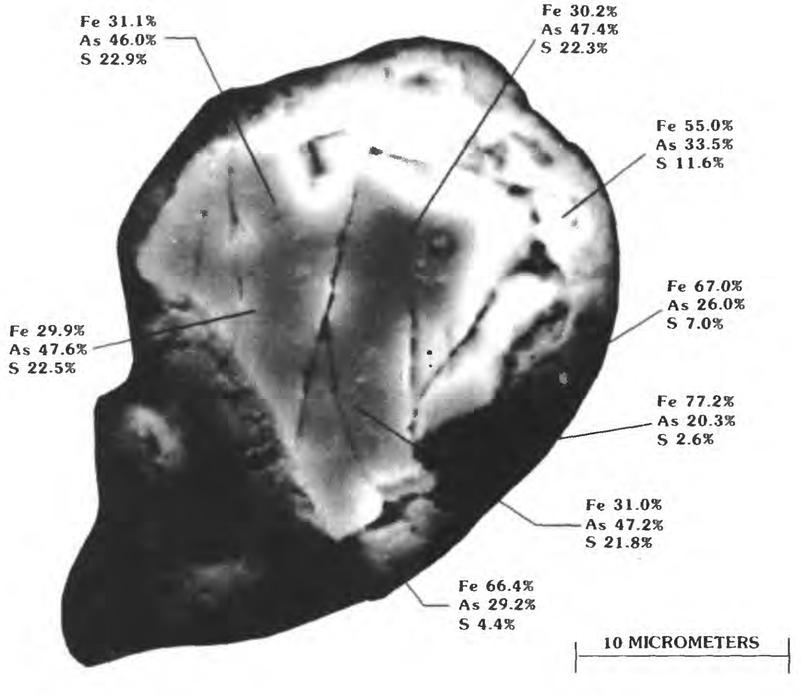


Figure D-12.—Selected analyses of iron, arsenic, and sulfur in an iron-oxide coated arsenopyrite grain from the Old Vale Bridge site; bar equals 10 μm.

associated with arsenopyrite. The As concentrations in the arsenopyrites are from 5 to 10 times higher than those found associated with the iron-oxide coatings, either in the very fine fractions or in the coarser material. Despite the apparent oxidized nature of these samples, and the presence of high As concentrations associated with iron-oxide coatings (finest fractions, see table D-4), arsenopyrite (a sulfide mineral) appears to be the major source of As in these segments owing to its presence in the coarser fractions which contribute most of the As to these samples. This is somewhat unexpected because sulfide minerals are not considered stable in oxidizing environments. It is possible that the iron-oxide rinds found on the arsenopyrites, and the other sulfide minerals found in the oxidized phases, prevent further oxidation of the underlying sulfide minerals and, thus, stabilize them.

The majority of the As found in both the oxidized and the reduced segments of the bank and flood-plain deposits would seem to be in the form of arsenopyrite. This would indicate that much of the As is in a less environmentally available form (associated with sulfides rather than iron oxides) than would be indicated by the apparent presence of significant quantities of oxidized bank and flood-plain deposits, which are estimated to constitute about 80 to 85 percent of this material along the Belle Fourche River (D.C. Marron, U.S. Geological Survey, oral commun., 1988). Finally, because arsenopyrite was found in both the oxidized and the reduced segments, either material could act as a source for the arsenopyrite found in the suspended sediments collected in the Cheyenne River and in the bed sediments of Lake Oahe.

CONCLUSIONS

Detailed examination of bank and flood-plain deposits from Whitewood Creek and the Belle Fourche River indicate that As is present in the form of arsenopyrite and also is associated with iron-oxide coatings. The As in the reduced segments largely is contributed by the less-than 63-μm fraction in the form of arsenopyrite. The As in the oxidized phases occurs in two forms: one associated with iron oxide coatings and one found in arsenopyrite; the As associated with the latter has a concentration 5 to 10 times higher than in the former. Some of the arsenopyrites found in the oxidized samples are surrounded by iron-oxide rinds. The As associated with the iron-oxide coatings is found predominantly in the very fine-size fractions. Despite the very high As concentrations determined for the very fine size-fractions of the oxidized samples, the major source of As in this material, as with the reduced segments, is arsenopyrite. The banks and flood plains of Whitewood Creek and the Belle Fourche River seem to be the primary source for the As and the arsenopyrite found in the suspended sediments collected in the Cheyenne River, and in the bed sediments of Lake Oahe.

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COUPLED CHEMICAL, BIOLOGICAL AND PHYSICAL PROCESSES IN WHITEWOOD CREEK, SOUTH DAKOTA: EVALUATION OF THE CONTROLS OF DISSOLVED ARSENIC

By Christopher C. Fuller[1], James A. Davis[1], Gary W. Zellwegger[1], and Kimball E. Goddard[2]

ABSTRACT

Coupled physical, chemical, and biological processes affect the concentration of dissolved arsenic in Whitewood Creek, South Dakota. In August 1987, dissolved arsenic concentrations were controlled primarily by adsorption and coprecipitation with iron oxyhydroxides (ferrihydrite) as ground water enriched in arsenic entered the stream. Periphyton photosynthesis induced a diurnal pH fluctuation in streamwater of 0.25 to 0.5 pH units and a concomitant diurnal cycle in arsenate (30 to 40 percent variation). The fluctuation in arsenate reflects the dynamic equilibrium of adsorption-desorption processes occurring in response to the pH cycle. Kinetics of the sorption processes are slow, and result in a cycle of dissolved arsenic that lags several hours behind the pH cycle.

INTRODUCTION

Adsorption processes are often invoked as a control on the concentrations of dissolved inorganic trace elements and contaminants in natural waters at concentrations below their solubilities (Drever, 1982; Morel, 1983). Numerous laboratory studies on the uptake of metals and oxyanions by synthetic oxides (Anderson and others, 1976; Davis and Leckie, 1980; Pierce and Moore, 1982), natural solids (Frost and Griffin, 1977; Lions and others, 1982), as well as solid-phase associations derived from selective extractions of sediments from natural waters (Tessier and others, 1985; Aggett and Roberts, 1986), have suggested the importance of this process of trace element partitioning. The cycling of dissolved arsenic (As) in surface-water systems is influenced by chemical, physical and biological processes of input and removal (Ferguson and Gavis, 1972; Holm and others, 1980). In oxic waters, dissolved As exists primarily as the arsenate oxyanion present as [AsO_4^{3-}], [$HAsO_4^{2-}$], [$H_2AsO_4^-$], species depending on pH. Dissolved arsenate will be referred to as [AsO_4] in this paper. This paper presents an evaluation of the role of adsorption-desorption reactions on iron (Fe) oxyhydroxides (ferrihydrite, as characterized by X-ray diffraction) in controlling [AsO_4] in a small, perennial stream that has been heavily contaminated by gold-mine tailings. The coupling of biological and physical processes to the sorption reactions in the cycling of [AsO_4] is discussed.

SITE DESCRIPTION

Whitewood Creek, S. Dak., a small perennial stream has been heavily impacted by the discharge, from 1876 to 1977, of about 100 million Mg (megagrams) of finely ground mill tailings containing arsenopyrite (FeAsS) and other metallic sulfide minerals. This discharge resulted in the development of contaminated flood-plain sediments (up to 11,000 μg As/g (micrograms of arsenic per gram of sediment)) over the course of the stream, some of which consist entirely of tailings (Goddard, in press). Field and mineralogic data indicate that a substantial fraction of the As is now associated with iron hydroxides and oxides. Slow release of As from the flood-plain deposits into ground and surface waters is occurring through oxidation of FeAsS and/or by dissolution of, or desorption from, As-rich ferrihydrite. Input of As to the stream results from the seepage of As- and Fe-bearing reducing ground water out of the flood-plain aquifers following periods of high stream discharge (Cherry and others, 1986). Dissolved As in the ground water is present as both arsenate and

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[1] U.S. Geological Survey, Menlo Park, Calif.
[2] U.S. Geological Survey, Rapid City, S. Dak.

arsenite whereas dissolved As in the stream essentially is in the oxidized form [AsO_4] (Fuller and others, 1987). Oxidation and precipitation of ferrous iron from the ground water upon contact with the atmosphere largely removes the dissolved As through coprecipitation with iron or subsequent adsoprtion onto the ferrihydrite. The buildup of As-rich iron oxides in the streambed and a downstream increase in dissolved As result. The great abundance of iron oxides in the sediments and flood plains of this stream, and the strong affinity of arsenate for iron oxyhydroxides (Pierce and Moore, 1982) are indicative of the control of dissolved As by reactions with the ferrihydrite surfaces. Further evidence for this lies in the constant molar ratio of As:Fe in iron precipitates in ground water seeps, and the fact that coarse- and fine-grained sediments contain a wide range of As and Fe content, but have a relatively constant As:Fe molar ratio (Fuller and others, 1987).

METHODS

The pH (8.0-9.0) of this high sulfate (6 mM (millimolar)), carbonate buffered (alkalinity 3 meq/L (milliequivalents per liter)) stream has been observed to increase during the day (Fuller and others, 1987). It was hypothesized that an increase in [AsO_4] should result if its concentration was controlled by reversible adsorption onto the abundant ferrihydrite. To elucidate the role of sorption processes in As partitioning, hourly sampling over a 3-day period at three sites over a 50-km (kilometer) reach of the stream was conducted in August 1987 (fig. D–13). Two downstream sites in the lower gradient reach of the stream were in areas where the flood plains were extensively contaminated and where visible ground water seeps were visible (Custer Camp, Sheeler Seeps), whereas an upstream site (Whitewood Creek above Whitewood), had no apparent inputs of As- or Fe-bearing ground water. At the most downstream site (Sheeler Seeps), lithium bromide (LiBr) was injected 2.8 km upstream from Sheeler Seeps to evaluate ground-water inputs and fluctuations in stream discharge (Bencala and others, 1987) in order to estimate the As input along the reach. In addition, dissolved As samples were collected along this reach. Just upstream from the Sheeler Seeps site, the ground water discharging from a large abandoned meander that contains contaminated sediments was sampled during this study and previously (Fuller and others, 1987; Goddard, in press). Methods of sampling and analyses have been presented earlier (Fuller and others, 1987). Streamwater dissolved As is greater than 95 percent as [AsO_4]. For the purpose of this paper, dissolved As data reported here is, therefore, assumed to be entirely as [AsO_4].

RESULTS AND DISCUSSION

A diurnal fluctuation in stream pH that varied as much as 0.5 units was observed at the three sites. The pH cycle results from algal photosynthesis that lowers the partial pressure of carbon dioxide (pCO_2) during the day as shown by the correlation of pH maxima with light-intensity maxima (fig. D-14a), and diurnal variations of dissolved oxygen and calculated pCO_2. A diurnal cycle in dissolved arsenate was observed at the two downstream sites (figs. D-14b, D-15). The fluctuation in [AsO_4], with an amplitude as great as 40 percent, lags behind the cycle of pH fluctuation by several hours. The trend of increasing [AsO_4] with pH at these sites (fig. D-16) is consistent with the pH dependence of arsenate adsorption by iron oxyhydroxides (Pierce and Moore, 1982; Goldberg, 1986). Although a diurnal fluctuation in pH of 0.5 units also was observed at the upstream site, no significant variation in [AsO_4] was measured.

In determining the importance of adsorption-desorption processes in the diurnal cycle of dissolved As, an evaluation of the potential sources and sinks of dissolved As that contribute to the diurnal cycle (variation of 0.21 μmol/L/d (micromole per liter per day) in [AsO_4]) was made for the Sheeler Seep site (table D-5). Results of the bromide injection indicate a 4 percent increase in discharge along the reach that is attributed to ground-water inflow. This inflow also is evident from a constant increase in sulfate over the reach resulting from sulfate-enriched ground water discharging from the flood plain aquifers and the underlying shale. The average ground-water dissolved As concentration measured at this site (3.8 μM (micromolar)) and the results of As-Fe coprecipitation experiments

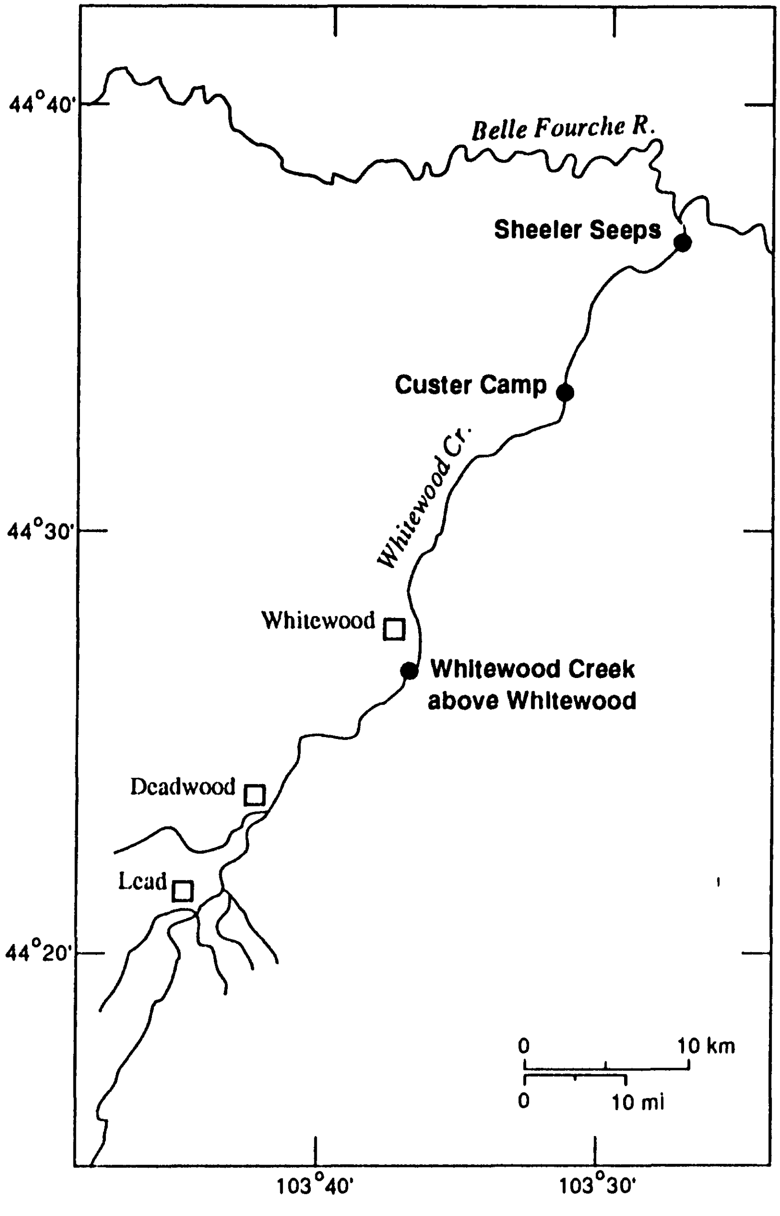

Figure D-13.—Location map.

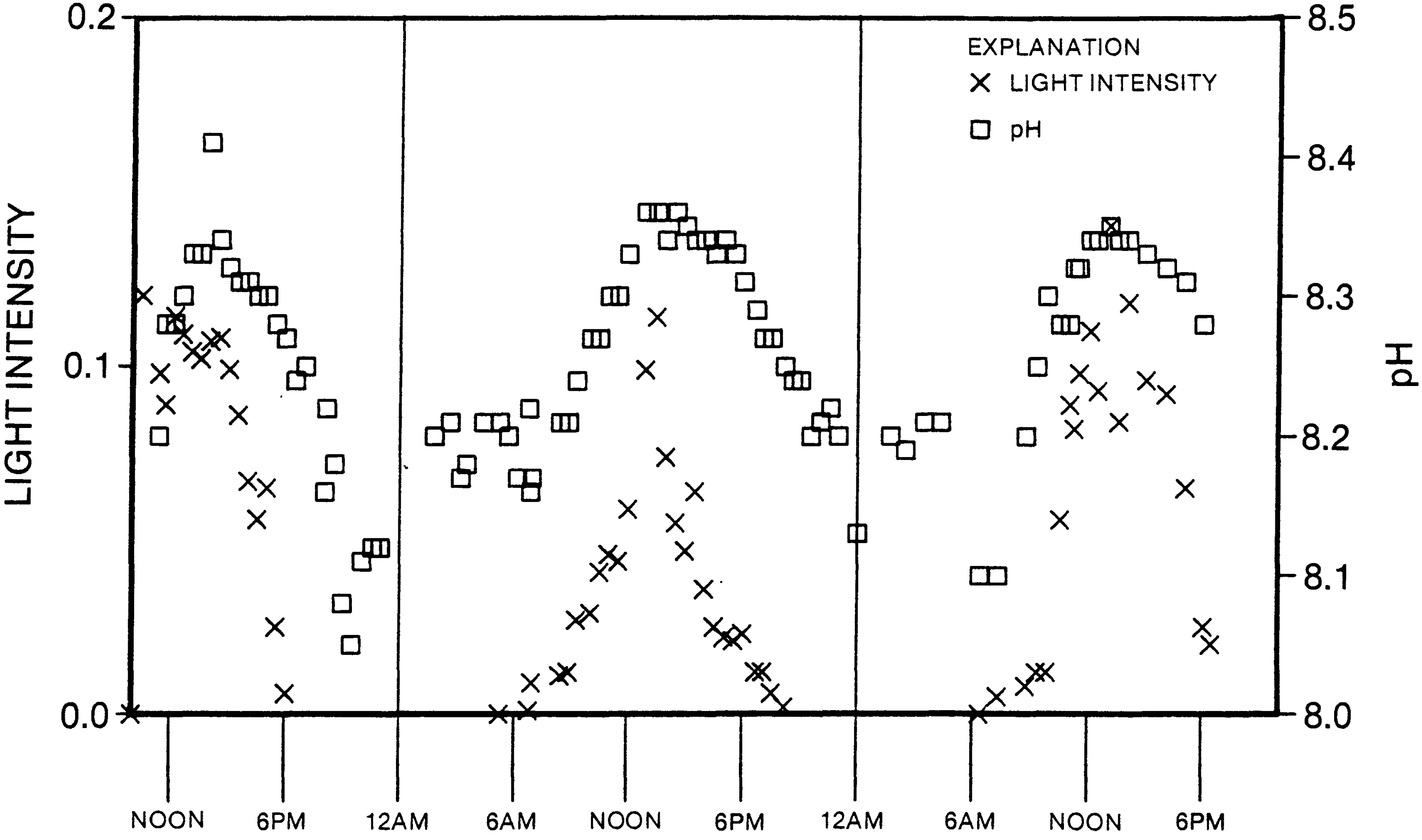

Figure D-14a. –Incident light intensity, in Einsteins per square meter per minute and stream pH versus time of day at Sheeler Seep site, August 11-13, 1987.

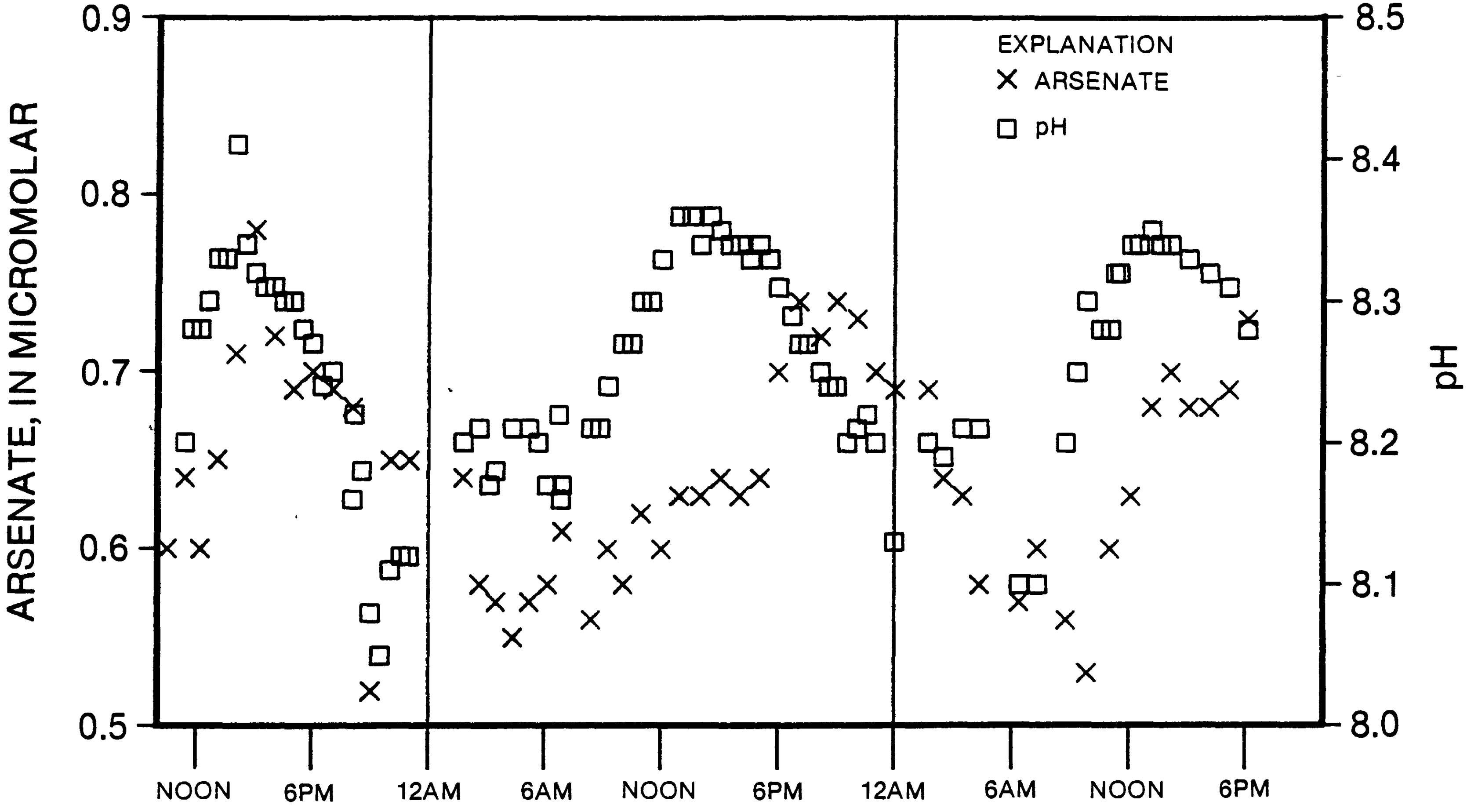

Figure D-14b. – Dissolved arsenate and pH versus time of day at Sheeler Seep site, August 11-13, 1987.

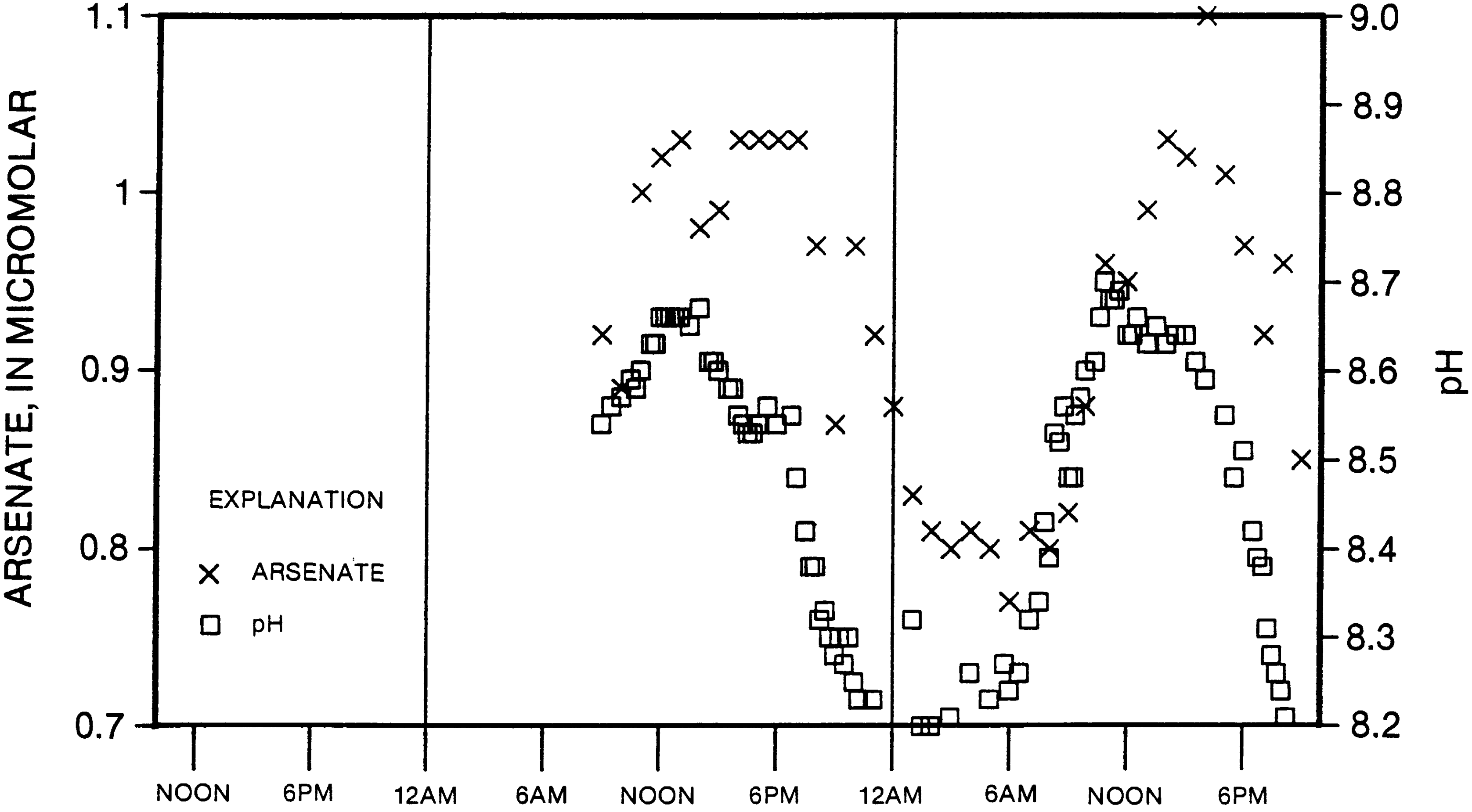

Figure D-15.–Dissolved arsenate and pH versus time of day at Custer Camp site, August 12-13, 1987.

Table D-5.–*Estimated sources and sinks of dissolved arsenic*

	Micromoles per liter per day
I. Ground Water Discharge	
A. no removal of As during iron precipitation:	+ 1.25
B. coprecipitation removes 92 percent As at pH 8.25:	+ .10
C. coprecipitation removes 90 percent As at pH 8.50:	+ .13
D. net As input over pH cycle	+ .03
II. Diffusive Flux from Sediments	+ .005
III. Aquatic Plant Uptake	
periphyton	- .033
IV. Desorption Potential from Suspended Sediments	+[1].006
V. Diurnal Fluctuation in $[AsO_4]$	.21

[1] Does not account for desorption on and in streambed sediments

(described below) were used to estimate a ground-water input of dissolved As to the stream of 1.25 μmol/L/d if there is no As removal during iron precipitation. Inputs of dissolved As of 0.10 and 0.13 μmol/L/d are estimated from laboratory data when uptake by coprecipitation with iron at pH 8.25 and 8.50, respectively, is accounted for and results in a net change in dissolved As input of 0.03 μmol/L/d during a pH cycle. A diffusive flux of dissolved As of 0.005 μmol/L/d is calculated from a porewater dissolved As of 4.7 μ mol/L/d (unpublished data on file with the Menlo Park office of the U.S. Geological Survey). This estimate is an upper limit because it does not account for As removal by adsorption near the sediment water interface and assumes that the streambed along the reach consists entirely of fine-grained reducing sediments. An uptake rate of $[AsO_4]$ in place of phosphate by periphyton (Andreae, 1978; Apte and others, 1986) of 0.033 μmol/L/d was calculated from the carbon fixation rate derived from the diurnal change in alkalinity (Stumm and Morgan, 1981), and the As to carbon (C) ratio, (As:C), measured in algal samples collected at this site 1 week before the diurnal sampling (J.S. Kuwabara, U.S. Geological Survey, written commun., 1988). The algal species present, *Cladophora* and *Ulothrix*, dominated the plant biomass. This estimate is an upper limit in as much as it assumes that the change in alkalinity is due only to photosynthesis. Assuming that this uptake of $[AsO_4]$ is directly correlated with phosphate uptake, which may be light enhanced (Stewart, 1974; Wetzel, 1975), biological uptake would diminish the observed diurnal fluctuation in $[AsO_4]$. The input of $[AsO_4]$ by desorption from suspended sediments of 0.006 mmol/L/d is estimated from the As concentration of suspended sediments (unpublished data on file with the Menlo Park office of the U.S. Geological Survey) and results of the As isotopic exchange study (described below). This estimate does not

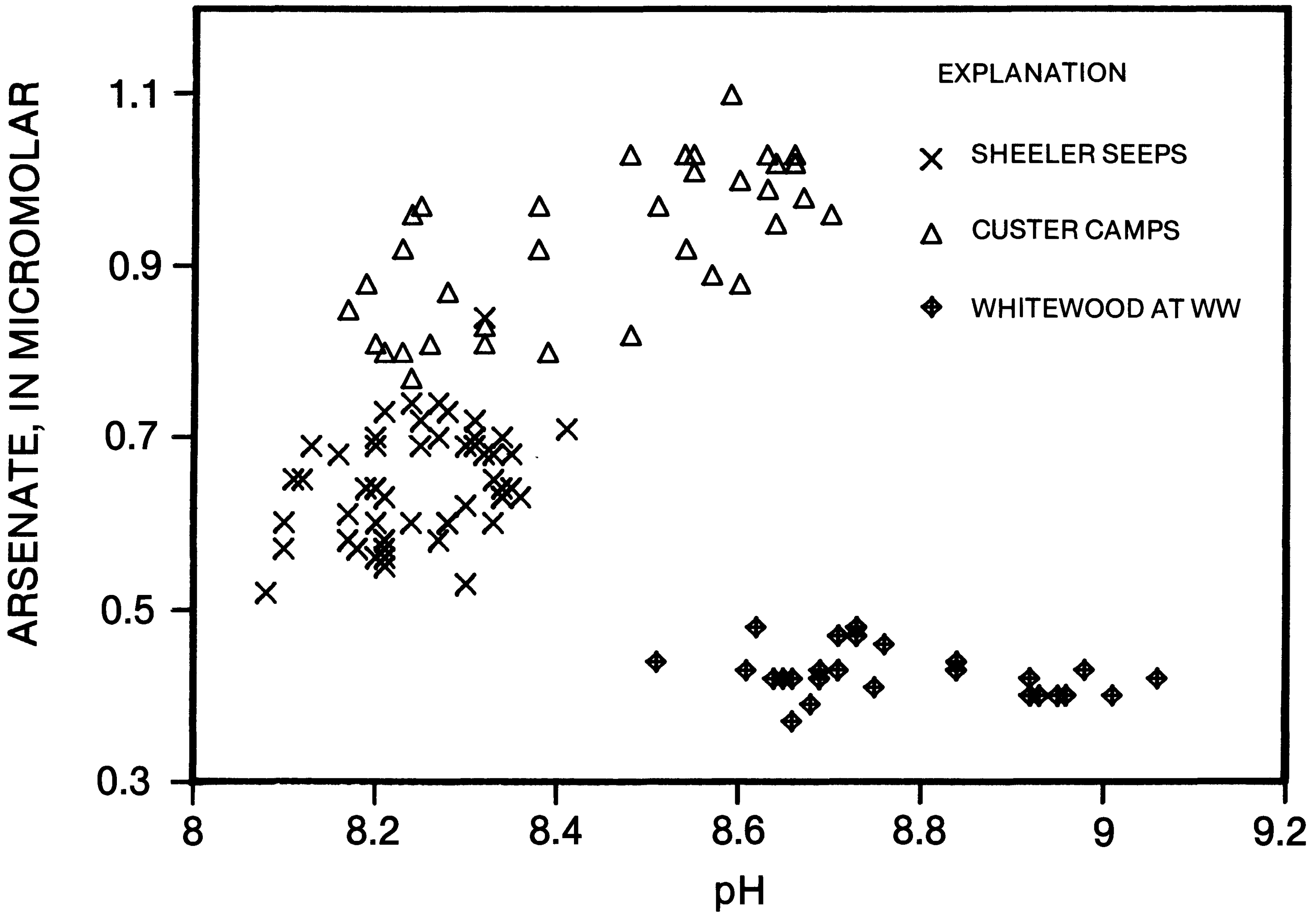

Figure D-16.—Dissolved arsenate versus pH in Whitewood Creek, August 11-13, 1987.

account for desorption of As in or on streambed sediments. Table D-5 summarizes these estimated sources and sinks of dissolved As. Comparision with the observed diurnal fluctuation in [AsO4] indicates that these processes are insufficient to result in the [AsO4] cycle.

Other physical and chemical processes, such as variation in stream discharge and ground-water inflow, may account for the [AsO4] fluctuation. The variations of [AsO4] measured along the 2.8-km reach (168-minute travel time) were within the range of [AsO4] in the concurrent diurnal sampling at Sheeler Seeps. These variations can be attributed to the increasing pH during the course of the sample collection. Thus, the diurnal cycle appears to occur throughout the reach. A variable, large, upstream point-source input cannot account for the observed cycle in [AsO4] inasmuch as the same cycle occurs concurrently at the two downstream sites more than 11 km apart. Coincident diurnal variations in both sulfate and the injected bromide observed at the diurnal sampling site suggest an increase in stream discharge from upstream sources that dilutes both constituents during the day rather than an increase in ground-water input along the reach at night. This fluctuation in discharge is insufficient to result in the observed diurnal variation in [AsO4] and, in addition, is out of phase with the [AsO4] cycle. Photoreduction of iron (McKnight and others, 1988) resulting in a release of its associated As was not evaluated because very low ferrous-iron concentrations suggest either rapid reoxidation and precipitation (with As coprecipitation) or negligible photoreduction. These estimates indicate that adsorption and desorption processes in response to the fluctuating pH must be largely responsible for the observed [As] variations, with ferrihydrite as the likely sorbent.

Laboratory sorption experiments were conducted to elucidate the role of surface chemical reactions of As with ferrihydrite in the partitioning of As in Whitewood Creek. The pH and time dependence of [AsO4] uptake by coprecipitation with iron was studied, as was adsorption and desorption as a function of time following pH changes. These experiments were conducted in an artificial stream water (ASW) of similar ionic composition and carbonate-buffering capacity as Whitewood Creek. In order to simulate ground water input to the stream, controlled additions of ferrous iron, Fe^{2+}, and [AsO4] (labeled with As-73) were made to the ASW to maintain a constant As:Fe molar ratio and to yield total concentrations measured in ground water (4 μM As and 200 μM Fe). The pH was held constant (+/-0.03 pH units) by acid and base additions with a pH controller.

Coprecipitation of As with Fe is rapid and is followed by constant [AsO4] concentration over the next 24 hours (fig. D-17). The magnitude of uptake by coprecipitation decreases with increasing pH and resulted in a linear increase in [AsO4] from pH 8.0 to 9.0 (data not shown). Upon an increase in pH of 0.5 units after 24 hours, release of [AsO4] to solution occurs over the next 4 hours followed by a slow release through 24 hours (fig. D-17). A similar two step-time dependence is observed for adsorption of [AsO4] back onto the ferrihydrite when the pH is lowered to its initial value at 48 hours. A hysterisis in [AsO4] was observed following adsorption and desorption in comparision to the initial uptake by coprecipitation. This may reflect differences in the properties of the ferrihydrite as a result of aging.

A study of [AsO4] uptake at pH 8.0 from filtered streamwater (collected at pH 8.4) onto ferrihydrite precipitates formed from ground water yielded a similar time dependence of uptake to that observed in the adsorption-desorption experiments. Following uptake, the reversible fraction of the sorbed As was estimated by As isotopic exchange. The exchange of As-73 with particle bound As occurs in two stages over time similar to that shown in figure D-17. From the uptake of As-73 after 96 hours, the calculated fraction of exchangable As (5 percent or 0.8 μM) is small compared to the total As. These data show that the arsenate sorption behavior with iron precipitates from the field is similar to that observed for laboratory-prepared ferrihydrite.

The results of these laboratory experiments are consistent with the diurnal fluctuations of [AsO4] observed in the stream. These data, along with the absence of other in-stream processes of sufficient magnitude to generate the observed cycle, provide strong evidence that the diurnal cycle in [AsO4] is

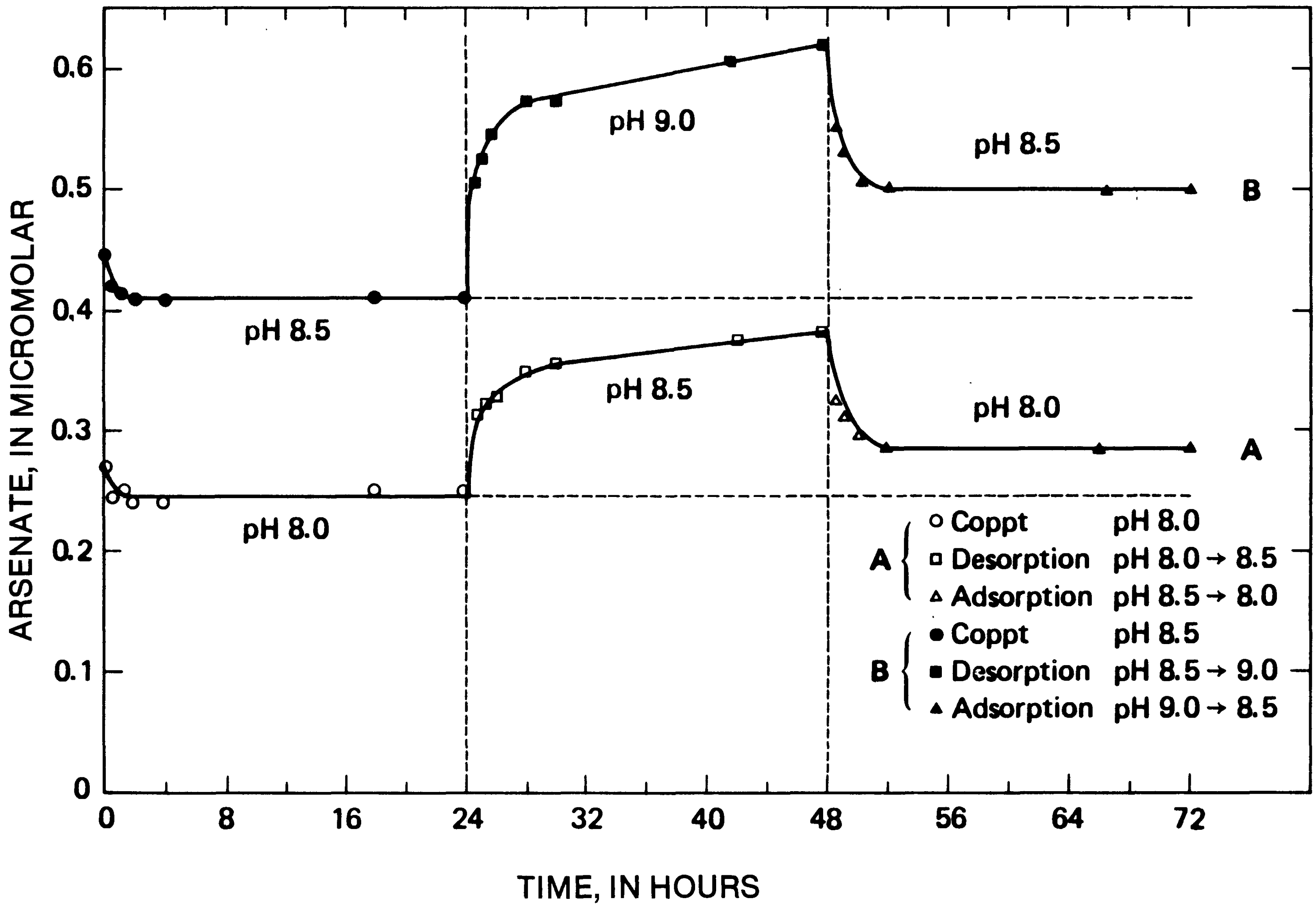

Figure D-17. –Dissolved arsenate versus time after coprecipitation with iron at pH 8.0 and 8.5.

the result of As adsorption-desorption processes on the surfaces of ferrihydrite. The reason for the absence of a diurnal cycle of $[AsO_4]$ at the Whitewood Creek at Whitewood site is not understood but may lie in the lack of a continuous source of As-rich ferrihydrite.

In summary, at the time of this study, dissolved As in Whitewood Creek is controlled primarily by adsorption and coprecipitation with ferrihydrite as reducing ground water containing dissolved As contacts the atmosphere and stream. Subsequent diurnal variations in $[AsO_4]$ result from shifts in the adsorption-desorption equilibrium in response to the biologically induced pH cycle. Kinetics of the adsorption-desorption processes cause the $[AsO_4]$ cycle to lag behind the pH cycle. Thus, the dynamic equilibrium of the chemical processes are tightly coupled to biological processes occurring in the stream. Continued laboratory studies on the processes and kinetics of As-Fe interactions are being conducted to enable further modeling of the field observations and to determine the mechanisms of the interactions. Evaluation of the occurrence of diurnal pH cycles in other natural waters and their effect on the partitioning of metals and other toxic substances need to be made.

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PERIPHYTON EFFECTS ON ARSENIC TRANSPORT IN WHITEWOOD CREEK, SOUTH DAKOTA

By James S. Kuwabara[1], Cecily C. Y. Chang[1], and Sofie P. Pasilis[1]

ABSTRACT

Increased periphyton abundance in Whitewood Creek, South Dakota, during the summer months suggests that chemical interactions involving arsenic and phosphorus between biota and the overlying water may significantly affect As transport and distribution in this mining-affected stream. Data used to predict arsenic transport for algae (for example, first-order uptake-rate constants, standing crop and accumulation factors) collected in the creek from upstream of mine discharge through a 57 kilometer affected reach have been determined. Cultures of Achnanthes minutissima (Bacillariophyceae) were isolated from four sites along a longitudinal gradient of dissolved arsenic within the study reach and then maintained at ambient dissolved arsenic concentrations. Arsenic uptake-rate constants for these isolates were determined as a function of dissolved arsenate and orthophosphate. All isolates appeared to have some exclusion mechanism by which phosphate was preferentially taken up over arsenate or by which excessive cell-associated arsenic was released. Initial uptake of both arsenate and orthophosphate appear to follow first order kinetics closely. Although uptake-rate constants increased slightly with increased dissolved arsenate concentrations, algae isolated from a site with elevated dissolved arsenic showed a significantly slower arsenic uptake relative to the same species isolated from the least contaminated site upstream. Over a 4-month sampling period during the summer of 1987, periphyton abundance increased downstream, then abruptly decreased at the site farthest downstream. Dissolved arsenic, temperature, physical substrate, and turbidity may explain these trends in periphyton standing crop.

INTRODUCTION

Biological processes can play an important role in the transport of reactive solutes in streams (Kuwabara and Helliker, 1988). For example, solute uptake by organisms may retard downstream transport, whereas metabolic reactions may result in a change in chemical speciation of that solute resulting in a change in its surface activity and transport behavior. The effects of these biological processes are difficult to quantify because characteristics of the benthic and planktonic communities may change dramatically temporally and spatially. These changing characteristics may influence, and be affected by, interacting chemical and hydrologic processes. Attempts to model the role of periphyton effects on arsenic (As) transport within an aquatic environment are complicated by a number of factors: (1) arsenate inhibits the growth of certain algal species at submicromolar concentrations, presumably because of interference with phosphate metabolism (Button and others, 1973; Sanders, 1979); (2) the effects of As speciation on uptake rates and periphyton concentration factors is not well known; (3) the manner in which prolonged exposure to elevated As concentrations affects metabolic reaction rates is not well understood; and (4) understanding the effects of physical and chemical factors (for example, light intensity and surface reactions with inorganic particles) is only now being developed. This paper presents results of a field and laboratory study that estimated As transport characteristics for periphyton along a mining-affected reach of Whitewood Creek, S. Dak., under various dissolved arsenate and orthophosphate concentrations. A first-order rate equation was assumed for this periphyton component.

Whitewood Creek (lat. 44°30′ N. long. 103°45′ E., fig. D-18), which is a perennial, snow-fed stream within the Black Hills of South Dakota, has served since 1876 as the receiving water for effluents from gold mining and municipal activities (for example, sewage treatment and power-generator cooling). Four sites along the creek were

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

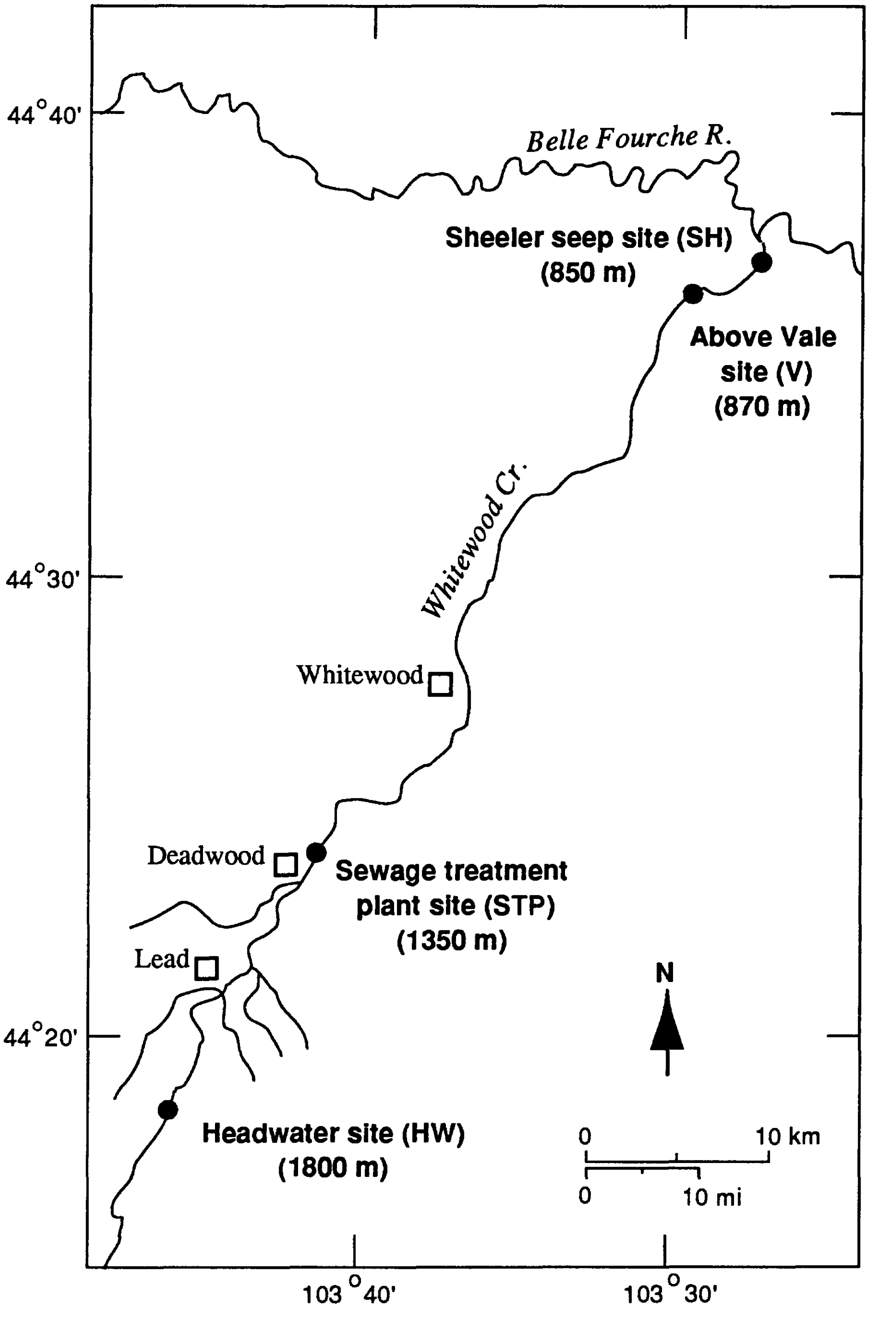

Figure D-18.–Map showing locations of sampling sites for this study (as filled in circles), and neighboring towns (marked by squares.)

selected for this study upstream from the mining activities to approximately 1-km (kilometer) upstream from the confluence of Whitewood Creek and the Belle Fourche River (fig. D-18). Although direct discharge of mine tailings into the creek ended in 1977, residual mine tailings form most of the bank and bottom sediment material over the 57-km study reach. These tailings contribute to a dissolved-As concentration gradient that increases in the downstream direction. Conversely, inputs of phosphorus (P) and other macronutrients from a sewage-treatment facility, at Deadwood, provides a dissolved P gradient that decreases in the downstream direction, except in downstream (arable) areas where irrigation waters from fertilized soils intermittently flow into the stream. Each year after snowmelt, a dense community of attached algae and submerged macrophytes quickly forms. A dense cover remains through the summer months. Coincidentally, peak dissolved As concentrations in the streamwater occur during the summer at downstream sites, possibly because of (1) a periphyton driven, diurnal pH fluctuation that causes release of particle-bound As; and (2) summer inputs of ground water that contains elevated dissolved As concentrations (Fuller and others, 1988, Goddard and others, 1988). The study reach, therefore, represents ideal field conditions for the examination and quantification of potentially important contributions of the periphyton to As mobilization and transport.

C.B. Hellquist of North Adams State College in North Adams, Mass., and R.L. Wong are gratefully acknowledged for taxonomic analyses of submerged macrophytes and benthic algae.

EXPERIMENTAL PROCEDURE

The experimental approach involved determination of As transport characteristics for algae and macrophytes collected at four sampling sites (fig. D-18): (1) a site 7 km upstream from the mining activities (1,800 meters elevation); (2) 15 km downstream from the first site and within the town of Deadwood (0.25 km downstream from treament plant discharge, 1,350 meters elevation); (3) 39 km farther downstream at a U.S. Geological Survey gaging station (870 meters elevation); and (4) approximately 1 km upstream from the confluence of Whitewood Creek and the Belle Fourche River (850 meters elevation). These sites are hereafter referred to as the Headwater (HW) site, the Sewage Treatment Plant (STP) site, the Whitewood above Vale (V) site, and the Sheeler Seep (SH) site, respectively (Kuwabara and others, 1988). Abundant ground-water seepage occurs as springs along the banks of the creek at the farthest downstream site.

Transport characteristics estimated include standing crop (ρ_b) or the accessible periphyton mass per unit streambed area, net sorption rate constant (λ_b), and accumulation factor (that is, biological partitioning coeffient, K_b), and may be used to describe a biological component of a comprehensive transport model describing hydrologic, chemical and biological processes. Assuming a first-order process, the rate of change of dissolved As resulting from periphyton accumulation would take the form:

$$(\rho_{b_j}/D_j)R_{b_j} = -(\rho_{b_j}/D_j)(\partial C_{b_j}/\partial t) =$$
$$-\lambda_{b_j}(\rho_{b_j}/D_j)(C_{b_j}-K_{b_j}C_j),$$

where the index j is a finite interval of the stream reach, D is the mean interval channel depth, R_b represents the temporal change in solute concentration associated with the periphyton (C_b), and C is the solute concentration in the stream as a function of time (t).

The As uptake by algal cells was studied in laboratory experiments as a function of dissolved arsenate and orthophosphate concentrations in media formulations. Unialgal cultures of the diatom*Achnanthes minutissima* (Kuetzing) Cleve collected along the study reach were used to determine uptake-rate constants. After isolation in liquid media and enriched agar plates, algal stocks were maintained in chemically defined media with added arsenate and orthophosphate concentrations similar to ambient levels at the sampling sites. *A. minutissima* was among the few species isolated from all four sites. *Stichococcus spp.* and *Scenedesmus spp.* also were isolated from all four sites and used in preliminary studies but were not as easily enumerated with the particle counter used because of the frequent formation of doublets and cell chains. Arsenate and phosphate uptake rate constants were determined from ^{73}As and ^{32}P-labeled experiments using cells, heat killed as described by Fisher and others (1984). Previous experiments (Kuwabara and others, 1988) indicated that use of heat-killed cells for short-term As and P uptake experiments yielded results comparable to living-cell cultures and avoided the need for biomass corrections. A 3^2 full-factorial experimental design (n (number of treatment replicates) = 3) was used to examine the interactive effects of As and P on uptake rates and accumulation of these solutes using *A. minutissima* isolates from the HW and above V sites. Results presented here consider only results of As uptake in these experiments. ^{73}As and ^{32}P-labeled stock solutions were used to achieve 0.0, 0.5, and 1.0 μM (micromolar) initial concentrations of dissolved As and P in the nine chemically defined media formulations. An inoculum of heat-killed cells was then added (10^6 cells per milliliter). After periods of 0.5, 1, 2, 4, 8 and 24 hours aliquots of the cell suspensions were centrifuged at 13,000 r/min (revolutions per minute) for 15 minutes. The supernatant was then removed and counted by liquid scintillation to determine solute removal from solution by the cells.

Periphyton abundance (ρb) at each of the four sites was estimated monthly from late May to September 1987, using ash-free dry weight and chlorophyll-a measurements (n = 9) of measured streambed areas (Franson, 1985). Measurements of channel width (n = 3), depth (n = 9) and channel velocity (n = 9) were made at all sites, as were temperature, specific conductance, dissolved oxygen and pH (table D-6). Arsenic concentrations in dominant periphyton species were determined by hydride generation, atomic absorption spectroscopy (Johns and Luoma, 1988).

RESULTS

Temporal changes in periphyton abundance differed among sites. As observed in the 1986 samples (Kuwabara and others, 1988), periphyton mass per unit streambed area generally increased with distance downstream from the HW site to the V site and then decreased abruptly at the most downstream (SH) site (table D-6). At the HW site, which was dominated throughout the summer by a submerged macrophyte (*Ranunculus longirostris*), biomass slightly increased from an average of 37 g/m^2 (grams per square meter) in late May to 60 g/m^2 in September (table D-6). Monthly differences were, however, not significant at the 95-percent confidence level (table D-6). The large confidence intervals relative to average ρ_b values, even with nine replicates per site, is indicative of a patchy periphyton distribution. At the STP site, a community dominated by *Ranunculus* during June and July gradually changed to a dense growth of the pondweed *Zannichellia palustris* and the chlorophytes *Cladophora spp* and *Ulothrix spp.* during August and September. Similar to the HW site, monthly standing crop values were not statistically different (table D-6). Because of high-flow conditions, periphyton growth was not established at the V site during the first sampling period in June. However, by July, a thick (approximately 20 cm (centimeters)) mat of *Ranunculus* and epiphytic diatoms blanketed more than half of the stream channel. As at the STP site, August and September samples showed a shift toward *Zannichellia* and filamentous chlorophyte species at the V site. Once the periphyton was established, standing crop was clearly most abundant at the V site, where estimated biomass was an order of magnitude higher than at other sites. Elevated stream discharge in late May also inhibited the establishment of a periphyton community at the SH site, but *Zannichellia* was observed in abundance by July under much lower flow conditions (table D-6). Epiphytic diatoms and filamentous chlorophytes dominated periphyton communities in August and September samples. Standing crop was consistently lower at the SH site than the other three upstream sites.

Autotrophic indices (AI, mass ratios of periphyton dry weight to chlorophyll-a) ranged from 80 at the SH site in July to 310 at the V site in September (table D-6). Tabled values represent the mean of three replicates with 95-percent confidence intervals consistently less than 10 percent of the mean. This index has been used as an indicator of environmental stress, whereby increasing values indicate increasing abundance of senescent or stressed cells or an increasing proportion of heterotrophic growth (Weber, 1973). All four sites in late May and July displayed AI values typical of unstressed periphyton communities (approximately 100 ± 50), whereas elevated values were measured at the V and SH sites in August and at the HW, V, and SH sites in September.

The arsenic concentrations in algal tissues consistently increased between the late May and August sampling dates at all four sites (table D-7). Concentrations observed in August and September samples were similar or showed a decrease in September. There was also a discernible increase in tissue As concentrations with distance downstream. However, the range of

Table D-6.—*Field data collected monthly during the summer of 1987 from four sites along Whitewood Creek, South Dakota: Headwater (HW), Sewage Treatment Plant (STP), Above Vale (V), and Sheeler Seep (SH) sites*

[Measured characteristics include: specific conductance (COND, in microsiemens per centimeter at 25 degrees Celsius), water temperature (TEMP, in degrees Celsius), pH, stream channel width (W, in meters) with 95-percent confidence interval (n = 6), mean channel depth (D, in meters) with 95-percent confidence interval (n = 9), mean velocity (V, in meters per second) with 95-percent confidence interval (n = 9), calculated mean discharge (Q, in cubic meters per second), standing crop (ρ_b, in grams dry weight per square meter) with 95-percent confidence interval (n = 9) and autotrophic index (AI, grams ash-free dry weight per gram chlorophyll-a). Sampling times are given in military format. The symbol "-" in the ρ_b or AI column indicates that the periphyton community at that site had not yet been established]

DATE	TIME	SITE	COND	TEMP	pH	W	D	V	Q	ρ_b	AI
5/27	930	HW	420	8.2	8.3	2.6±0.1	0.12±0.05	0.82±0.02	0.3	37±15	120
5/27	1430	STP	545	15.2	8.1	7.7± .5	.38± .09	.94± .12	2.8	34±17	110
5/28	1300	V	890	18.4	8.2	21.6±1.6	.35± .12	.30± .11	2.3	-	-
5/28	1550	SH	980	20.0	8.2	3.9± .4	.38± .15	.77± .20	1.1	-	-
7/7	1255	HW	450	16.0	8.3	2.4± .3	.10± .02	.58± .10	.1	52±19	110
7/8	1040	STP	760	17.0	8.4	7.3± .5	.24± .04	.74± .11	1.3	71±51	120
7/9	1300	V	1180	21.5	8.6	17.9± .7	.05± .02	.39± .14	.4	469±65	90
7/10	1610	SH	1310	28.0	8.6	3.4± .5	.24± .11	.86± .16	.7	28±5	80
8/19	940	HW	429	9.0	8.7	2.5± .3	.15± .03	.51± .16	.2	51±27	140
8/19	1300	STP	899	17.6	8.3	7.1± .3	.23± .06	.65± .19	1.1	54±19	100
8/26	1400	V	1108	17.0	8.0	18.0± .5	.21± .18	.13± .03	.5	280±30	180
8/26	1015	SH	1245	14.5	8.1	3.6± .3	.27± .04	.72± .20	.7	29±14	160
9/16	1315	HW	563	11.1	8.3	1.7± .2	.10± .02	.25±0.05	.1	60±34	170
9/16	1730	STP	930	16.8	7.9	6.5± .7	.19± .04	.53±0.07	.7	82±60	120
9/28	1745	V	1167	18.3	8.1	17.8± .8	.33± .06	.07±0.01	.4	237±25	310
9/28	1435	SH	1222	19.5	8.3	3.7± .4	.24± .05	.46±0.09	.4	7±4	280

concentrations observed during the growth period at the upstream (HW) site was much greater than that observed at the downstream sites (table D-7). Arsenic in submerged macrophyte tissue was slightly higher than found in the macroalgae although general concentrations trends at each site were very similar between plant groups (table D-7).

Short-term uptake-kinetics experiments using *A. minutissima* indicate that a first-order rate equation closely describes the observed algal uptake of arsenate. Fit of the kinetic data for both HW and V isolates at the nine treatment combinations to a first-order model (Dixon, 1985) yielded consistently high coefficients of determination (table D-8). Uptake rate constants were significantly increased by elevating dissolved arsenate concentrations. A comparison of rate constants for HW and V isolates shows significantly lower constants for the apparently As-tolerant V isolate. The accumulation of As by both isolates was inhibited by increasing orthophosphate concentrations. The V isolate had slightly lower K_b values than did the HW isolate. Increasing dissolved arsenate concentrations in the media did not result in a corresponding increase in biologically sorbed As (note in table D-8 that the K_b values significantly decreased at higher dissolved As concentrations).

Table D-7.—*Total arsenic concentrations (microgram solute per gram dry tissue) with 95-percent confidence intervals (4 replicates) in dominant periphyton species collected from four sites along Whitewood Creek, South Dakota*

[The headwater and most upstream site (HW), sewage treatment plant site (STP), above Vale site (V) and Sheeler seep site (and most downstream sampling site for this study, SH). Symbol "-" indicates that the periphyton community had not yet been established at that site]

	Date (month/day/year)			
Sampling site	5/27-28/87	7/7-10/87	8/19-26/87	9/16-28/87
HW - Macroalgae[1]	1,465 ± 38	1,633 ± 33	1,884 ± 43	1,931 ± 50
- Macrophyte[2]	1,552 ± 16	1,866 ± 9	2,180 ± 52	1,991 ± 83
STP - Macroalgae	1,709 ± 22	1,819 ± 31	1,903 ± 18	1,933 ± 50
- Macrophyte	1,757 ± 14	1,971 ± 8	2,030 ± 49	2,099 ±112
V - Macroalgae	-	2,051 ± 45	2,151 ± 15	2,117 ± 94
- Macrophyte	-	2,390 ± 8	2,479 ± 39	2,184 ± 95
SH - Macroalgae	-	2,358 ± 91	2,418 ± 24	2,317 ±189
- Macrophyte	-	2,480 ± 16	2,572 ± 42	2,352 ± 23

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[1] Samples dominated by filamentous chlorophytes and epiphytic diatoms. Specific changes in community structure are described in the text.

[2] Early summer samples typically dominated by the submerged macrophyte, *Ranunculus longirostris* and associated algal epiphytes, whereas later samples commonly dominated by the pondweed, *Zannichellia palustris*. Specific changes in dominant macrophyte species are discussed in the text.

Table D-8.—*Results from experiments examining arsenate uptake by Achnanthes minutissima isolates from the Headwater site (HW, low (less than 0.1 micromolar) dissolved arsenic exposure) and the above Vale site (V, elevated (approximately 1 micromolar)* dissolved arsenic exposure)

[Uptake rate constants (λ_b, in reciprocal hours) and accumulation factors (K_b, ratio of micromoles solute per gram algae to micromoles solute per gram media). Confidence intervals (95 percent) reflect the multivariate regression from a 3^2 full factorial design (n = 3) sampled at elapsed times of 0.5, 1.0, 2.0, 4.0, 8.0 and 24.0 hours after inoculation. The coefficients of determination (r^2) are given for a fit of the kinetic data to a first order model (Dixon, 1985). Details of the experimental design are provided in the text]

Treatments		Transport characteristics		
(Micromolar solute added)				
As	P	λ_b	K_b	r^2
HW isolates				
0.5	0.0	0.73 ± 0.08	1,790 ± 70	0.96
5	.5	.56 ± .08	1,340 ± 90	.92
.5	1.0	.94 ± .13	990 ± 50	.92
1.0	.0	1.08 ± .11	990 ± 20	.96
1.0	.5	1.37 ± .22	800 ± 30	.90
1.0	1.0	1.77 ± .17	500 ± 30	.84
V isolate				
.5	.0	.39 ± .02	1,750 ± 30	.99
.5	.5	.48 ± .06	1,240 ± 30	.98
5	1.0	.57 ± .07	960 ± 30	.99
1.0	.0	.74 ± .08	870 ± 30	.98
1.0	.5	.81 ± .11	630 ± 30	.94
1.0	1.0	1.09 ± .19	500 ± 20	.97

DISCUSSION

Inhibition of As uptake with increasing dissolved orthophosphate concentrations that was observed for the freshwater diatom *A. minutissima* is an interesting, but not surprising observation. Preferential uptake of P over As previously has been reported for chlorophytes (Kuwabara and others, 1988) and for marine diatoms (Morris and McCartney, 1984). In contrast, Button and others (1973) found that the yeast *Rhodotorula rubra* sorbed P and As indiscriminately. Although the exclusion mechanism for the test algae reported on here has not been identified, uptake results from the HW site isolate suggest that the mechanism is not acquired by prolonged As exposure.

Differences between algal isolates in As uptake and accumulation suggest that *A. minutissima* from the V site exhibited As tolerance in two ways. First, this isolate accumulated slightly less As than did controls (the HW isolate). Secondly, the V isolate consistently demonstrated slower As sorption kinetics than did the HW isolate. Both observations represent distinctive advantages for cells exposed to elevated and fluctuating dissolved As concentrations.

Increasing algal abundance with distance downstream may be attributed to inputs of macronutrients from the water-treatment-plant effluent, ground-water inputs, and irrigation runoff from fertilized land. In addition, temperature effects on algal growth rates may contribute to the downstream increase in algal abundance (table D-6). At the SH site, decreased abundance may be caused by scarcity of firm substrate needed to establish a dense algal community. Visibly high turbidity also may hinder photosynthetic activity at this site. Although periphyton growth was patchy, especially at the SH site, replicate ash-free, dry-weight measurements indicated similar biomass concentrations within the patches.

Elevated AI values, particularly at the V and SH sites in August and September 1987, suggest an adverse change in the condition of the periphyton community. Senescence of periphytic tissue was visibly evident in these samples and probably represents typical growth progression within these mats. It is interesting to note that the elevated AI observed in August 1986, at the STP site (Kuwabara and others, 1988) was not observed in 1987, probably because of a shift in community structure of periphyton at the STP site in 1987 to include new growth of *Z. palustris* and various filamentous chlorophytes.

It is clear from these studies that algal isolates from Whitewood Creek have the ability to take up orthophosphate over arsenate preferentially. Given the As transport characteristics reported here for *A. minutissima*, the rapid growth of periphyton biomass between late May and July at the V and SH sites represents both a rapid and significant accumulation of As (table D-7) within this single biological component. Furthermore, *A. minutissima*, which was exposed to elevated concentrations of dissolved As, seems to be able to slow down the kinetics of cellular As uptake. In view of the above observations, the limitations of these results are equally clear. The trends in the transport characteristics presented above pose a number of additional complex questions related to the modeling of periphyton effects on stream transport of As: (1) What causes large annual variations in community structure of the type seen between 1986 and 1987 samples? (2) How do solute sorption processes differ between the algae and submerged macrophytes seen in abundance in 1987? (3) How does the state of the periphyton affect As uptake and accumulation (that is, what other physical and chemical perturbations that account for changes in observed autotrophic indices, in addition to elevated orthophosphate concentrations, affect As uptake)? (4) How long does it take for periphyton species to adapt to ambient As concentrations by way of changing uptake characteristics?

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(p.257 follows)

TEMPORAL AND SPATIAL VARIABILITY OF ARSENIC IN BENTHIC INSECTS FROM WHITEWOOD CREEK, SOUTH DAKOTA

By Daniel J. Cain[1], Steven V. Fend[1], and James L. Carter[1]

ABSTRACT

Whole body concentrations of arsenic were determined for benthic insects in Whitewood Creek, a stream contaminated with arsenic-bearing tailings from mining operations near its headwaters. Insects were collected in late May through early June of 1986 and 1987. Arsenic concentrations in insects appeared greater in 1987 than in 1986 at a station in the lower reach of the stream, but not at a station directly below the mine. Small differences in arsenic concentration between years also were evident in some taxa at a station above the mine. Although substantial differences in arsenic concentrations among taxa within stations were apparent, arsenic in all taxa collected from the contaminated reach was greater than in taxa from uncontaminated stations. Arsenic in Hydropsyche spp. and Baetis tricaudatus generally reflected the total arsenic concentrations of sediments. Trophic level and size appeared to be important variables affecting arsenic concentrations in insects. Results of experiments where insects were transferred from uncontaminated stations to a contaminated station showed that arsenic accumulation in herbivores and omnivores was more rapid than in predators. However, data indicate that nonspecific sorption of arsenic to the exoskeleton also contributed substantially to the total arsenic body burden.

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INTRODUCTION

The determination of elemental concentrations in tissues of organisms is now a widely accepted and extensively applied technique to quantify contaminants in aquatic systems. Analysis of organisms complements direct measures of abiotic components of the system--that is, water and sediment--and unlike those analyses provides a measure of the biologically available concentration of a contaminant. Some variables, both biotic and abiotic, can affect contaminant concentrations in organisms, and these variables need to be considered to assure that results obtained from bioindicators accurately reflect trends, both spatial and temporal, in the bioavailability of contaminants. These variables have been discussed in detail by Phillips (1980).

The emphasis in aquatic biological monitoring has grown principally in the direction of its application to the marine and estuarine environments. As a result of this effort, certain species (for example, the mussel *Mytilus edulis*) were selected to monitor contamination over wide geographic areas (Goldberg and others, 1978). In freshwater, the development of indicator organisms, particularly for application over wide spatial scales, has progressed more slowly. However, the growing concern over the quality of surface waters clearly underscores the need to apply this technique to these systems.

The findings of a 2-year study that evaluates benthic insects as indicators of arsenic (As) contamination are reported in this paper. The study was conducted in 1986 and 1987 on Whitewood Creek and the Belle Fourche River, S. Dak. (fig. D-19). Whitewood Creek is a small, perennial stream located in the southwesten part of the State. The stream has been heavily impacted by the discharge of tailings from gold mining operations near its headwaters at Lead, S. Dak. (Goddard, in press). Between 1870 and 1977, when this method of disposal ceased, approximately 100 million Mg (megagrams) of material was discharged into Whitewood Creek. The tailings material, which contains large quantities of arsenopyrite (FeAsS), has been transported downstream. Some of these

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

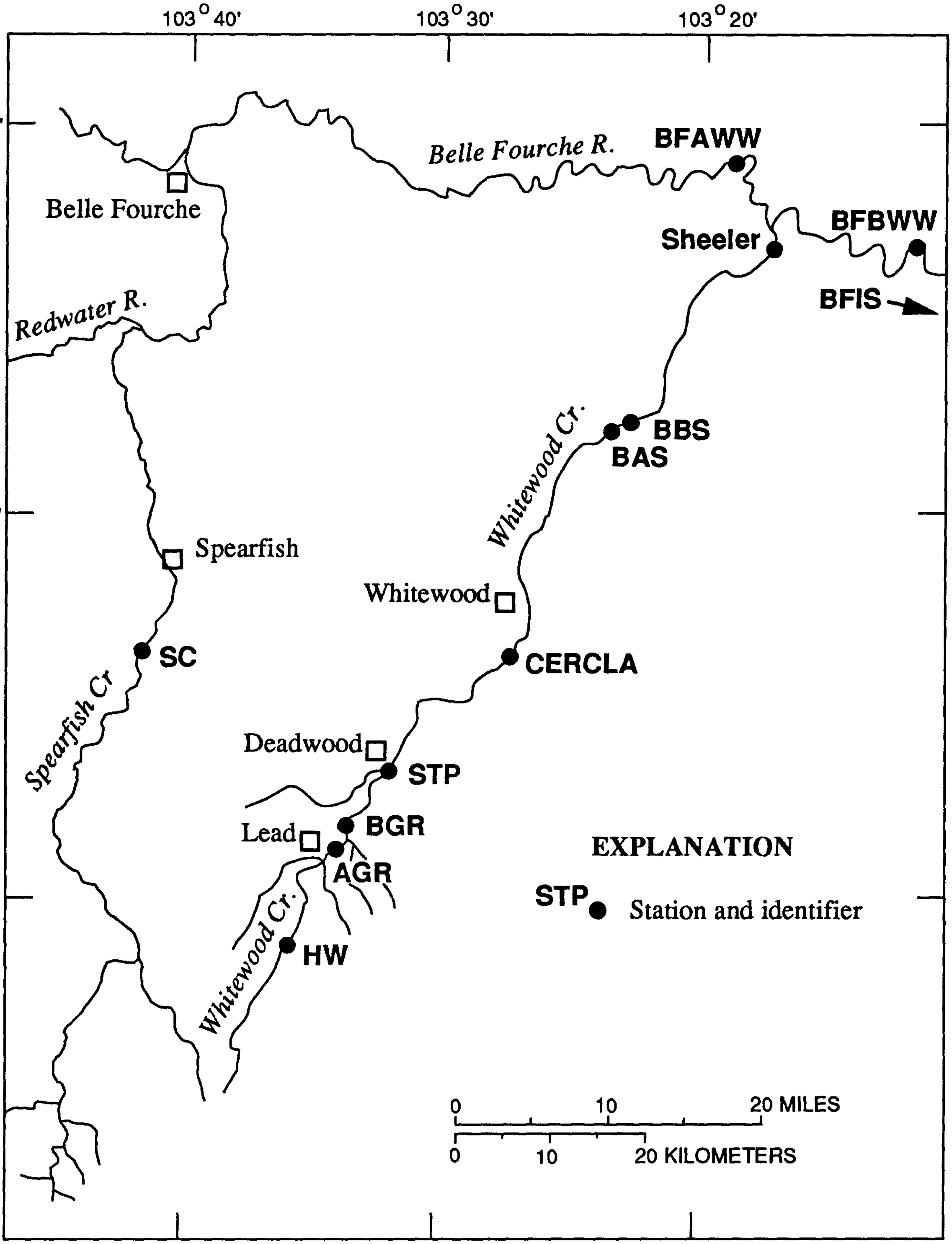

Figure D-19.—Map showing location of stations sampled in 1986 and 1987.

materials are now stored in overbank deposits along Whitewood Creek, the Belle Fourche River, and the Cheyenne River. Dissolved As and ferrous iron (Fe^{2+}) enter Whitewood Creek with ground water that seeps from these contaminated alluvial sediments (Cherry and others, 1986; Fuller and others, 1988). Subsequent oxidation has resulted in the formation of As-enriched Fe-oxide deposits along the streambed (Fuller and others, 1987).

Analysis of samples collected in June 1986 indicated that all insect species within the contaminated sections of Whitewood Creek and the Belle Fourche River have elevated As concentrations (Cain and others, 1987). Concentrations were specific to insect species, and downstream trends were difficult to evaluate because of the discontinuous distribution of species. Data also indicated that sorption of As to the exoskeleton may be an important mechanism of accumulation in benthic insects in this system. Additional sampling was done in 1987 to ascertain the degree of interannual variability in As concentration of benthic insects. Differences in As bioaccumulation among species and its relation to trophic level and taxonomic relation were further examined. The spatial variability in As concentration in specific taxa were assessed relative to the As concentrations of sediments.

MATERIALS AND METHODS

Biological Samples

The locations of stations where benthic insects were collected in 1986 and 1987 are shown in figure D-19. (Appendix 1 gives a complete listing of station names.) Samples were collected at ten stations in 1986 (Cain and others, 1987). Four of these stations were sampled again between May 27 and June 1, 1987 (HW, BGR, CERCLA, and BBS). Additionally, three new locations, stations AGR, BAS, and SC, were sampled in 1987. Only the data from these seven stations are presented in this paper. The approximate locations of stations AGR and BGR are, respectively, 1 km (kilometer) above and 150 meters below Gold Run Creek, the historical point of tailings discharge into Whitewood Creek. Station BAS is approximately 100 meters above a site where ground water seeps into Whitewood Creek. Samples also were collected within the plume of this seep which was visible by the Fe-oxyhydroxide deposition at station BBS. Two stations, Headwater of Whitewood Creek (HW) and Spearfish Creek (SC) were outside the area affected by tailings from the mine at Lead, and thus served as background stations.

Specimens of all species that were collected were temporarily preserved in formalin and then permanently transferred to 85 percent ethanol for taxonomic identification. Insects collected for As analysis were sorted initially, on site, by taxon at the levels of order and family. They were kept in nonaerated streamwater in plastic bags that were placed on ice for about 6 hours to allow some cleaning of their digestive tracts and then frozen. In the laboratory, the samples were thawed and further sorted to the family, genus, and species level. Identifications were based on the samples permanently preserved in ethanol. Within each taxonomic group, individuals of similar size were pooled into samples to attain sufficient biomass (approximately 100 mg (milligrams) dry weight) for As determinations. The samples were homogenized, lyophilized, ashed, and analyzed for As by hydride-generation atomic absorption spectroscopy. The analytical accuracy was verified by routinely analyzing National Bureau of Standards reference material 50 (albacore tuna).

Sediments

Streambed sediments were collected with a polypropylene scoop from shallow water along the left and right edges of the stream and composited into a single sample. The first 5 to 10 mm (millimeters) of surficial sediment was carefully removed and then sieved with streamwater through a 63-micrometer nylon screen into acid-washed polypropylene jars. Sediment was allowed to settle for 24 hours and then water was decanted and the sediment stored frozen until analysis. The total As concentration of samples was determined by dissolution of the sample in a hydrofluoric-perchloric acid mixture. Aliquots of the sample solution were first passed through an ion-exchange resin to remove aluminum then analyzed by inductively coupled plasma spectrometry (Moore and others, 1988).

Transfer Experiment

In a separate experiment, insects from stations HW and SC were transferred to the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) station to assess rates of As accumulation within the contaminated zone of Whitewood Creek. Specimens of *Hesperophylax occidentalis* were collected from station HW, and *Hydropsyche oslari, Hesperoperla pacifica,* and *Rhyacophila* sp. were collected from SC. These taxa were selected because they were relatively large, abundant at the control stations, and represented different trophic levels. At each control station, the collected specimens were separated into three equal groups. One group was immediately processed for the determination of As, following the procedure described above, to establish the As concentrations of these taxa at the control stations at the start of the experiment (0 hours). The other two groups were sealed into separate plastic (nitex), 500 μ (micron) mesh bags. One bag was returned to the control stream for the duration of the experiment to determine if being held in the bag affected As concentrations in the insects. The other bag containing the remaining group was transferred to CERCLA within 2 hours of collection. After 48 hours, all bags were recovered.

Statistical Analyses

When the sample sizes were adequate, As concentrations of insects were statistically analyzed for significant differences. The arsenic concentrations were analyzed within the same taxon among different stations and among different taxa at the same station. Sample variances were tested for homogeneity by a two-tailed F-test. Samples that were homogeneous were analyzed by the t-test and ANOVA. In some cases, data were log-transformed to meet the assumptions of homogeneity of variances. Samples that were significantly heterogeneous were analyzed by the Mann-Whitney and Kruskal-Wallis tests. Differences were considered significant if $p \leq 0.05$ for a 2- tailed test.

RESULTS AND DISCUSSION

The arsenic concentrations of taxa collected at stations HW and BGR in 1986 were similar to samples collected in 1987 (table D-9). The concentration in *Hesperoperla pacifica* at station HW was significantly higher in 1987, but the difference in concentration between the 2 years was only about 2 μg/g (micrograms per gram). At the CERCLA station, the As concentration of *Hydropsyche* spp. in 1987 was two times greater than in 1986. However, this difference was not significant. It should be noted that the concentration for *Hydropsyche* spp. in 1987 is the mean of concentrations for two taxa, the species *H. bronta* and samples composed of two morphologically and ecologically similar species *H. slossonae* and *H. oslari.* All three species were collected at the CERCLA station in 1986, but they were not separated for chemical analysis. *Hydropsyche bronta* was only differentiated from the other two species in 1987. It is possible that differences in the species composition of the samples contributed to the difference in As concentrations between years, although at the CERCLA station, only small differences in As concentrations ($p > 0.05$; ANOVA) were observed between Hydropsyche species in 1987 (table D-10).

The arsenic concentrations in all species increased below the HW station. Average background As concentrations in benthic insects, represented by samples taken at stations HW and SC, ranged from 3 to 16 μg/g (table D-10). Arsenic in the mayfly, *Ephemerella inermis*, more than doubled at station AGR. Below station AGR, mean As concentrations ranged from 10 to 625 mg/g depending upon station and species. The influence of ground-water input of As was evident by the differences in As concentration of taxa collected at stations BBS and BAS. The As in *Choroterpes* sp., *Tricorythodes* sp., and *Ambrysus* sp., which were collected within the plume of the seep at station BBS, were greatly elevated compared to samples of these taxa collected 100 meters upstream at station BAS. *Hydropsyche* sp. was collected from the midchannel, outside of the plume at BBS, which may explain why the As concentrations of this taxon were similar at stations BBS and BAS. A detailed evaluation of the longitudinal distribution of bioavailable As in Whitewood Creek was complicated by the lack of species common to all stations, variabilty within small sample sizes, and conflicting trends between species. For example, As concentrations in

Table D-9.—*Arsenic concentrations of three benthic insect taxa collected from Whitewood Creek in June 1986 and May 1987*

[Values are in micrograms per gram dry weight; mean ± 1 standard error of the mean. Sample size in parentheses. ND = not determined]

Station	*Ephemerella inermis*		*Hydropsyche* spp.[1]		*Hesperoperla pacifica*	
	1986	1987	1986	1987	1986	1987
HW	11±0.5 (2)	16±0.2 (2)	ND	ND	0.8±0.05 (2)	[2]3.2±0.3 (3)
BGR	65±8 (3)	59±20 (2)	22 (1)	28±8 (2)	ND	ND
CERCLA	ND	ND	46±4 (2)	89±9 (2)	ND	ND

[1] Samples of different Hydropsyche spp. collected in 1987 were combined for comparison with samples collected in 1986. Values for 1987 are means of the concentrations of H. bronta and H. slossonae/oslari. Samples were not separated by species in 1986, and therefore represent a mixture of the different species.

[2] Indicates significant difference between years ($p < 0.05$).

Hydropsyche spp. collected in both 1986 and 1987 appeared to increase below HW, peak at the CERCLA station, and then decrease downstream. However, in *Baetis tricaudatus*, As concentrations peaked at station BGR and were lowest at the CERCLA station (table D-11).

The As concentrations in sediments increased substantially below station HW (table D-11). However, concentrations in the insects did not consistently follow changes in the As concentration of sediments down Whitewood Creek. Differences in responses of different species (as noted above) to sediment As concentrations also were evident.

Within stations, differences in the As concentrations of insects could be distinguished on the basis of taxonomic differences, tropic level differences, and the body size of individual insects. There was substantial variability in As concentration among taxa, but some trends were evident among orders and families. Arsenic concentrations were consistently higher in the order Ephemoroptera (*Baetis tricaudatus, Choroterpes* sp., *Ephemerella inermis, Tricorythodes* sp.) and in the trichopteran family Hydropsychidae (*Hydropsyche* spp. and *Cheumatopsyche* spp.) than in the order Plecoptera (*Isoperla* sp. and *Hesperoperla* sp.) and the trichopteran families Limnephilidae and Rhyacophilidae (table D-10). There was less variation among closely related taxa. At CERCLA, where there were sufficient data for statistical analysis, there was no difference in As concentration ($p > 0.05$; ANOVA) among three morphologically and ecologically similar taxa within the family Hydropsychidae (*H. bronta, H. slossonae/oslari,* and *Cheumatopsyche* spp.). Similarly, two mayfly species (*B. tricaudatus* and *E. inermis*) had similar As concentrations at stations AGR and BGR (table D-10).

Table D-10.—*Arsenic concentrations of benthic insects collected from Whitewood Creek and Spearfish Creek in May-June 1987*

[Values are in micrograms per gram dry weight. Standard deviation of the mean concentration shown. Sample size given in parenthesis. The caddisflies *Limnephilus* sp. and *Hesperophylax* sp. were not separated prior to As determination]

Trophic level	Taxa	Station						
		HW	AGR	BGR	CERCLA	BAS	BBS	SC
Herbivore								
	Baetis tricaudatus	10 (1)	65±15 (4)	80±15 (3)	24±2 (2)			
	Choroterpes sp. (=*Neochoroterpes*)					156±28 (9)	278±86 (3)	
	Ephemerella inermis	16±0.2 (2)	40±1 (2)	59±28 (2)				
	Tricorythodes sp.					92±20 (3)	625±80 (3)	
	Hesperophylax occidentalis	6±3 (2)						
	Limnephilus sp. & *Hesperophylax* sp.		8 (1)	10±0.03 (2)				
Herbivore/Omnivore								
	Cheumatopsyche spp.				56±8 (3)	59 (1)		
Omnivore								
	Hydropsyche bronta			20 (1)	80±4 (2)	29 (1)		
	Hydropsyche oslari							7±3 (2)
	Hydropsyche slossonae & oslari		58±10 (3)	37±6 (5)	98±26 (3)			
	Hydropsyche sp.					66±25 (9)	77±15 (3)	
Predator								
	Rhyacophila acropedes gr.		4 (1)	64 (1)				2 (1)
	Isoperla *quinquepunctata*				10±4 (2)			
	Hesperoperla pacifica	3±0.5 (3)	5±1 (3)					2±0.2 (2)
	Ambrysus sp.					25±5 (7)	73±42 (3)	

Table D-11. – *Concentration of arsenic in fine (< 63 micrometer) streambed sediments and in benthic insects collected at stations on Whitewood Creek in 1987*

[Values are in micrograms per gram dry weight. Mean and 1 standard error of the mean. Sample size is given in parentheses]

Station	Sediment	Taxon		
		Hydropsyche spp.	*Baetis tricaudatus*	*Ephemerella inermis*
HW	15 (1)		10 (1)	16±0.2 (2)
AGR	440 (1)	58±10 (3)	65±15 (4)	40±1 (2)
BGR	460±10 (2)	37±6 (5)	80±15 (3)	59±28 (2)
CERCLA	610±140 (2)	98±26 (3)	24±2 (2)	
BAS	930 (1)	66±25 (9)		
BBS	1100 (1)	77±15 (3)		

Trophic level appeared to affect As bioaccumulation. The As concentrations generally were lower in predators than in herbivores, with concentrations in omnivores falling somewhere in between (table D-10). Exceptions to this pattern were observed in just two cases; elevated As concentrations in a single *Rhyacophila* sp. (predator) sample collected at station BGR, and low As in *Limnephilus* sp., a herbivore, collected at stations AGR and BGR. In the case of *Limnephilus* sp., As levels may have been affected by the animals' stage of development. When those specimens were collected, they were in an inactive, prepupal state, sealed in cases, and presumably had evacuated their guts. The gut contents are potentially a major source of contamination (Elwood and others, 1976).

The As concentration also appeared to be dependent upon the size of the insect regardless of species (fig. D-20). Correlations of mean dry weight per insect and As concentration at stations HW, BGR, and BBS were significant (r = -0.942, r = -0.968, and r = -0.850, respectively) even though species composition changed completely from station HW to station BBS. Furthermore, in some instances concentrations of species with different habits (that is, trophic level) overlapped. However, it was difficult to differentiate possible effects of trophic level from size. Herbivores with the highest As concentrations were typically the smallest specimens collected and predators the largest. In *Limnephilus* sp., a large herbiverous caddisfly, As concentrations were low, but this could have been related to its developmental stage as explained above.

The As concentrations of insects transferred from uncontaminated stations (HW and SC) to the CERCLA station for 2 days increased in varying amounts relative to controls (table D-12). The concentration in *Hydropsyche oslari* increased roughly seven times and was one-half the concentration of resident specimens. In contrast, only a slight increase in As concentration was apparent in *Rhyacophila* sp. At the control stations, As concentrations of insects held in bags for 2 days (bagged control) and those sampled directly from the stream at the start of the experiment (unbagged control) were similar, indicating that the bags used in the transfer experiment had no apparent effect on insect As concentrations. Arsenic accumulation in the transferred taxa could be distinguished on the basis of both trophic level and size. Rates of As accumulation were much higher in the herbivore (*Hesperophylax occidentalis*) and the omnivore (*H. oslari*) than in the two predators (*Hesperoperla pacifica* and *Rhyacophila* sp.). Predators were presumably unable to feed because the mesh size of the bags excluded most prey. Thus, a potential source of As contamination could have been reduced in this group of insects. Fine organic material in or on the bag could have been consumed by the herbivore and omnivore. The As concentrations of individual samples among *H. pacifica*, *H. oslari*, and *H. occidentalis* were negatively correlated with dry body weight (r = -0.840), but As in

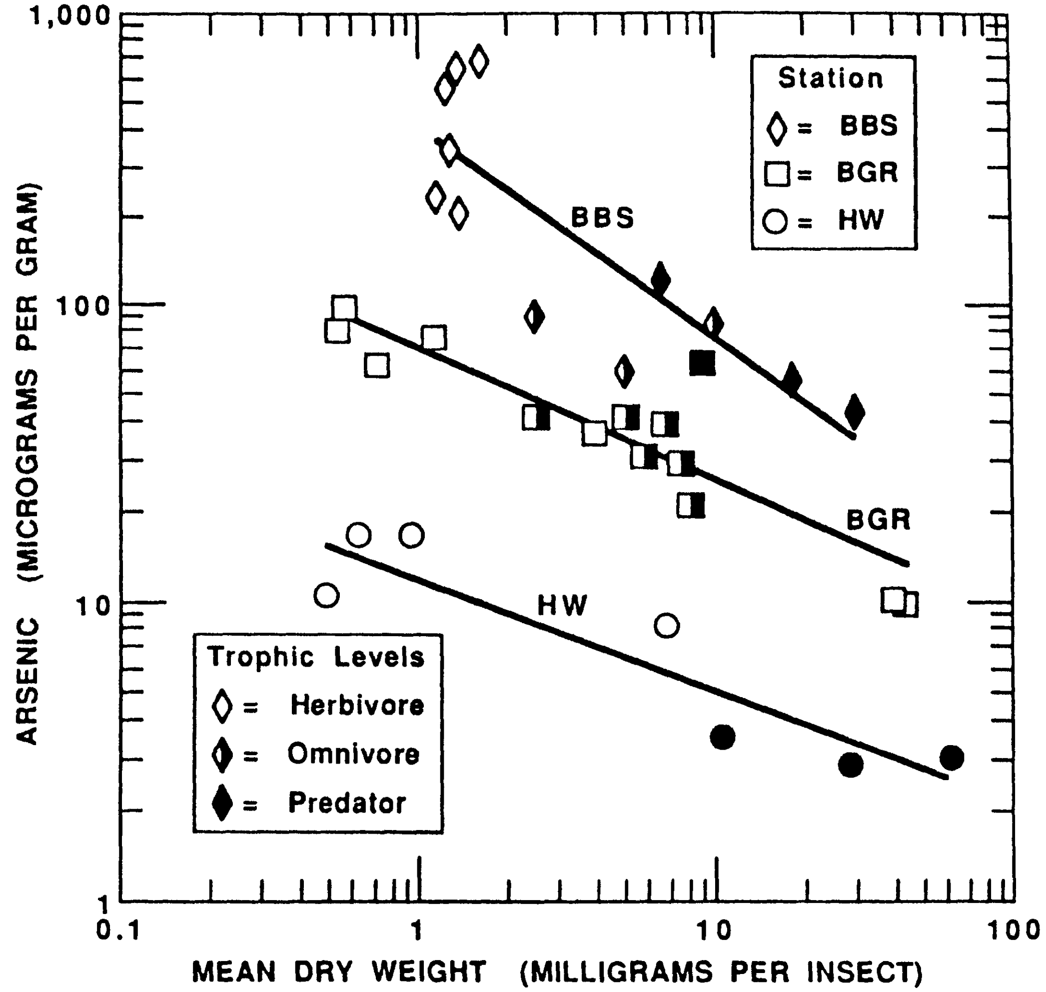

Figure D-20.—The relation of arsenic concentrations and the dry weight of individual benthic insects collected at three stations on Whitewood Creek. Data were fitted by correlation. The different shading patterns for the station symbols differentiate taxa by habit.

Table D-12.– *Arsenic concentrations in controls and insects transferred to the CERCLA station for 2 days*

[Values are the means and 1 standard error of the mean in micrograms per gram dry weight; sample sizes are given in parentheses]

Taxon	Control (unbagged)	Control (bagged)	Transfer (bagged)	CERCLA resident
Hydropsyche oslari	6.69±1.96 (3)	5.92±1.40 (3)	[1]42.0±5.0 (3)	98±15 (3)
Hesperophylax occidentalis	11.9±0.4 (2)	5.4 (1)	40.9±28.0 (2)	
Hesperoperla pacifica	1.86±0.12 (2)	1.36±0.31 (6)	[1]6.63±1.10 (3)	
Rhyacophila acropedes gr.	2.12 (1)	2.30 (1)	3.12±0.22 (2)	

[1] Indicates a significant difference between control (bagged) and transferred group at ($p \leq 0.05$).

Rhyacophila sp. was low relative to its body weight on the basis of the relation among the three other taxa.

The specific mechanism(s) of accumulation could not be resolved quantitatively. Trophic level appeared to play a role in As accumulation because predators generally had lower body burdens and accumulated As more slowly than did herbivores. This observation is consistent with the suggestion that As is transferred inefficiently through aquatic food webs (Moore and Ramamoorthy, 1984). Effects of trophic level may be modified by the size of the animal as suggested by the relation between dry weight and As concentrations. Dry weight may be indicative of a number of allometric and behavioral characteristics, including the surface area:mass ratio of the animal, volume of the gut, and changes in food preference as the animal grows.

Several lines of evidence suggest that sorption of As to external body surfaces contributed greatly to the As burden in these insects. The negative correlation of concentration with body weight of larvae would be expected because the surface area:mass ratio typically decreases as an animal grows (Smock, 1983). The relation between As concentration and dry weight was observed for individuals of the same species as well as for different species and, in some cases, cut across tropic levels indicating that food preference was not the only factor influencing As body burdens. Furthermore, As concentrations in different life forms that shed the larval exoskeleton (pupa and adult) were only 15 to 50 percent of the concentrations in the larvae (table D-13). Thus, much of the variability in As concentration of larval life forms of insects collected at a given station could be explained simply as a function of their size. These findings are consistent with those of Krantzberg and Stokes (1988) who concluded that adsorption of metals to the exoskeleton was an important component of the total metal body burden in midge larvae.

In summary, results of two consecutive yearly samplings of the benthic-insect community showed that all taxa collected within a 73-km reach of Whitewood Creek and the Belle Fourche River had As concentrations higher than what could be considered background for the watershed. The As concentrations increased below Lead and peaked at the CERCLA station. The As concentrations in the insects reflected differences

Table D-13.–*Arsenic concentrations in different life forms of insects collected from Whitewood Creek and Spearfish Creek in 1986 and 1987*

[Values are in micrograms per gram dry weight. Sample sizes range from one to three. Mean and 1 standard error of the mean given for taxa with sample sizes greater than one]

Station	Taxon	Life Stage		
		Larva	Pupa	Adult
AGR	Limnephilid	7.62	2.64	
BGR	Limnephilid	9.98±0.02	5.14±0.63	
STP	Limnephilid[1]	19.5	3.6	
CERCLA	Limnephilid[1]	12.4±1.8	2.0±0.02	
	Hydropsyche bronta	80.0±2.9		
	H. slossonae	97.6±14.8		
	H. bronta/slossonae			3.34±0.06
	Isoperla sp.	10.4±2.54		4.39±0.49
SC	*Rhyacophila* spp.	2.12	1.94	

[1] Samples collected in 1986.

between unenriched and contaminated streambed sediments in Whitewood Creek. However, it was apparent that body size and trophic level of the insect also influenced As concentrations in these taxa. Additional research is required to resolve the sources of bioavailable As and the mechanism(s) of As accumulation by the insect.

Differences in As concentration of taxa between years and the variability in As among taxa emphasized some important considerations related to using benthic insects as bioindicators. Collection of small benthic insects such as mayflies and caddisflies to obtain sufficient biomass for chemical analysis is often an extremely labor-intensive activity. Consequently, the numbers of samples of any particular taxa for any given station are commonly low. Typically, when organisms are exposed to a contaminant, the individual variability in the concentration of that contaminant increases dramatically. Unfortunately, the combination of small sample size and high sample variabilty severely reduces the power of statistical analyses and the ability to critically evaluate temporal and spatial trends in contaminant concentrations. From a practical standpoint, it is valuable to know at what level taxa can be lumped into a composite sample. It also may be necessary to make assumptions about the relative potential for contaminant accumulation by different taxa when comparing sites with different species compositions. Analyses of Whitewood Creek samples indicated that mayflies and the caddisflies Hydropsychidae had consistently elevated concentrations of As and that differences in As concentrations among species within these groups were not great. Thus, species within these groups could be combined when necessary to make interstation comparisons. However, this approach may not be appropriate for other elements or at other sites.

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Appendix 1.

Station	Location
HW	Whitewood Creek, upstream of Lead
AGR	Whitewood Creek, approximately 1 km upstream of Gold Run Creek
BGR	Whitewood Creek, 100 meters downstream of Gold Run Creek
STP	Whitewood Creek, 100 meters downstream of the Deadwood Sewage Treatment Plant
CERCLA	Whitewood Creek near Whitewood at the Comprehensive Environmental Response and Liability Act Site
BAS	Whitewood Creek, 50 meters downstream of the bridge near the Berger Ranch (approximately 20 km downstream of Whitewood)

BBS	Whitewood Creek, 150 meters downstream of the bridge near the Berger Ranch
Sheeler	Whitewood Creek near the confluence of the Belle Fourche River
BFAWW	Belle Fourche River, upstream of the confluence of Whitewood Creek
BFBWW	Belle Fourche River, 100 meters downstream of the Vale Bridge
BFIS	Belle Fourche River, 200 meters upstream of the bridge on Interstate 34, about 32 km east of Sturgis
CH	Cheyenne River, downstream of the confluence of the Belle Fourche River (not shown in fig. D-19)
SC	Spearfish Creek

CHAPTER E – ORGANIC COMPOUNDS IN THE LOWER CALCASIEU RIVER

(p. 271 follows)

FATE AND TRANSPORT OF ORGANIC COMPOUNDS AND TRACE ELEMENTS IN THE LOWER CALCASIEU RIVER, LOUISIANA

By Charles R. Demas[1] and Dennis K. Demcheck[1]

ABSTRACT

A field study was initiated in 1985 by the U.S. Geological Survey to determine processes that control the fate and transport of manmade organic compounds and trace elements in the industrial reach and in the transition zone between brackish and freshwater of the lower Calcasieu River.

Volatile and halogenated organic compounds, and four trace elements (iron, manganese, mercury, and chromium) were selected for study on the basis of results of reconnaissance sampling. Both classes of organic compounds and the four trace elements were determined to move in distinctly different ways in the aquatic environment and were either dissolved in the water column, associated with suspended sediment, or attached to bottom material.

Concentrations of volatile organic compounds in the lower Calcasieu River were found to depend on wind speed and density. Longitudinal movement of volatile organic compounds in the river was affected by the presence of salinity gradients, which restricted vertical mixing in the water column and provided, in one instance, a means of upstream transport from their source. Halogenated organic compounds, in contrast, were associated primarily with the bottom material which serves as a sink for these compounds because of their low solubility in brackish water.

INTRODUCTION

The lower Calcasieu River in southwestern Louisiana (fig. E-1) is a typical example of a Gulf Coast river that has been adversely affected by human activities. Previous unpublished studies by State and Federal agencies (Philip Crocker, U.S. Environmental Protection Agency, written commun., 1985; Michael Schurtz, Louisiana Department of Environmental Quality, written commun., 1985) have attributed the occurrence of hazardous organic compounds and trace elements in the water, bottom material, and aquatic organisms of the river to industrial activity in the basin. None of these studies, however, has determined the processes that control the fate and transport of these organic compounds and trace elements in relation to the physical and chemical characteristics of the river.

In 1985, the U.S. Geological Survey began a field study to determine the processes that control the fate and transport of organic compounds and trace elements in the industrial reach and in the transition zone between brackish and freshwater of the lower Calcasieu River. The purpose of this paper is to provide an overview of the Calcasieu River Surface Water Toxics Study by providing a description of the study area, summarizing results from completed U.S. Geological Survey investigations, and prefacing papers in this chapter of the Proceedings.

The lower Calcasieu River is a tidally affected stream that lies within the Coastal Plain. The upper and middle parts of the Calcasieu River basin are characterized by hardwood forests, cypress, and related vegetation. Rice and soybeans are the principal crops grown in the upper and middle basin. Long-term water-quality data (1968-present) collected at the U.S. Geological Survey National Stream Quality Assessment Network (NASQAN) site near Kinder (fig. E-1) indicate that the upper reach of the Calcasieu River contains low concentrations of dissolved solids. Specific conductances range from 13 to 187 μS/cm at 25 °C (microsiemens per centimeter at 25 degrees Celsius). Discharge at the Kinder site averages 2,500 ft^3/s (cubic feet per second) and ranges from 200 to 183,000 ft^3/s for the period of record (1938-present). Runoff of agricultural chemicals into this reach of the river appears to be minor; however, chlordane, diazinon, and aldrin have been detected in water at the Kinder site.

The lower reaches of the Calcasieu River are bordered by swamp and marshland and can be divided into two sections. The first section is bordered upstream by a saltwater barrier and downstream by the Intracoastal Waterway. The

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[1] U.S. Geological Survey, Baton Rouge, La.

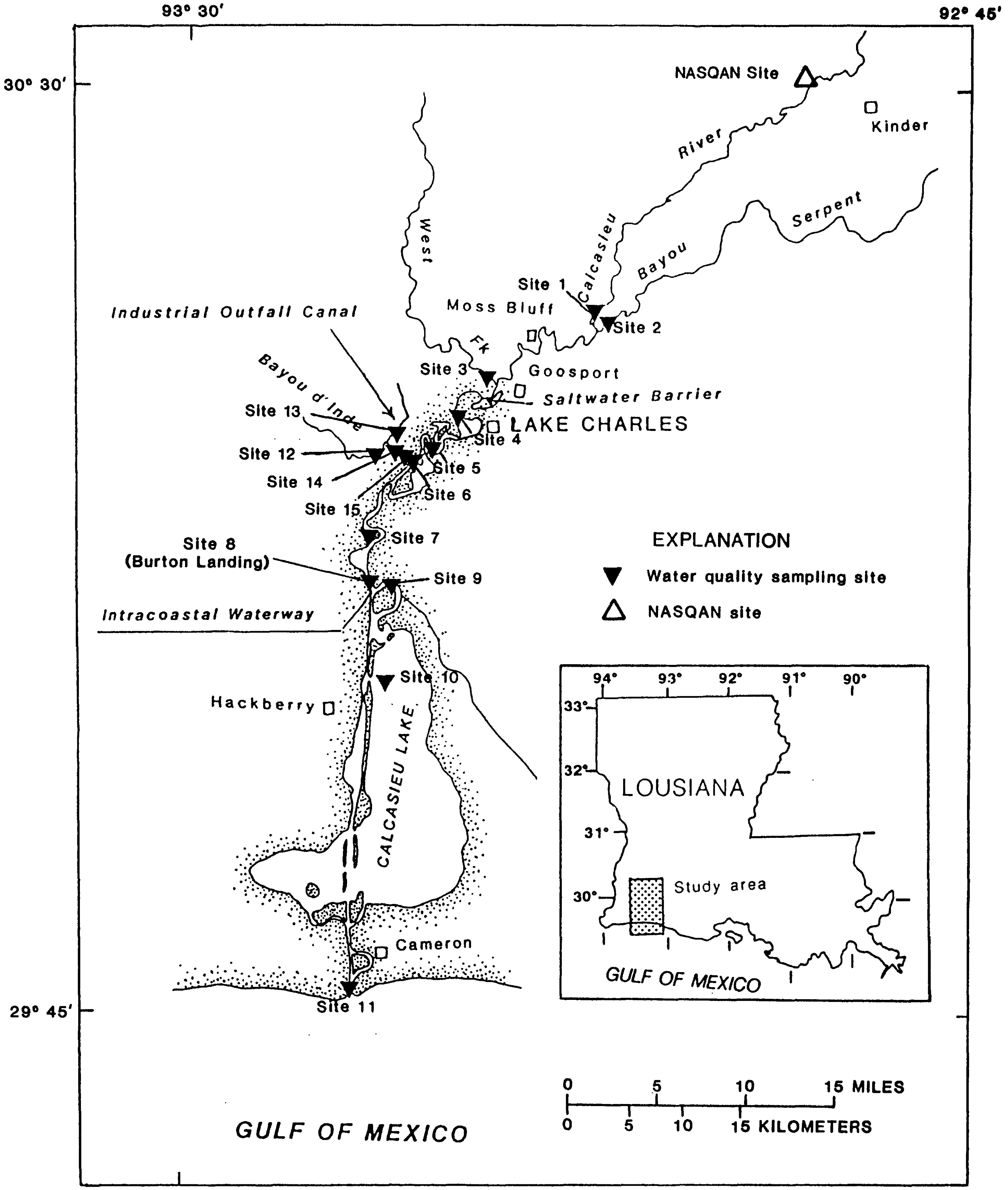

Figure E-1.—Study area and water-quality sampling sites of lower Calcasieu River, Louisiana.

Lake Charles urban area and industrial complex dominate land use in this section of the study area. Approximately 32 industrial plants are located along this 14-mile section of the river. The specific conductance of the water ranges from 200 to 33,000 μS/cm and dissolved organic carbon (DOC) ranges from 3 to 4 mg/L (milligrams per liter) in this section of the river. Petrochemical and agricultural-chemical plants along this section use the lower Calcasieu River for water supply, navigation, and assimilation of effluent discharge. Byproducts (table E-1), such as oil and grease, phenols, and metals, are discharged into the river by chemical industries in the Lake Charles area. The second section is bordered upstream by the Intracoastal Waterway and downstream by the Gulf of Mexico. Commercial and sport fishing, and support facilities for oil and gas drilling are major industries in this section of the river.

RESULTS

Two classes of organic compounds (volatile and acid- base/neutral extractable) and four trace elements (iron, manganese, mercury, and chromium) were selected for study on the basis of the results of two reconnaissance sampling surveys conducted in 1985 of the lower Calcasieu River at the sites listed in table E-2. Both classes of organic compounds and the four trace elements were determined to move in distinctly different ways in the aquatic environment and were either dissolved in the water column, associated with suspended sediment, or attached to bottom material.

Volatile organic compounds (VOC) were selected for study on the basis of the widespread odor of organic compounds detected in the air during the first reconnaissance sampling survey. Detection of these compounds at low concentrations in water samples led to an investigation of the effects of wind speed, sampling techniques, and density of the compound on the presence, location in the water column, and concentration of these compounds in the lower Calcasieu River (Demas and others, 1988).

Analysis of river-water samples collected under different wind conditions during four reconnaissance sampling surveys indicate that wind speed, and the turbulence it created in the river, was a primary factor in controlling the concentrations of VOC. For example, water samples were collected during moderate (15.3 mi/h (miles per hour)) and low (7.5 mi/h) wind conditions in May and August 1985 from a reach of the lower Calcasieu River extending from Lake Charles to Burton Landing, La. (fig. E-1). Samples were depth integrated from water columns with similar temperature and specific-conductance values. Results indicated that only four VOC were detected at two sites (sites 5 and 6) during moderate wind conditions, compared to six compounds detected at four sites (sites 5 through 8) during low wind conditions. Also, VOC such as bromoform (fig. E-2), chloroform, 1,2-dichloroethane, and chlorodibromomethane were detected in concentrations as much as five times greater during low wind conditions as compared to moderate wind conditions. Thus, sampling for VOC during moderate to strong wind conditions may lead to erroneous conclusions about the presence and potential effect of these compounds in the aquatic environment.

Water samples were collected at different depths in the water column from the same reach to determine the effects of different densities of organic compounds on the distribution of VOC in the lower Calcasieu River (Demas and others, 1988). This sampling was conducted to ascertain if the density of a VOC determines the location in the water column where that compound might be concentrated. Position of a compound in the water column is very important in determining the types of sampling equipment and methods needed to describe accurately the presence and concentration levels of organic compounds in the river. For example, a VOC such as bromoform, which has a density of 2.9, might be expected to be present in greater concentrations at a position lower in the water column than a lighter VOC, such as 1,2-dichloroethane, which has a density of 1.3. If this occurred in the river, then depth-integrated or water-surface samples would indicate an abnormally low concentration of bromoform in the river, whereas point water samples would indicate the position in the water column where the bromoform was concentrated and, therefore, might have the greatest effect on the environment. Accordingly, point samples were collected in May 1986 during low wind conditions (6.9 mi/h) and April 1987 during moderate wind conditions (17.0 mi/h). Results from the May 1986 sampling (fig. E-3) indicate that different densities of organic compounds had little effect on the vertical distribution of these volatiles in the water column.

Table E-1.—*Major industrial categories wastewater characteristics of the Greater Lake Charles area, Louisiana*

[T, temperature; BOD, biochemical oxygen demand; TSS, total suspended solids; O and G, oil and grease; COD, chemical oxygen demand; NH_3, ammonia; TOC, total organic carbon; TOX, total organic halides; Cr, chromium; Hex. Cr, hexavalent chromium; N, nitrogen; NO_3, nitrate; FC, fecal coliform; Cl, chloride; P, phosphorus; Zn, zinc; Cu, copper; Ni, nickel; Hg, mercury; Pb, lead; sulfide, H_2S]

Industrial category	Number of plants present	Byproducts	Wastewater characteristics monitored
Chemical-manufacturing plants	4	Chemicals	pH, TSS, O and G, BOD, TOX, total P, TOC, NH_3, total Kjeldahl N, NO_3, total Cr
		Polypropylene, high density polyethylene, polyolyolefins	T, BOD, pH, COD, TSS, O and G, NH_3 TOC
		Chemicals	T, pH, TSS, BOD, COD, NH_3, chlorinated hydrocarbons
		Chemicals	Hg, Pb, Cr, TSS, BOD, total chlorinated hydrocarbons
		Polymens, polyvinyl chloride	BOD, TSS, FC
Specialty chemical-manufacturing plants	1	Specialty chemicals-olefins	TSS, Cu, Ni, Lime, dichlorobromomethane, bromoform, chloroform, TOC, chlorodibromomethane, sodium aluminate
Synthetic-rubber plant	1	Synthetic rubber and latex	T, BOD, COD, Cr, pH, TSS, O and O and G, NH_3
Paint plant	1	Paint	TOC, O and G, pH
Oil refineries and related industries	5	Oil refinery; produces naphtha, distillate and residual oil, and liquified propane gas	NH_3, H_2S, C1, O and G, phenols, P
		Products of petroleum cracking catalysts	T, BOD, pH, TSS, NH_3
		Oil products	BOD, COD, TSS, O and G, phenols, NH_3, H_2S, total Cr, Hex. Cr, pH, flow
		Petrochemicals	BOD, TSS, TOC, phenols, H_2S, O and G, NH_3, Zn
		Regasification of liquified natural gas	T, TSS, BOD, O and G
		Ammonia	NH_3, O and G, Cr
Fertilizer	1	Municipal sewage	NH_3, BOD, FC, pH, TSS
Domestic sewage treatment plants	1	Grinding and distribution of barite	Treated sanitary wastewater
Oil and gas drilling	1	Cryogenic air separation	O and G, Cr, pH
Others	3	Cement Calcium chloride	T, pH Runoff

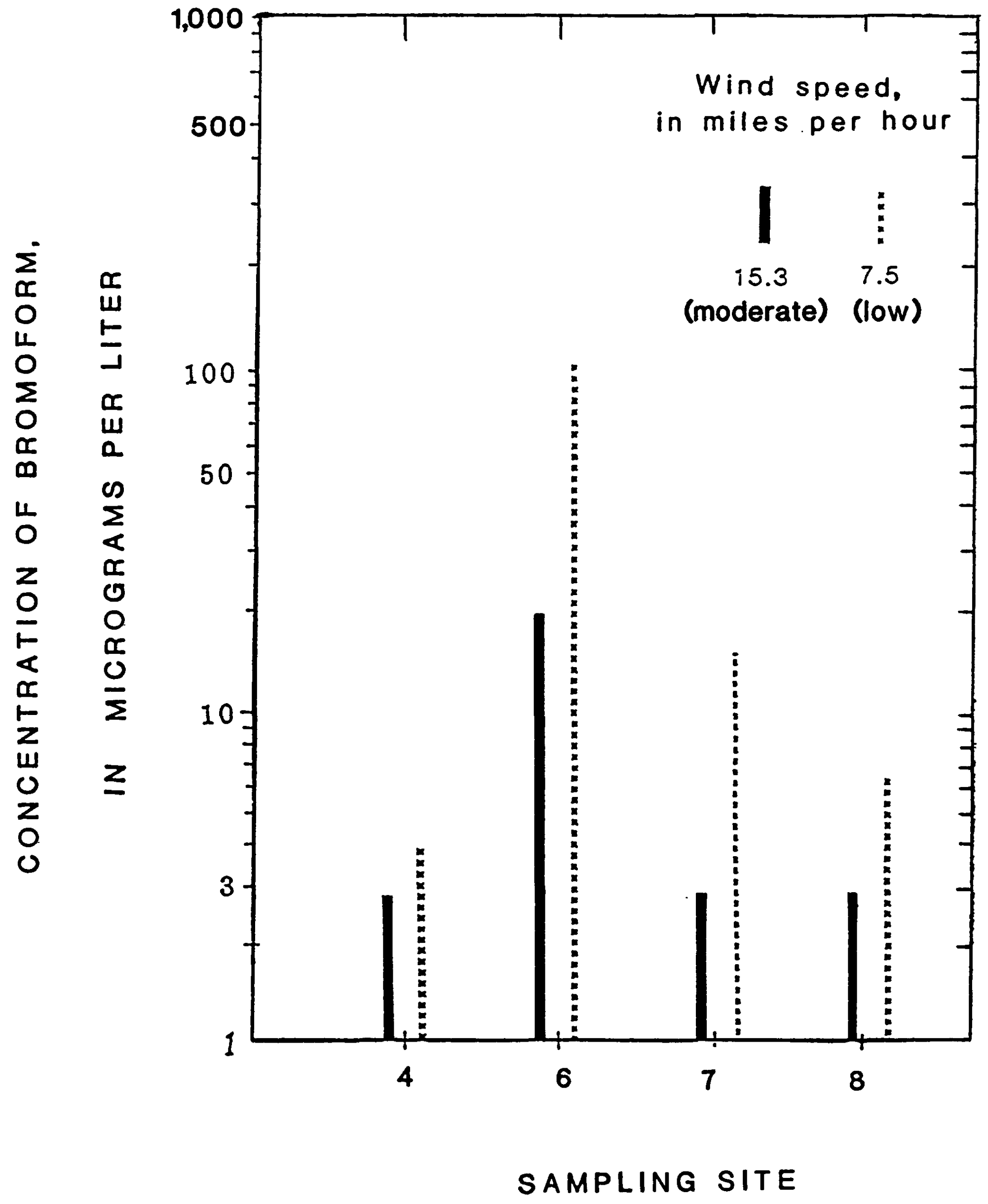

Figure E-2.—Concentration of bromoform under moderate and low wind conditions, May and Ausust 1985, respectively, in the lower Calcasieu River.

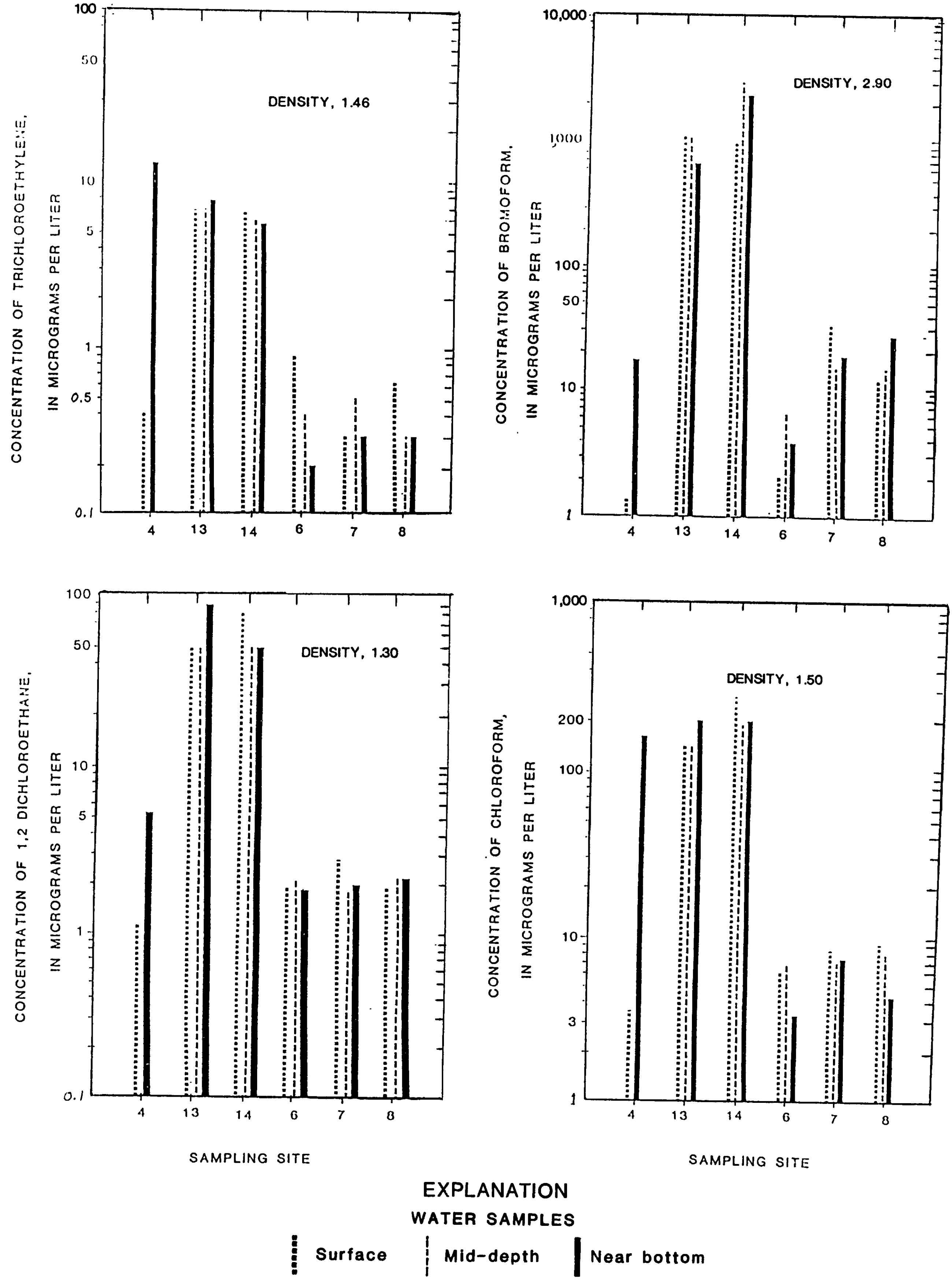

Figure E-3.—Vertical distribution of four volatile organic compounds of different densities collected May 1986, lower Calcasieu River.

Concentrations of VOC at different depths were similar for the six sampling sites (fig. E-3) except at site 4. For example, the vertical distribution of bromoform at site 13 was similar to that of 1,2-dichloroethane and trichloroethylene (density 1.5). Bromoform was present in similar concentrations (1,000 μg/L) (micrograms per liter) at all three depths sampled. This indicates that results of VOC analyses of depth-integrated and water-surface samples accurately describe the presence and concentration levels of these organic compounds in the lower Calcasieu River under most conditions.

The exception to the above observation occurred at site 4 where the concentration of VOC near the bottom is much greater than the concentration at the water surface. Vertical differences in concentrations observed at site 4 can be explained by the results of flow, dye, and density studies. Flow studies (Curwick, 1988) indicate that the slow-moving water currents in the river preclude much vertical mixing in the water column because of the small vertical velocity gradients. Therefore, the comparatively dense saltwater moves almost exclusively near the bottom. The saltwater travels some distance upstream because of the longitudinal salinity gradient between the freshwater upstream and the denser saltwater in the Gulf of Mexico. Dye studies conducted in 1979 and 1987 (Curwick, 1988) also indicate slow vertical mixing in the water column when the densities of surface and bottom water are significantly different. These differences in water density (measured as differences in specific conductance) were most pronounced at site 4 where the bottom sample had the highest concentrations of VOC (bromoform, 17 μg/L; chloroform, 160 μg/L; trichloroethylene, 13 μg/L; 1,2-dichloroethane, 5.4 μg/L). The high concentration of volatiles was present in a part of the water column that had a specific conductance of 12,500 μS/cm--a value similar to downstream sites. In contrast, surface samples, which contained lower concentrations of VOC (bromoform, 1.3 μg/L; chloroform, 3.4 μg/L; trichloroethylene, 0.4 μg/L; 1,2-dichloroethane, 1.1 μg/L) were from relatively low-specific-conductance water (2,500 μS/cm) compared to downstream sites 7 (sites 6, 13, and 14). This phenomenon also was observed in samples collected during moderate wind conditions (17 mi/h) in April 1987. These results indicate that (1) upstream movement of VOC occurs along the bottom when salinity gradients are present in the lower Calcasieu River, (2) VOC detected in the bottom water sample at site 4 came from downstream, and (3) presence of the salinity gradient at site 4 inhibited movement of

Table E-2.—Location of water-quality sampling site for the lower Calcasieu River, Louisiana

Sampling Site No. (see fig. 1)	Location
1	Calcasieu River east of Moss Bluff.
2	Bayou Serpent east of Moss Bluff.
3	West Fork Calcasieu River west northwest of Goosport.
4	Calcasieu River at buoy 130 at Lake Charles.
5	Calcasieu River at buoy 114 at Lake Charles.
6	Calcasieu River at Bayou d' Inde.
7	Calcasieu River 3.9 miles south of Hollywood.
8	Calcasieu River at Burton Landing.
9	Calcasieu River at Devil's Elbow.
10	Calcasieu Lake northeast of Hackberry.
11	Calcalieu River at buoy 47 southwest of Cameron.
12	Bayou d' Inde 0.25 mile upstream from an industrial outfall.
13	Industrial outfall at Bayou d' Inde.
14	Bayou d' Inde 0.25 mile downstream from an industrial outfall.
15	Bayou d' Inde 0.50 mile downstream from an industrial outfall.

VOC from the lower part of the water column to the near surface part of the water column. Data from dye and volatile-organic compound studies (Curwick, 1988; Demas and others, 1988) also indicate that salinity gradients inhibit vertical movement of VOC in the water column. Presence of VOC at site 4 and their movement upstream with the saltwater wedge could not have been determined without point samples. Thus, a sampling scheme for VOC in areas where salinity gradients exist needs to include some point samples to obtain an accurate picture of the distribution of these compounds in the aquatics environment.

Acid-base/neutral extractable organic compounds also were studied in the lower Calcasieu River. One group of compounds detected in water, bottom material, and biotic samples was the halogenated organic compounds (HOC), which includes the haloarenes, a class of chlorinated aromatic compounds that are toxic to aquatic organisms. (See Demas and others, 1988, in press; Pereira and others, 1988, in press; for details of sampling and analysis.)

Haloarenes have relatively high octanol partition coefficients, log P (octanol/water) values, that are characteristic of compounds that sorb strongly to natural organic compounds present in bottom material and bioconcentrate in lipid tissues of aquatic organisms (Pereira and others, 1988). Haloarenes are even less soluble in saltwater because of an increase in the octanol/estuarine-water partition coefficient (K_{OW^*}), as shown in table E-3 (Pereira and others, 1988). Naturally occurring organic compounds, such as humic and fulvic compounds, indicate similar changes in solubility: DOC decreased from 5 or 6 mg/L in the freshwater reach of the river to 3 or 4 mg/L downstream from the saltwater barrier. Most of this decrease in DOC resulted from changes in the hydrophobic fraction; the hydrophillic fraction remained relatively constant. Removal of the hydrophobic fraction of the DOC from the water column may also facilitate the transfer of HOC from the water column to bottom material by providing additional organic material to which the HOC can attach in the bottom material. Because of the decrease in solubility of HOC in saltwater and the presence of natural organic carbon, bottom material in the lower Calcasieu River functions as a major sink for these compounds. For example, hexachlorobenzene (table E-4) was detected in bottom material at a concentration of 350 mg/kg (milligrams per kilogram). This same compound was detected on suspended sediment at a concentration of 2.5 mg/kg and in water at a concentration of 0.000008 mg/L. Clearly, these compounds concentrate in the bottom material.

The reduced solubility of HOC in saltwater also was found to enhance moderately the partitioning of the organic compounds into biota and bottom material (Pereira and others, 1988). Concentrations of HOC in biota and water were not in equilibrium relative to concentrations in bottom material apparently because of differences in K_{OW^*}. Compounds with K_{OW^*} values less than 5.2 showed a relatively greater tendency toward equilibrium with the water column than did compounds with K_{OW^*} values greater than 5.2.

Table E-3.—*Partition coefficients of selected haloarene isomers*

[K_{OW^*} = octanol/estuarine-water partition coefficient;
K_{OW} = octanol/distilled-water partition coefficient]

Compound	Log K_{OW^*}	Log K_{OW}
Chlorobenzene	2.92	2.84
1,3-Dichlorobenzene	3.58	3.50
1,4-Dichlorobenzene	3.56	3.47
1,3,5-Trichlorobenzene	4.40	4.31
1,2,4-Trichlorobenzene	4.09	4.02
Pentachlorobenzene	5.27	5.20
Hexachlorobenzene	5.59	5.50
Hexachloro-1,3-butadiene	5.17	4.90

Table E-4. – *Concentrations of halogenated organic compounds in water, suspended sediment, and bottom material in Bayou d' Inde, Louisiana, near an industrial outfall*

[Suspended sediment in parts per million; water in parts per million; bottom material in parts per million; mm, millimeter; ND, not detected; >, greater than; <, less than]

Compound	Water column	Suspended sediment	Bottom material Coarse (>0.63mm)	Bottom material Fine (<0.63 mm)
Chlorobenzene	0.000018	0.02	0.07	ND
1,3-Dichlorobenzene	.000048	.07	3.2	0.57
1,4-Dichlorobenzene	.000074	.09	2.7	.43
1,3,5-Trichlorobenzene	ND	.07	2.8	.42
1,2,4-Trichlorobenzene	.000040	.37	10	1.6
Pentachlorobenzene	.000032	1.2	53	.17
Hexachlorobenzene	.000008	2.5	350	.73
Hexachloro-1,3-butadiene	.001298	1.8	53	.81

These latter compounds are more hydrophobic and kinetically restricted in their exchange between bottom material and water, making them less bioavailable. This lack of equilibrium between HOC concentrations in bottom material and the water column suggests that mixing is limited, resulting in slow diffusion of the sorbed contaminants from bottom sediments. In contrast, HOC concentrations in biota were in equilibrium to concentrations in water and suspended sediment.

Bioconcentration factors of HOC in four biotic species correlated reasonably well with triolein/water partition coefficients (table E-5) from Pereira and others, in press. Bioconcentration factors indicate that the primary means of uptake of these compounds could be passive diffusion; however, more information is needed to determine if uptake also occurs by other routes, such as active uptake through the digestive tract.

Other work on the movement of VOC and HOC in the lower Calcasieu River reported elsewhere in this Proceedings includes (1) transport of VOC through an industrial outfall canal into Bayou d' Inde and the Calcasieu River determined by dye and VOC concurrent sampling (Demcheck and others, 1989, this Proceedings), (2) remobilization of HOC from bottom material into the water column when HOC are exposed to waters with differing ionic strength (Demas and Demcheck, 1989, this proceedings), and (3) uptake of VOC and HOC by *Rangia cuneata* from selected areas of the lower Calcasieu River (Demas and Demcheck, 1988b). Results from the first study partially explain the role of

Table E-5. – *Bioconcentration factors of halogenated organic compounds in different biota, lower Calcasieu River, Louisiana*

Compound	Lipid-based log (bioconcentration factor) Atlantic croakers	Blue crabs	Spotted sea trout	Blue catfish
1,3-Dichlorobenzene	3.60	3.86	3.25	3.40
1,4-Dichlorobenzene	3.91	4.53	4.09	3.51
1,3,5-Trichlorobenzene	4.40	4.45	3.51	4.22
1,2,4-Trichlorobenzene	4.76	4.90	3.54	4.68
Pentachlorobenzene	5.93	6.12	4.96	5.57
Hexachlorobenzene	6.42	6.71	5.96	5.98
Hexachloro-1, 3-butadiene	4.50	3.97	4.06	4.55

volatilization in the movement and dispersal of VOC into the Calcasieu River. Results from the second study indicate that HOC can be remobilized back into the water column when bottom material is exposed to low ionic-strength waters. Such conditions are present in the Calcasieu River during periods of freshwater flooding and exposure of mudflats to rain during low tides. Results from the third study provide insight into uptake rates of VOC and HOC by aquatic organisms in the lower Calcasieu River and use of these organisms for detection of these compounds in areas where low concentrations are present in water.

Trace element analyses during the reconnaissance stage of the study indicated that barium, chromium, copper, iron, manganese, and mercury were present in detectable concentrations in water and/or bottom material (Demas and others, in press.) Previous information indicate that mercury and chromium contamination of water, bottom material, and biota existed during the early 1970's (Michael Schurtz, Louisiana Department of Environmental Quality, oral commun., 1986). Iron, manganese, chromium, and mercury were selected for study in both water and bottom material on the basis of results from the reconnaissance sampling surveys. Analysis of these selected trace elements has enhanced understanding of the effect of oxide coatings, natural organic compounds, and manmade organic compounds on the transport of trace elements in the river (Simon, 1989, this Proceedings). Also, radon-222 was investigated as a possible tracer of exchange mechanisms across the bottom material-water interface in one of the lakes connected to the Calcasieu River (Demas and others, 1989, this Proceedings).

SUMMARY AND CONCLUSIONS

A field study was initiated in 1985 by the U.S. Geological Survey to determine processes that control the fate and transport of manmade organic compounds and trace elements in the industrial reach and in the transition zone between brackish and freshwater of the lower Calcasieu River. Two classes of organic compounds, volatile and halogenated, and four trace elements (iron, manganese, mercury, and chromium) were selected for study on the basis of results of reconnaissance sampling surveys.

Presence and magnitude of concentrations of VOC in the lower Calcasieu River were dependent on wind speed and water density. Vertical upstream movement of VOC in the river was affected by the presence of salinity gradients, which restricted vertical mixing in the water column and provided, in one instance, a means of transporting VOC upstream from their source. HOC, in contrast, were detected primarily in the bottom material, which functions as a sink for HOC because of their low solubility in brackish water.

The movement and fate of iron, manganese, mercury, and chromium in water and bottom material also was investigated following the results of reconnaissance sampling surveys. Analysis of these trace elements has enhanced understanding of the effect of oxide coatings, natural organic compounds, and manmade organic compounds on the transport of these trace elements in the lower Calcasieu River.

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(p.283 follows)

REMOBILIZATION OF ORGANIC COMPOUNDS FROM BOTTOM MATERIAL COLLECTED FROM BAYOU D' INDE, LOUISIANA, UPON EXPOSURE TO DIFFERING IONIC-STRENGTH WATERS

By Charles R. Demas[1] and Dennis K. Demcheck[1]

ABSTRACT

Bayou d' Inde, a small tributary of the lower Calcasieu River in southwestern Louisiana, has a heavy organic contaminant load in its bottom material. In April 1987, the U.S. Geological Survey conducted a series of experiments to determine under what conditions movement of these organic compounds from Bayou d' Inde bottom material into the water column would occur.

Bottom material from Bayou d' Inde near an industrial outfall canal, brackish water from Bayou d' Inde, freshwater from the Calcasieu River near Kinder, Louisiana, and deionized water were analyzed for acid-base/neutral organic compounds. Results showed high concentrations, in the milligram per kilogram range, of chlorinated compounds in the bottom material and below levels of detection in the water samples. Modified elutriate tests were then performed on the bottom material and water. Tests indicated that mixing bottom material with brackish water from Bayou d' Inde resulted in no remobilization of organic compounds into the water column. Mixing bottom material with low ionic-strength waters, represented by Calcasieu River water near Kinder and deionized water, however, resulted in the remobilization of 1,2-dichlorobenzene and hexachlorobutadiene into the water at concentrations of 7 and 15 micrograms per liter, respectively. On the basis of these results, potential environmental repercussions could occur if dredging of contaminated bottom material took place during periods of freshwater inflow.

INTRODUCTION

Recent investigations (Pereira and others, 1988; Demas, in press) of the fate and movement of toxic substances in the lower Calcasieu River (fig. E-4) revealed extremely high concentrations (as much as 279 (mg/kg) milligrams per kilogram of hexachloroethane, for example) of several classes of organic compounds in the bottom material of Bayou d' Inde. Results indicated that these organic compounds appeared to precipitate out of the water column in the presence of saltwater and partition onto the bottom sediments. Recently (1988), several proposals have been submitted to State and Federal agencies to dredge the lower reaches of Bayou d' Inde for navigation and flood-control purposes. It was unknown from earlier studies how strongly organic compounds, such as hexachlorobenzene and hexachlorobutadiene, were bound to the bottom material and whether exposure to low ionic-strength waters would remobilize any of these compounds. During dredging, bottom material would be mixed with water ranging in salinity from 0 to 12 ppt (parts per thousand), and deposition of dredged material in spoil banks would expose this material to rain.

This paper describes the conditions under which remobilization of these organic compounds from Bayou d' Inde bottom material into the water column would occur. Three different ionic-strength waters (Bayou d' Inde at mouth, Calcasieu River near Kinder, and deionized water) were mixed with Bayou d' Inde bottom material to represent waters that are present within the Bayou d' Inde system during different hydrologic conditions.

MATERIALS AND METHODS

In April 1987, 24 liters of bottom material were collected at one vertical from Bayou d' Inde near its confluence with an industrial outfall canal (fig. E-4) using a stainless-steel sampler and stored in clean, fired glass bottles at 4 °C (degrees Celsius) until processed. Native water was collected at the mouth of Bayou d' Inde and the Calcasieu River near Kinder (fig. E-4) using prerinsed (pesticide-grade methanol and deionized water) 16-liter glass carboys and stored at 4 °C until used. Deionized water was obtained from the Louisiana District Laboratory of the

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[1] U.S. Geological Survey, Baton Rouge, La.

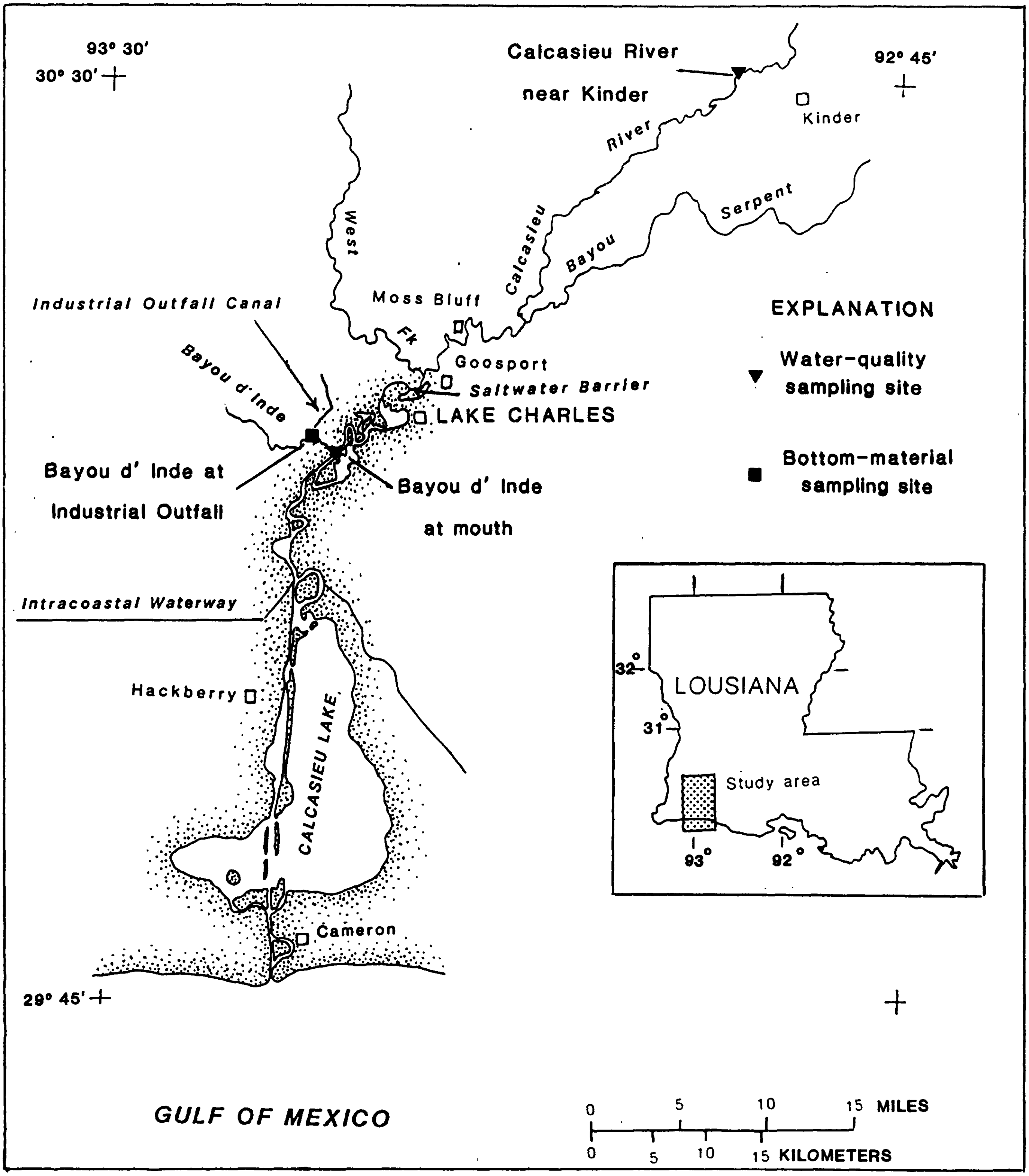

Figure E-4.–Study area and sampling sites on Bayou d' Inde and the lower Calcasieu River, Louisiana.

U.S. Geological Survey. Water temperature, pH, dissolved oxygen, salinity, specific conductance, and oxidation-reduction potential were recorded at the time of collection of bottom-material and native-water samples using a seven parameter *in situ* water-quality monitor.

Bottom-material samples were composited and mixed after collection by use of a Teflon[2]-coated industrial pastry mixer for 30 minutes to ensure that representative subsamples were used. One set of subsamples of bottom material (after compositing), native water, and deionized water were placed in clean, fired 1-liter glass bottles and sent to the Tennessee Valley Authority (TVA) Chemical Laboratory, Chattanooga, Tenn., for chemical analysis. Another set of subsamples of bottom material, native water, and deionized water was set aside for the study using standard elutriate methods developed by Keeley and Engler (1974). In three tests, bottom material from Bayou d' Inde was mixed with native water from either Bayou d' Inde, Calcasieu River near Kinder, or deionized water. A 1:4 volumetric ratio of bottom material to water was used in each test. Each mixture was placed in the mixer and vigorously mixed for 30 minutes. A part of the bottom material water mixture was poured into Imhoff cones immediately after mixing and rates of deposition were recorded (American Public Health Association and others, 1981). The remainder of the bottom material water mixture was placed in a clean, 16-liter glass carboy and refrigerated at 4 °C for 1 hour. After settling for 1 hour, half of the bottom material-water mixture was decanted into clean, fired, 1-liter glass bottles and sent to the TVA laboratory for analysis; this represents the fine material that would remain suspended in the water column after dredging. The other half of the mixture was centrifuged and then filtered using 1 μm (micrometer) effective pore size, glass- fiber filters in a positive pressure stainless-steel filter apparatus pressurized with ultrapure nitrogen gas. Filtered water was collected in clean, fired, 1-liter glass bottles and sent to the TVA Laboratory for analysis. All samples, bottom material and water, were analyzed according to U.S. Environmental Protection Agency (1979) method-625.

RESULTS AND DISCUSSION

Bottom material, native water, and deionized water were analyzed for acid-base/neutral organic compounds at the detection limits listed in table E-6. None of the compounds listed in table E-6 were present at detectable concentrations in water samples collected from Bayou d' Inde near its mouth, from the Calcasieu River near Kinder, or from the deionized water used in the remobilization study. These waters were selected because they represent conditions present in the Calcasieu River-Bayou d' Inde system during normal flow periods (Bayou d' Inde water), high runoff (Calcasieu River near Kinder water) and rainfall (deionized water). Simulated rainfall was investigated because dredging procedures used in the lower Calcasieu River commonly require disposal of dredged material in spoil banks bordering the navigation channels. The edges of these spoil banks have drainage pipes to allow rainwater to percolate down through the exposed spoil banks (bottom material) and discharge into the river.

Bottom material collected from Bayou d' Inde near an industrial outfall contained several organic compounds, such as hexachlorobenzene and hexachlorobutadiene in concentrations, as much as 50,000 μg/kg (micrograms per kilogram) (table E-7). The organic compounds detected in the bottom material are hydrophobic and generally restricted locally in their distribution to the Bayou d' Inde area of the Calcasieu River (Pereira and others, 1988; Demas, in press). Pereira and others (1988) reported that partition coefficients for octanol-Bayou d' Inde water, determined using methodology developed by Chiou and others (1982), were approximately 20 percent higher than those reported for the same compounds in distilled water. This implies that the solubility of these compounds in brackish water is reduced compared to freshwater. This decrease in solubility may account for the high concentrations of hexachlorobenzene and hexachlorobutadiene found in bottom material and the lack of detection of these same compounds in the overlying water column. Physical and chemical constituents recorded during time of collection (table E-8) indicate that salinity concentrations of 6.7 ppt at the mouth of Bayou d' Inde and 7.2 ppt at Bayou d' Inde at confluence with an industrial outfall canal were

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

Table E-6.—*Detection limits for acid-base/neutral extractable organic compounds analyzed in water samples collected from Bayou d' Inde and Calcasieu River near Kinder, Louisiana, and in deionized water, April 1987*

Organic compound	Lowest level of dectection (micrograms per liter)	Organic compound	Lowest level of dectection (micrograms per liter)
Acenaphthene	5.0	N-nitrosodimethylamine	5.0
Acenaphthylene	5.0	N-nitrosodi-N-propylamine	5.0
Anthracene	5.0	Nitrosodiphenylamine	5.0
Benzo[a]anthracene		Pentachlorophenol	5.0
1,2-benzathracene	5.0	Phenanthrene	5.0
Benzo[a]pyrene	10.0	Phenol	5.0
Benzo[b]fluoranthene	10.0	Pyrene	5.0
Benzo[g,h,i]perylene	10.0	1,2-Dichlorobenzene	5.0
Benzo[k]fluoranthene	10.0	1,2,4-Trichlorobenzene	5.0
Butyl benzyl phthalate	5.0	1,3-Dichlorobenzene	5.0
4-Chloro-3-methylphenol	30.0	1,4-Dichlorobenzene	5.0
Chrysene	10.0	Bis (2-chloroethoxy) methane	5.0
Di-n-Butyl phthalate	5.0	Bis (2-chloroethyl) ether	5.0
Di-n-Octylphthalate	10.0	Bis (2-chloroisopropyl) ether	5.0
Diethyl phthalate	5.0	2- Chloronaphthalene	5.0
Dimethyl phthalate	5.0	2-Chlorophenol	5.0
4,6-Dinitro-2-methylphenol	30.0	Bis (2-ethylheyl) phthalate	5.0
Fluoranthene	5.0	2-Nitrophenol	5.0
Fluorene	5.0	2,4-Dichlorophenol	5.0
Hexachlorobenzene	5.0	2,4-Dimethylphenol	5.0
Hexachlorobutadiene	5.0	2,4-Dinitrophenol	20.0
Hexachlorocyclopentadiene	5.0	2,4-Dinitrotoluene	5.0
Hexachloroethane	5.0	2,4,6-Trichlorophenol	20.0
Indeno (1,2,3-CD) pyrene	10.0	2,6-Dinitrotoluene	5.0
Isophorone	5.0	4- Bromophenyl phenyl ether	5.0
Naphthalene	5.0	4-Chlorophenyl phenyl ether	5.0
Nitrobenzene	5.0	4-Nitrophenol	30.0

similar to a salinity of 8.0 ppt for the Bayou d' Inde water used earlier to determine octanolwater partition coefficients.

The lack of detection of hexachlorobenzene and hexachlorobutadiene in the overlying water during previous studies indicated that the bottom material served as a sink for these compounds during brackish and saltwater conditions in Bayou d' Inde. Possible remobilization of these compounds was investigated by mixing bottom material from Bayou d' Inde near an industrial outfall with water collected from the mouth of Bayou d' Inde (specific conductance—12,300 μS/cm (microsiemens per centimeter) at 25 °C, salinity—6.7 ppt), Calcasieu River near Kinder (specific conductance—57 μS/cm, salinity—0.0 ppt) and deionized water (specific conductance—4 μS/cm, salinity—0.0 ppt). Previous studies using elutriate tests and actual dredge samples from brackish to saltwater areas of the Calcasieu River (Grimwood and others, 1977) and from brackish and saltwater areas of the Pacific Northwest (G.J. Fuhrer, 1989) have shown little remobilization of metals or organophosphorus insecticides from bottom material into saline waters. Data from the present study showed similar results in the lack of remobilization of the chlorinated organic

Table E-7.—*Organic compounds in three subsamples of bottom material from the mouth of an industrial outfall near Bayou d' Inde, Louisiana, April 15, 1987*
[ND, not detected]

Organic compound	Concentrations, in micrograms per kilogram		
	Subsample		
	1	2	3
1,2-Dichlorobenzene	ND	ND	2,300
1,3-Dichlorobenzene	ND	ND	470
1,2,4-Trichlorobenzene	7,600	7,700	8,100
Hexachlorobenzene	28,000	37,000	50,000
Hexachlorobutadiene	17,000	18,000	25,000
4-Chlorodiphenyl ether		14,000	14,000
4-Bromodiphenyl ether	ND	ND	9,900
Phenanthrene	5,800	5,800	5,800
Fluoranthene	5,700	5,500	5,500
Pyrene	ND	4,800	4,800
Hexachloroethane	ND	ND	1,100
Bis (2-ethylhexyl) phthalate	14,000	14,000	13,000

Table E-8.—*In situ measurements of physical characteristics of the Calcasieu River system, Louisiana, April 15, 1987*
[°C, degrees Celsius; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; ppt, parts per thousand; mV, millivolts]

Depth (meters)	Temperature (°C)	pH (units)	Dissolved oxygen (mg/L)	Specific-Conductance (µS/cm)	Salinity (ppt)	Oxidation-reduction potential (mV)
Calcasieu River near Kinder						
0.5	18.8	7.2	7.8	57	0.0	+84
Bayou d' Inde at mouth						
.5	24.6	8.8	9.4	12,300	6.7	+173
1.5	22.7	8.6	9.5	12,290	6.7	+174
2.8	22.0	8.4	9.0	12,330	6.7	+177
Bayou d' Inde near industrial outfall						
.5	29.4	7.4	9.0	13,120	7.3	+151
1.0	29.4	7.4	8.6	13,100	7.2	+153
2.5	28.0	7.4	8.8	13,050	7.0	+148

Note : For the purposes of this paper, salinities ranging from 6 to 12 parts per thousand are referred to as brackish.

compounds present in bottom material from Bayou d' Inde (table E-9). None of the compounds detected in the bottom material (table E-7) were detected in the unfiltered or filtered water sampled from the bottom material-Bayou d' Inde water mixture. This suggests that these organic compounds detected in Bayou d' Inde are strongly attached to the bottom material and do not readily dissolve into the water column during periods of brackish and saltwater presence in the Calcasieu River-Bayou d' Inde system. Also, settleable-matter data, which refers to the volume of suspended matter that settles out within a 1-hour period (table E-9), indicate relatively rapid deposition of the resuspended bottom material in the presence of brackish and saltwater. For example, 325 mL (milliliter) of material settled out of suspension in 1 hour in the Bayou d' Inde water-bottom material mixture. This appears to be the condition in Bayou d' Inde where concentrations of these organic contaminants in bottom material decrease substantially in a downstream direction from the entrance of the industrial outfall canal (Pereira and others, 1988). This indicates that the organic contaminants are associated with particulate matter that settles out rapidly in the presence of saltwater.

Bottom material-low ionic strength water mixtures, in contrast to the brackish water mixtures, showed a significant increase in 1,2-dichlorobenzene and hexachlorobutadiene concentrations (table E-9). 1,2-dichlorobenzene was detected at the 7- and 8-μg/L (micrograms per liter) level in the Calcasieu River near Kinder unfiltered and filtered water mixture samples and at the 7-μg/L level in the unfiltered deionized water mixture sample. It was not detected in the filtered deionized water sample. Hexachlorobutadiene was detected at the 15-μg/L level in the unfiltered deionized water mixture sample only. It appears that the compounds detected in the two low ionic-strength samples are associated with colloidal material that was resuspended during the mixing process. J.A. Leenher (U.S. Geological Survey, oral commun., 1987) reported that suspended sediment transported in the Calcasieu River was predominantly in the 0.7- to 0.2-μm range which will pass through the 1.0- μm glass-fiber filter used in processing water samples for organic analysis. Settleable-matter data further support this observation. For example, only 10 mL/L (milliliter per liter) of material in the Calcasieu River near Kinder sample and 15 mL/L of material in the deionized water sample settled out in 1 hour. In contrast, 325 mL/L of material settled out from the Bayou d' Inde sample during the same time period, indicating that, once suspended in low ionic-strength water, contaminated bottom material from Bayou d' Inde could be transported downstream until it comes

Table E-9.—*Organic compounds detected in elutriate samples, and settleable matter results from Bayou d' Inde bottom material exposed to water of three ionic strengths*
[BDI = water from Bayou d' Inde at mouth; Kinder = water from Calcasieu near Kinder; LAB = deionized water; μg/L, micrograms per liter]

Sample type	Organic chemicals	Settleable matter (milliliters per liter)
BDI total elutriate	None	325
BDI filtered elutriate	None	
Kinder total	1,2-dichlorobenzene at 7 μg/L	10
Kinder filtered	1,2-dichlorobenzene at 8 μg/L	
LAB total	1,2-dichlorobenzene at 7 μg/L; hexachlorobutadiene at 15 μg/L	15
LAB filtered	None	

in contact with brackish or saltwater and settles out. This suggests that dredging activities in the lower Calcasieu River-Bayou d' Inde area be conducted only during periods when brackish or saltwater is present in the system to minimize dispersion and remobilization of organic contaminants present in the bottom material. Also, by avoiding disposal of any dredged material in spoil banks from contaminated areas, possible remobilization of chlorinated organic compounds on exposure to rain could be minimized.

Although concentrations of 1,2-dichlorobenzene and hexachlorobutadiene remobilized into the low ionic-strength waters were small compared to the concentrations detected in bottom material, their potential environmental effects may be significant. Pereira and others (1988) reported bioconcentration factors ranging from 3.79 to 4.46 for 1,2-dichlorobenzene, and 3.97 to 4.50 for hexachlorobutadiene for three species of finfish and one species of shellfish collected from the Calcasieu River-Bayou d'Inde area. They also reported that concentrations of chlorinated organic compounds in these organisms were in equilibrium with the concentrations reported for water and suspended sediment and not in equilibrium with bottom material. Concentrations of the chlorinated organic compounds, such 1,2-dichlorobenzene and hexachlorobutadiene, were detected in the 0.001- to 1.3-μg/L range in water. The concentration of hexachlorobutadiene in blue catfish, *Ictalurus furcatus*, captured concurrently with collection of the water samples during Pereira's study, was 4,100 μg/kg. If, in fact, these aquatic organisms do reach equilibrium with concentrations of these organic compounds in the water column, then, the increase in concentrations of 1,2-dichlorobenzene and hexachlorobutadiene observed in the low ionic-strength mix waters could result in a significant increase in biological uptake of these compounds. This increase in biological uptake could occur in the contaminated areas if bottom material in these areas were mixed with low ionic-strength waters during dredging operations.

SUMMARY AND CONCLUSIONS

Bottom material from Bayou d' Inde near an industrial outfall canal, water from Bayou d' Inde, Calcasieu River near Kinder, and deionized water were analyzed for acid-base/neutral organic compounds. Analytical results indicate that high concentrations of chlorinated organic compounds were present in bottom material and absent from corresponding water samples. Modified elutriate tests were performed on the Bayou d' Inde bottom material and water to determine how strongly the chlorinated organic compounds were attached to bottom material and whether remobilization would occur on exposure to different ionic-strength water. Tests indicated that mixing of bottom material with Bayou d' Inde brackish water resulted in no remobilization of organic compounds from bottom material. Low ionic-strength waters represented by Calcasieu River water near Kinder and deionized water, in contrast, resulted in remobilization of 1,2-dichlorobenzene and hexachlorobutadiene into the water at concentrations ranging from 7 to 15 μg/L, respectively. On the basis of these results, resuspension of contaminated bottom material during periods of freshwater inflow potentially could adversely affect the water quality of the lower Calcasieu River.

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THE USE OF RADON-222 AS A TRACER OF TRANSPORT ACROSS THE BED SEDIMENT-WATER INTERFACE IN PRIEN LAKE, LOUISIANA

By Charles R. Demas,[1] Philip B. Curwick,[2] and Dennis K. Demcheck[1]

ABSTRACT

Data from flux-chamber studies (December 1987 through February 1988) and analyses of core samples from Prien Lake, Louisiana, indicate a net movement of radon-222 from the bed sediment to the overlying water column. Apparent diffusion coefficients calculated from core and flux measurements exceeded the calculated molecular diffusion coefficient by two to seven times. Results indicate that factors, such as physical diffusion stirring of the bed sediments and increased water movement from the bed caused by wind-magnified tides and bubbling of gases such as methane from the bed sediment, may accentuate the movement of radon from the bed sediment to the overlying water column.

The movement of radon-222 from the bed sediments to the overlying water column indicates that mechanisms exist for the movement of organic compounds and trace elements present in the interstitial pore water to the overlying water column.

INTRODUCTION

Chemical transport across the bed sediment-water interface is one of the most important processes regulating the chemical composition of overlying water of lakes and estuaries (Martens and others, 1980). Striking differences in chemistry commonly exist between pore water and the water above the interface. For example, the overlying waters are usually oxygenated and relatively depleted in nutrients. Interstitial waters in these environments usually are anaerobic very near the bed-sediment surface and enriched in nutrients, manmade organic compounds, and some trace elements. Thus, bed sediments consume oxygen from, and return nutrients and possibly some organic compounds and trace elements to, the overlying water column. The movement of substances dissolved in pore water across the bed sediment-water interface can have a major effect on the water quality of the overlying water (Hammond and others, 1977).

Previous studies (Pereira and others, 1988; Demas, in press) have detected large concentrations of manmade organic compounds and some trace elements in the bed sediment in the lower Calcasieu River system (fig. E-5). This study was undertaken to determine if transport of organic compounds and trace elements is occurring between interstitial pore water and the overlying surface waters. Prien Lake (fig. E-5) was selected for study on the basis of grain-size distribution in the bed sediment and results of previous work (T.F. Kraemer, U.S. Geological Survey, written commun., 1988). The radon- 222 (^{222}Rn) analysis requires that a bed-sediment sample be an equal mixture of sand and fines because ^{222}Rn in pore water moves too rapidly for accurate measurements in porous sand-bed sediment and, conversely, movement of ^{222}Rn in pore water is too slow in clay-bed sediment.

This paper evaluates the usefulness of ^{222}Rn as a tracer to estimate the rate of transport of water-soluble compounds across the bed sediment-water interface in the lower Calcasieu River system. Flux chambers were deployed in Prien Lake, La., starting in late December 1987 and ending in early February 1988 to determine movement of ^{222}Rn from the bed sediment to the overlying water column. Core samples also were collected to verify flux- chamber results and provide information on diffusion coefficients of ^{222}Rn in Prien Lake.

DATA COLLECTION AND ANALYSIS

Three approaches can be employed to estimate the rate of transport of dissolved substances across the bed sediment-water interface: (1) direct measurement of flux to overlying water either in core samples returned to the laboratory or in a confining device placed on the bed-sediment surface, (2) measurement of gradients in interstitial waters and calculation of diffusive flux, and (3) construction of a mass balance for a

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[1] U.S. Geological Survey, Baton Rouge, La.

[2] Ecotech, Baton Rouge, La.

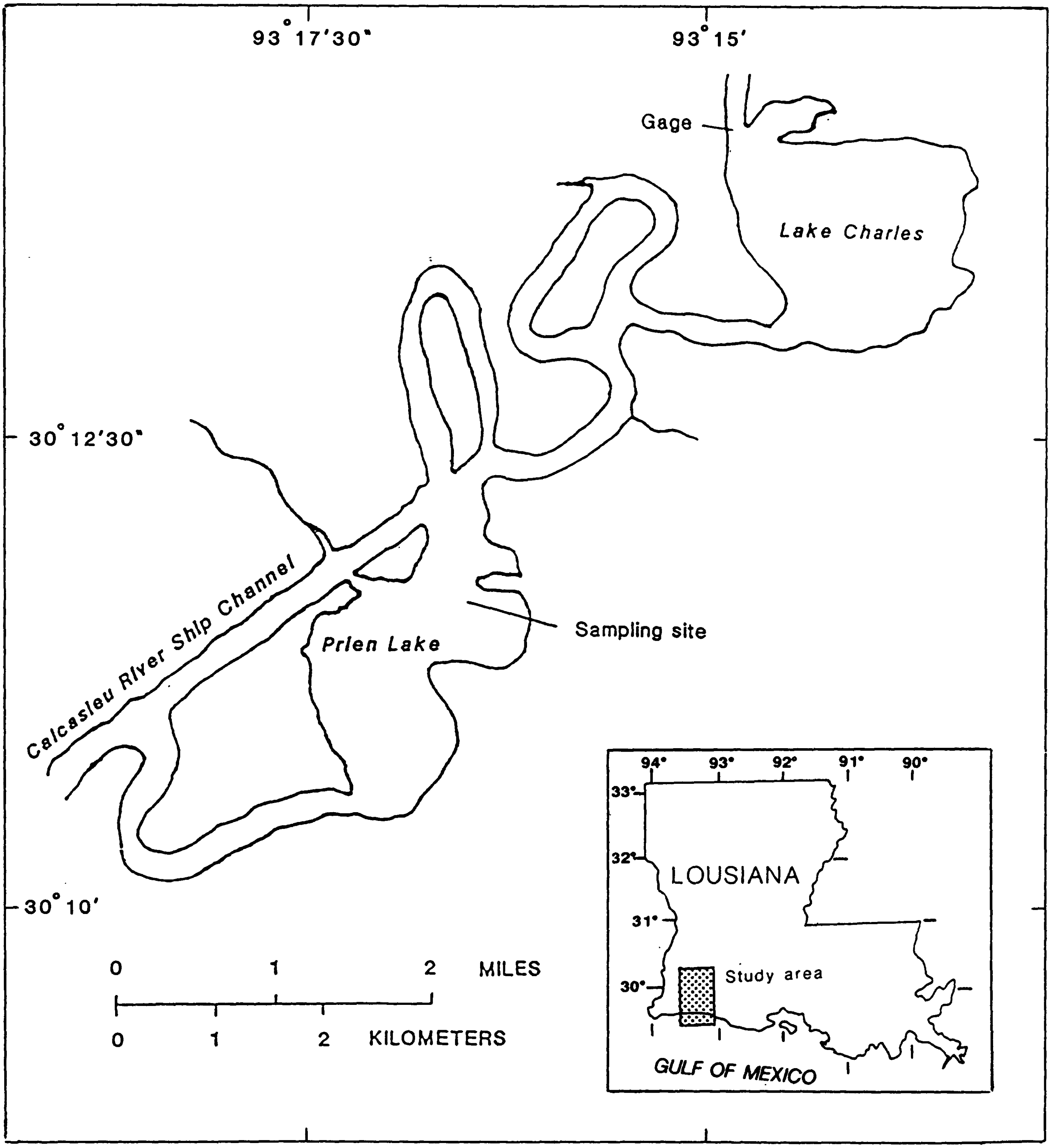

Figure E-5.—Radon-222 tracer study area, Prien Lake, Louisiana.

substance in the water column that includes transport to or from the bed sediments (Hammond and others, 1977). The direct-measurement approach was used for this study, and fluxes were measured in core samples and confining devices.

Theory

Naturally occurring ^{222}Rn can be used as a tracer to estimate the rate of transport across the bed sediment-water interface. As a noble gas, ^{222}Rn (half-life 3.83 days) is free of biological interactions and, therefore, its distribution is controlled by a balance between diffusion and advection, radioactive decay, and production from its parent, radium-226 (^{226}Ra) (half- life 1,600 years) (Hammond and others, 1977; Key and others, 1979; Martens and others, 1980). The short half-life of ^{222}Rn indicates that ^{222}Rn should be in secular equilibrium with ^{226}Ra (that is, the decay rate of ^{222}Rn equals the decay rate of ^{226}Ra) within the bed sediment. ^{226}Ra is associated with the bed sediment particles and, therefore, is enriched within the bed sediment by several orders of magnitude over its concentration in the water column. Much of the ^{222}Rn produced from the ^{226}Ra in the bed sediment diffuses to the surrounding pore water, causing an enrichment of ^{222}Rn in the pore water in contrast to ^{222}Rn activity in the water column. Because of the large concentration gradient between pore water and surface water, ^{222}Rn diffuses upward, forming a radon deficit (the difference between ^{222}Rn concentration predicted from ^{226}Ra decay and the actual ^{222}Rn concentration) in the upper 10 to 20 cm (centimeters) of the bed sediment (Key and others, 1979). The amount and depth within the bed sediment of the deficit are controlled in quiescent bed sediment by molecular diffusion. However, transport of ^{222}Rn to the overlying water column can be enhanced when physical stirring and biological movement of the bed sediment occurs. This results in an increased ^{222}Rn deficit observed in the bed sediment at depths greater than the 10 to 20 cm caused by molecular diffusion.

The general equation describing radon distribution in the bed sediment assuming a constant diffusion coefficient and porosity is

$$dC/dt = (d/dz)[D_s(dC/dz)] + \lambda \times C_{eq} - \lambda \times C, \qquad (1)$$

where

d = total depth;

C = measured ^{222}Rn concentration, in atoms per cubic centimeter or disintegrations per minute per cubic centimeter of bulk bed sediment;

t = deployment time, in seconds;

z = distance to the bed sediment from the interface, in centimeters;

D_s = diffusion coefficient for ^{222}Rn in bed sediment including the effects of tortuosity and porosity, in square centimeters per second;

λ = decay constant for ^{222}Rn and is equal to 2.098×10^{-6} per second; and

C_{eq} = ^{222}Rn concentration in pore space in equilibrium with sedimentary ^{226}Ra (or the concentration of radon deep within the bed sediment where upward diffusion is insignificant).

If the following simple boundary conditions are applied:

$C = C_{eq}$ at Z = infinity, and $C = C_o$ at $z = 0$,

the steady-state solution to the above equation is:

$$C = C_{eq}[1 - \exp -(\lambda/D_s)\, 0.5\, zt] + C_o \exp[-(\lambda/D_s)\, 0.5\, z]. \qquad (2)$$

The flux of radon across the bed sediment-water interface may be obtained by differentiating the above equation for the interface concentration gradient and applying Fick's first law,

$$J = -D_s(dC/dz) \text{ at } z = 0 \qquad (3)$$

to yield, .

$$J = -(\lambda \times D_s)\, 0.5\, (C_{eq} - C_o) \qquad (4)$$

Flux Measurement

Transport rates of ^{222}Rn across the bed sediment-water interface were determined by use of two variations of the direct measurement method. The first variation by direct measurement used *in situ* chambers placed on the bottom of the lake by divers from which ^{222}Rn was measured and compared between chambers open and closed to the bed sediment of the lake. The second variation by direct measurement involved integrating the depth deficiency of

^{222}Rn versus ^{226}Ra in core samples from the bed sediment of the lake.

In situ fluxes of ^{222}Rn from the bed sediment were measured using aluminum chambers originally designed and operated by Region IV of the U.S. Environmental Protection Agency (USEPA) for sediment oxygen- demand studies. The chamber is a cylinder with a center core that forms an annular ring (fig. E-6). The lid is fastened to the top of the chamber with four wing nuts. The lid is removed during deployment, which facilitates purging of the chamber as it passes through the water column. Divers positioned the chamber on the bottom of the lake and then lowered and fastened the lid. The chamber in the deployed position isolates 65 liters of water over 0.27 m^2 (square meter) of the bed sediment.

Water is circulated within the chamber by a 12-volt direct contact pump delivering approximately 600 liters per hour through diffusers. Because of the annular design and orientation of the diffusers, a unidirectional flow of about 0.02 to 0.03 m/s (meter per second) is attained over the bottom. Further details of the chamber design are given by Murphy and Hicks (1986).

Once the chamber and lid are in position, divers extract water samples of approximately 200 mL (milliliters) per sample. Duplicate samples were collected from each chamber. These samples were drawn into evacuated samplers through a short tube with a valve extending from the chamber, sealed and brought to the surface to be analyzed for ^{222}Rn.

Gradient Measurement

Sedimentary ^{222}Rn and ^{226}Ra activities were obtained from hand cores. The corer was 4.7 cm in diameter, 51 cm in length, and had a plastic or stainless steel liner. The cores were extruded and sectioned into 2.5- to 5.1-cm-long segments with the aid of a plunger forced up from the bottom of the core liner. These segments were transferred and sealed in glass flasks containing approximately 200 mL of ambient water. The mixture was then agitated to form a slurry. The ^{222}Rn was removed by bubbling ambient air through the slurry and extracting the ^{222}Rn into Lucas cells. ^{226}Ra was determined by the same procedure after the radon-free slurries were resealed for a minimum of 2 weeks to allow ingrowth of the daughter, ^{222}Rn. The ^{222}Rn determined after this 2- week period represents the ^{222}Rn concentration (C_{eq}) in equilibrium with sedimentary ^{226}Ra. Sedimentary ^{222}Rn/^{226}Ra activities were calculated using C and C_{eq} (Hammond and others, 1977; Hartman and Hammond, 1984).

^{222}Rn activities in both the water and sediment slurries were counted in a Lucas-type cell constructed of acrylic plastic using a dual counting system. The alpha particles emitted from ^{222}Rn decay produce scintillations on the activated zinc sulfide coating inside the counting cell. Photons of light emitted are detected by a photomultiplier tube and counted in a light-tight cylinder. Each cell was calibrated against a standard of known activity of ^{222}Rn in water.

The radon counting equipment was set up in the Louisiana District Laboratory of the U.S. Geological Survey after the first deployment and in a hotel located near the lake after the second deployment. Duplicate water samples were collected from the flux chambers. Duplicate samples were analyzed on both photomuliplier tubes to remove any bias in the results from using one tube over the other.

RESULTS

Experiments in Prien Lake were conducted in late December 1987 through February 1988. The flux chambers were deployed two times at two locations in the lake that ranged in depth from 0.91 to 1.52 meters during the studies. Initial radon concentrations were measured in both the open and closed flux chambers at time of deployment. Background radon concentrations were measured in the closed flux chamber that contained only near-bottom water. ^{222}Rn activity increased in chambers opened to the bed sediment on both occasions (table E-10). Little or no increase in ^{222}Rn activity was observed in the chambers closed to the bed sediment, indicating negligible production of ^{222}Rn within the water column.

The increases in radon concentration in the chambers were used to calculate the ^{222}Rn flux. By definition the flux per unit area can be calculated as

$$J = \frac{V \times \lambda[C_t\, C_o \exp(-\lambda \times t)]}{A[1 - \exp(-\lambda \times t)]} \qquad (5)$$

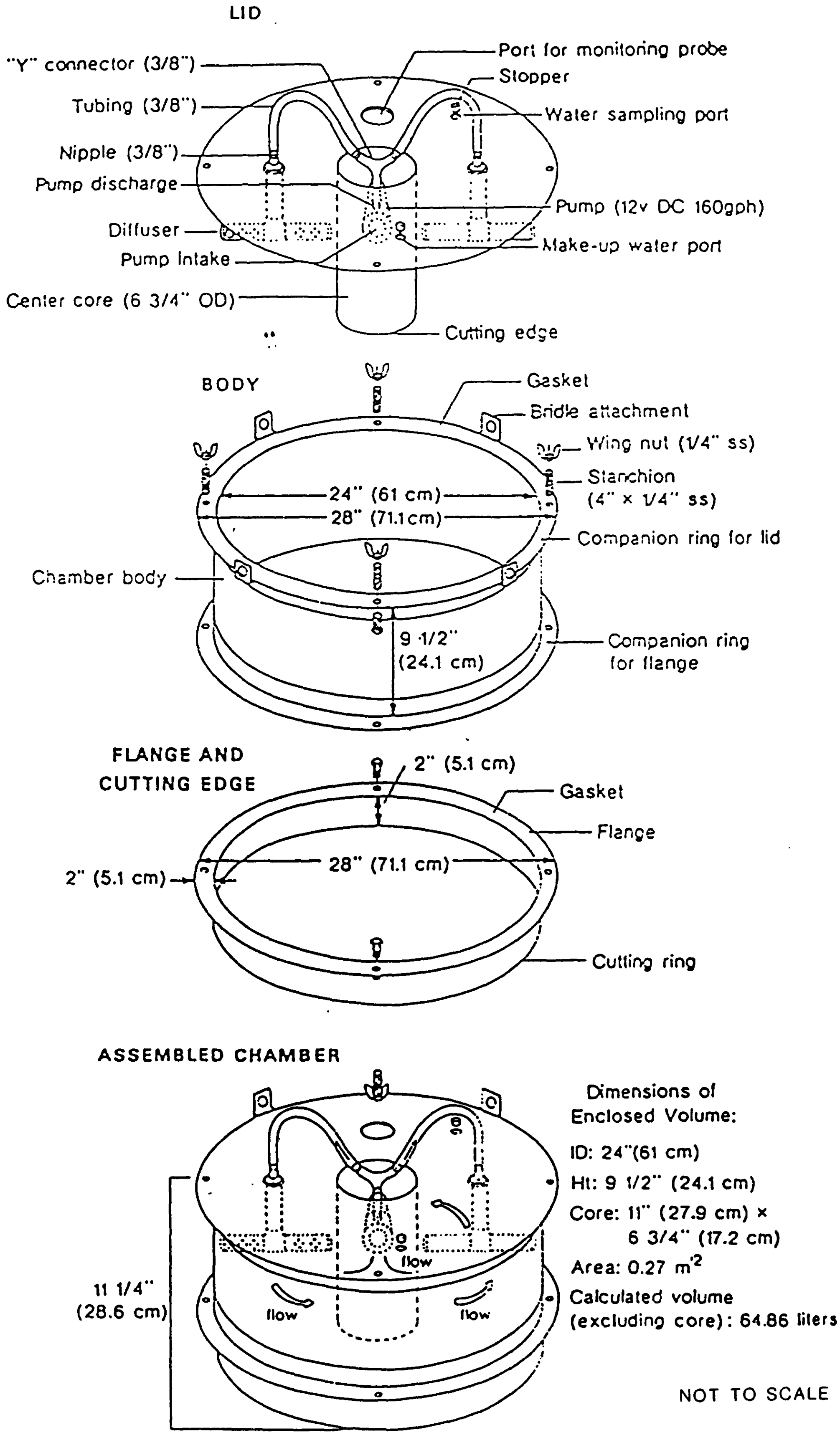

Figure E-6.—Schematic of *in situ* flux chamber.

Table E-10.—*Activity of radon-222 in flux chambers deployed in Prien Lake, Louisiana*

[Dpm/L, disintegrations per minute per liter]

Date	Sampling time	Radon-222 activity Closed chamber (dpm/L)	Radon-222 activity Open chamber (dpm/L)	Time (hours)
		First deployment		
12-23-87	10:30	2.1	0.4	0.0
1- 6-88	09:30	1.9	19.3	360.0
1-13-88	11:15	3.3	12.6	528.8
		Second deployment		
1-27-88	14:00	2.0	2.3	0.0
1-29-88	10:00	1.6	26.8	44.0
2- 1-88	11:30	4.0	29.3	117.5
2- 9-88	15:00	1.4	19.3	313.0

where V is the total volume of the chamber, A is the surface area of the bed sediment trapped by the chamber and is calculated using the radius of the chamber, and t is the time between taking the initial (C_o) and final (C_t) radon concentrations. Flux values for the open chambers ranged from 51 to 357 (atoms/m^2)/s (atoms per square meters per second) (table E-11). These values indicate positive movement of radon from the bed sediment to the overlying water column. The positive fluxes observed for the open chambers indicate that mechanisms exist for the movement of organic compounds and trace elements present in the interstitial pore water with the overlying water column.

Data from ^{222}Rn studies on core samples collected from Prien Lake support results from the flux-chamber studies. Core data (table E-12) show a ^{222}Rn deficit decreasing with depth in the upper 20 cm of the bed sediment (fig. E-7). These profiles are similar to those described by Hammond and others (1977), Key and others (1979), and Hartman and Hammond (1984) and indicate net movement of ^{222}Rn from the upper layers of the bed sediment to the overlying water column.

Apparent diffusion coefficients were calculated from equation 3 and the fluxes measured in table E-11. These values can be compared to the molecular diffusivity of ^{222}Rn in water, $D = 1.37 \times 10^{-5}$ 25 °C (degrees Celsius). In bed sediment, this value must be reduced for the effects of tortuosity and porosity. Estimating the tortuosity of Prien Lake bed sediment as 1.10 and a porosity of 85 percent the adjusted molecular diffusivity is $D_s = eD/t \times t = 0.96 \times 10^{-5}$ cm^2/s (square centimeters per second). In contrast, diffusion coefficients in table E-11 range from 2.6 to 7.4×10^{-5}. These results indicate that other processes, in addition to molecular diffusion, may play a role in the upward migration of dissolved-chemical species in Prien Lake. Other commonly identified processes that transport dissolved species through interstitial waters and across the bed sediment-water interface include bioturbation of bed sediments by burrowing benthic organisms and physical stirring of bed sediments by wind-driven waves and tidal currents. The relatively shallow depths (0.91-3.04 meters) of this lake would aid the physical stirring of bed sediments by wind-driven waves and windmagnified tides. Tidal currents in the lower Calcasieu River-Prien Lake system are not normally strong enough to cause significant resuspension of bed sediments; however, this was not the condition during the two deployment periods. During both studies, strong northerly winds prevailed, and stages at the Lake Charles gage (fig. E-8) showed a wide

Table E-11.—*In situ radon-222 sediment-water flux and calculated apparent sediment diffusivities*

[--, core not collected]

Date	Time (hours)	Radon flux (atoms per square meter per second)		Diffusivity (square centimeters per second)
		Individual	Mean	
		First deployment		
1- 6-88	360.0	298	298	--
1-13-88	528.0	51	174	--
		Second deployment		
1-29-88	44.0	357	357	7.4 × 10-5
2- 1-88	117.5	194	275	4.4 × 10-5
2- 9-88	313.0	85	212	2.6 × 10-5

range in tidal fluctuations from the Gulf of Mexico. The variations in tide stages resulted in large changes in water levels at Prien Lake. Radon activity did not increase at a constant rate in the open chambers, which can partially be explained by the increased water movement from the bed sediment to the chambers because of the pumping action caused by the fluctuating water levels. This same phenomenon was observed by Hammond and others (1977) in the Hudson River Estuary, N.Y., along the shoreline and shallower sections that were most affected by the changing water levels caused by tidal action.

Enhanced fluxes also may result from bubbling caused by significant methane and ammonium ion production in organic-rich flocculent material that rests on the bottom of the lake (Martens and others, 1980). This phenomenon may partially explain the enhanced fluxes observed for the Prien Lake samples. Divers noted gas bubbles emanating from the bed

Table E-12.—*Distribution of radon-222/radium-226 within a bed-sediment core collected from Prien Lake, Louisiana, January 1988*

Depth from surface (centimeters)	Radon-222/Radium-226 activity ratios
0- 3	0.52
3- 6	.64
6- 9	.84
9-12	.85
12-15	.82
15-21	.90
21-27	1.00
27-33	.89
33-39	1.00
39-48	.93

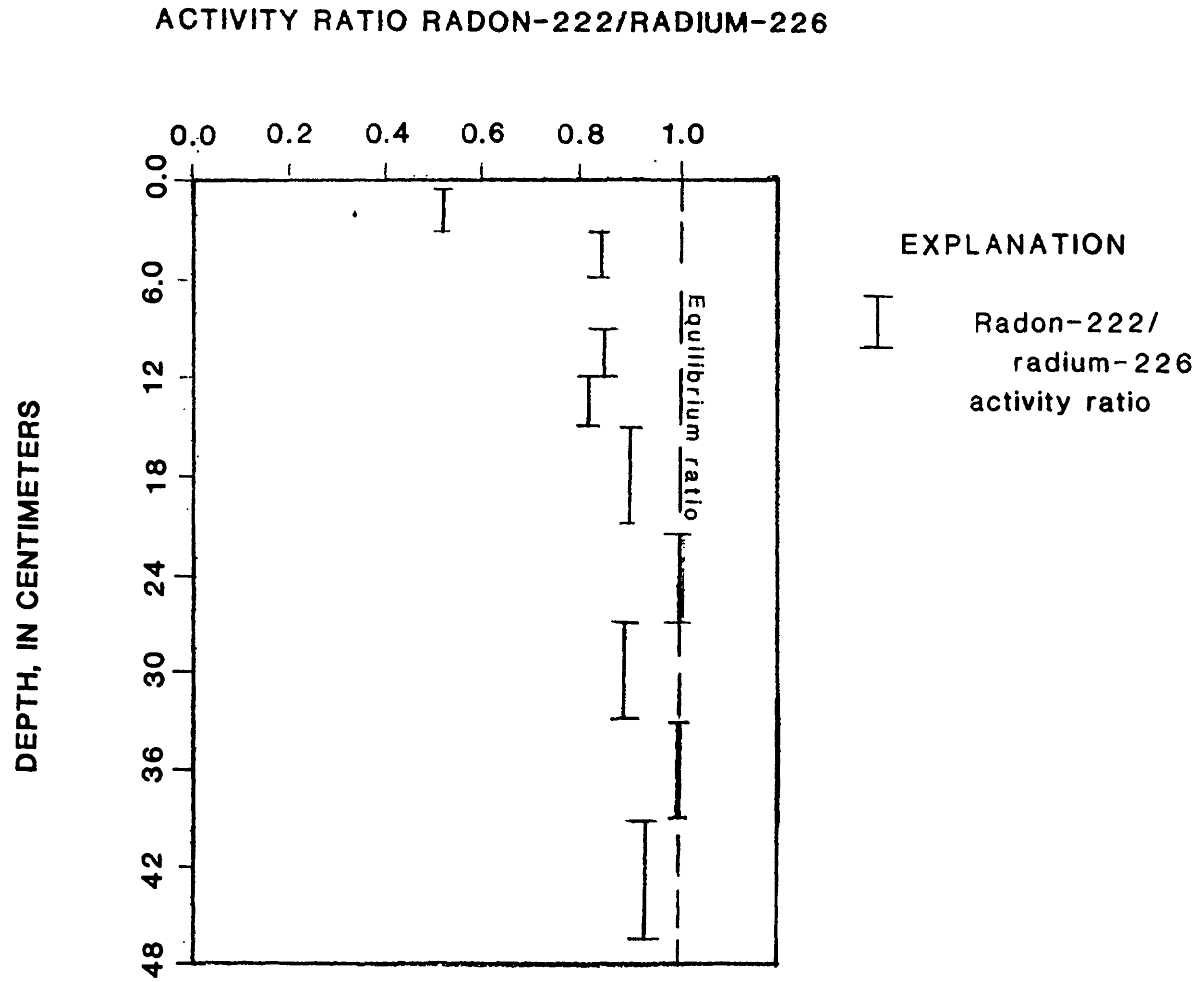

Figure E-7. – Profile of activity ratios of actual radon-222/radium-226 supported radon-222 in a sediment core from Prien Lake, Louisiana.

sediment in Prien Lake several times during the deployment and collection phases of the study. Also, some gas pockets were observed at different depths in core samples collected for radon from Prien Lake.

CONCLUSIONS

^{222}Rn flux-chamber studies conducted during two periods in late December 1987 through February 1988 showed little change in activity in chambers closed to the bed sediment of Prien Lake and significant increases in chambers open to the bed sediment. Results indicated that negligible radon production occurred in the water column compared to radon generated from bed sediment. Flux values calculated from the open chambers ranged from 51 to 357 (atoms/m^2)/s. These values indicate movement of radon from the bed sediment to the overlying water column.

Data from ^{222}Rn studies of a core sample collected from Prien Lake supported conclusions drawn from the flux-chamber studies. Core data showed ^{222}Rn deficits decreased with depth in the upper 20 cm of the bed sediment, indicating a net movement of radon from the bed sediment to the overlying water column.

Apparent diffusion coefficients calculated from core and flux measurements exceeded the calculated molecular diffusion coefficient by two to seven times. Results indicate that factors, such

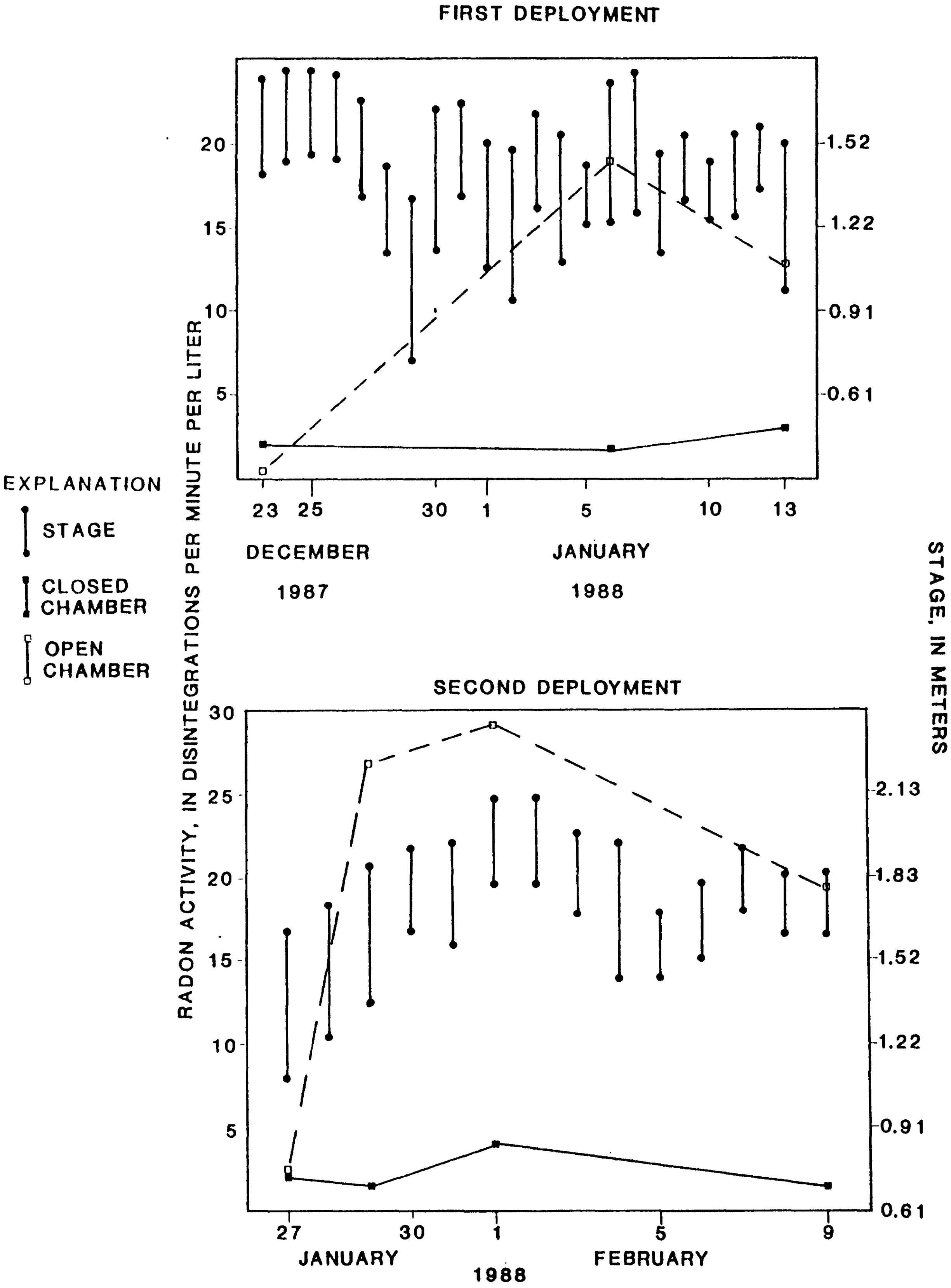

Figure E-8—Water stage changes at the Lake Charles gage in relation to radon-222 activity in flux chambers during two deployment in Prien Lake, Louisiana,December 1987 through February 1988.

as physical stirring of the bed sediments and increased water movement through the lake bed caused by wind-magnified tides, and bubbling of gases, such as methane, from the bed sediments may accentuate the movement of radon from the bed sediment to the overlying water column.

The movement of radon from the bed sediment to the overlying water column indicate that mechanisms exist for the movement of organic compounds and trace elements present in the interstitial pore water to the overlying water column.

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PHASE ASSOCIATION OF TRACE METALS IN SEDIMENTS FROM THE CALCASIEU RIVER, LOUISIANA

By Nancy S. Simon

ABSTRACT

Statistical evaluation of data from a detailed study of extraction techniques for sediments has resulted in the identification of four mechanisms for retention of chromium by bottom sediments in the Calcasieu River, Louisiana. Chromium is partitioned in iron-oxide phases, manganese-oxide phases, labile organic matter, and refractory organic matter. Chromium retained by sediment in cores collected either upstream or downstream from petrochemical plant outfalls is associated with iron oxides and with organic matter subject to degradative reactions. In sediment taken from two sites close to petrochemical discharge, manganese oxides and refractory organic matter played major roles in the retention of chromium by sediment solids. These conclusions were based on sediment organic-carbon and nitrogen data, sediment total metal-concentration data, surface- adsorption studies, data from extractions with pyrophosphate-plus-hydrogen peroxide or hydrogen peroxide-plus-dilute hydrochloric acid, and interstitial-water metal analyses. The data indicate that the difference between chromium retention by metal oxides or organic matter could be inferred by using only the extraction data and the sediment organic-carbon and nitrogen data. Identification of metal phase association is a factor in determining metal bioavailability and mobility. Organically bound chromium could be mobilized in either oxic or anoxic environments or, possibly, under acidic conditions. Chromium associated with metal oxides could be mobilized in reducing or acidic conditions.

INTRODUCTION

The U.S. Geological Survey standard technique I-5485-78 (Skougstad and others, 1979, p. 19) is used to destroy organic matter in, and desorb and solubilize readily acid-soluble metals from, bottom sediment material. The metal-concentration data obtained by using this technique are thought to be related to the amount of metals in surface coatings—that is, the recoverable metals from the sediment sample. The recoverable metals associated with organic matter are considered to be the bioavailable metals (Gupta and Chen, 1975). Data from a reconnaissance study in 1985 of sediment from the Calcasieu River indicated that only concentrations of iron, manganese, and chromium were above background levels (C. R. Demas, U.S. Geological Survey, oral commun., 1985). Chromium is a trace metal on the hazardous substances list published by the U.S. Environmental Protection Agency. This paper describes the phase associations of chromium in Calcasieu River sediments by using data from extraction techniques that are readily available.

METHODS

Four sediment cores were collected with a gravity corer in May 1986 at sites Buoy 130 (B-130), Bayou d' Inde (BDI), Citgo, and Burton Landing (Burton) (fig. E-9). The cores were sectioned in a nitrogen-filled glove box and the material was transferred to screw-capped centrifuge tubes. After centrifugation, the tubes were returned to the nitrogen-filled glove box and the supernatant was filtered through 0.2-μm (micrometer) polycarbonate membranes and transferred to glass vials. The volume of extractable water for several samples was too small for chemical analyses. Interstitial-water ammonium and adsorbed ammonium were determined on site by using an ammonia electrode and the method described in Simon and Kennedy (1987, p. 13). Filtrates collected for metal analyses were acidified with distilled ultrapure nitric acid to a pH of approximately 2. Samples for anion analysis were diluted with ion-chromatography eluent. The vials containing interstitial-water samples were chilled and returned to the laboratory. The interstitial-water concentrations of chloride, bromide, sulfate, and orthophosphate were determined in the laboratory using separator-suppressor ion chromatograph and the procedure of Simon and Kennedy (1987).

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

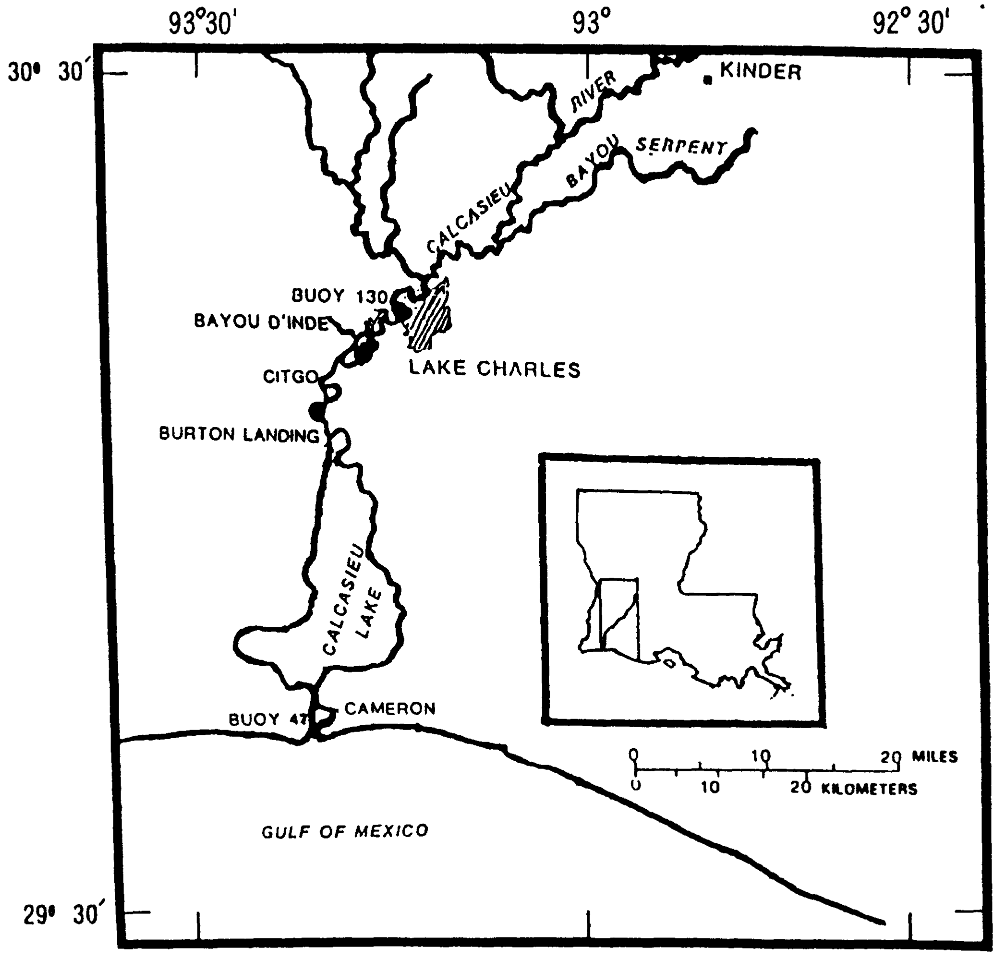

Figure E-9.—Calcasieu River surface water toxics study area.

Chromium, manganese, and iron analyses were done using atomic absorption spectrophotometry. The standard deviation for chromium, manganese, and iron was 10 + 1 ppb (parts per billion) equivalent to micrograms per gram. National Bureau of Standards "Trace Elements in Water, 1643b" was used as a control.

The sediment remaining in the centrifuge tubes was chilled and returned to the laboratory where it was freeze-dried and ground to pass through an 80 mesh sieve in preparation for extraction procedures. Laboratory tests have shown that there is no statistical difference between extraction data from air-dried and freeze-dried sediment (N.S. Simon, unpublished data on file at the U.S. Geological Survey in Reston, Va.). The extraction techniques included (1) oxidation of organic matter with 30-percent hydrogen peroxide and extraction with 0.2 percent isothermally distilled hydrochloric acid, and (2) oxidation of organic matter with hydrogen peroxide in the presence of 0.25 μmol (micromole) sodium pyrophosphate. The treatment with peroxide-plus-dilute hydrochloric acid is the method used for total recoverable metals in sediments used by the U.S. Geological Survey, as described by Skougstad and others (1979, p. 19). The treatment with peroxide-plus-pyrophosphate that is done at a pH of approximately 8, is a modification of the method that uses peroxide-plus-hydrochloric acid. The peroxide oxidizes organic matter, and the pyrophosphate extracts organically-bound iron and associated organic matter and complexes solubilized iron to prevent its loss from solution through precipitation or resorption by the solid phase. Solutions were analyzed in replicate for chromium, manganese, and iron using an atomic absorption spectrophotometer with Zeeman correction. Use of the Zeeman correction eliminated the need to extract the samples to prevent interferences during atomic absorption analysis. Analyses for sediment total-metal concentrations in cores collected in May 1986 were done by U.S. Geological Survey Branch of Analytical Services, Geologic Division, using

$HF/HNO_3/HClO_4$ digests and inductively-coupled-plasma spectrophotometry.

RESULTS

Concentrations of ammonium and selected trace metals in interstitial water and adsorbed ammonium data from the sediment cores collected in May 1986 are presented in table E-13. Adsorbed ammonium and concentrations of interstitial-water ammonium were the highest at sites B-130 and BDI. At these sites the concentrations of chromium in interstitial water were higher than at Citgo and Burton sites. Rapid decreases in sulfate concentration in interstitial water occurred with depth in the sediment at sites B-130 and BDI.

Total extractable metal-concentration data for sediment from cores collected in May 1986 are presented in table E-14. A summary of the statistical evaluation of cores collected in May 1986 is presented in table E-15. A discussion of the salient statistics for each location is given below. Positive correlations among the concentrations of metals in the sediments indicates similarities among diagenetic processes affecting metal concentrations.

Total chromium concentrations were similar for all sediment samples. At B-130 the total chromium concentrations in sediment were slightly, although not significantly, lower. The chromium concentrations in the sediments from the B-130 and Burton sites, which are upstream and downstream from inputs from petrochemical plants, are correlated, at a value of greater than 0.90, with the total iron and manganese concentrations. Chromium concentrations are less well correlated with total iron and total manganese at the BDI site and not correlated at all at the Citgo site. These two sites are affected by local inputs from petrochemical plants.

Total iron and manganese concentrations in sediments were variable. At the B-130, BDI, and Burton sites the correlation coefficients for total sediment iron and manganese were greater than 0.90. All total metal concentrations in the sediment from the Citgo site are poorly correlated.

At site B-130, chromium concentrations, in interstitial water and sediment extracts, consistently correlate positively with the corresponding iron concentrations. Chromium can coprecipitate with iron. The data imply that this mechanism occurs at this site. There is also a strong correlation between iron and chromium in the peroxide-plus-pyrophosphate extract that could indicate that chromium was present associated with organic matter or was present as a sulfide. The correlation between chromium in interstitial water and organic carbon in sediment was positive. This could indicate that degradation of carbon was not contributing to the increase in interstitial-water concentrations of chromium with depth. Because there was a rapid decrease in sulfate concentration in interstitial water, the presence of sulfides in the sediment is likely. These data indicate that chromium could be present as sulfides rather than associated with organic matter. Chromium sulfide would not be subject to dissolution in the bed sediments.

At the BDI site, chromium concentrations correlate most often with manganese concentrations. Chromium can coprecipitate with iron. Although there is a correlation of chromium with iron in the peroxide-plus-hydrochloric acid extraction data, the dominant phase association appears to be with manganese oxides. There appears to be no correlation between chromium concentrations and organic carbon.

For the Citgo site data, the only significant correlation of chromium is with the iron in the solution that resulted from extraction of sediment with hydrogen peroxide and pyrophosphate. This combination can extract iron associated with organic matter. Pyrophosphate is thought to have little effect on amorphous or crystalline iron (Bascomb and Thanigasalam, 1978, p. 386; Pickering, 1981, p. 243). Organic carbon and sulfides can be oxidized by peroxide. The source of the chromium extracted in the procedure could therefore be either organic carbon or a sulfide phase. The carbon-to-nitrogen (C:N) ratio in the sediment solids from the Citgo site ranged from 26:1 to 33:1. The ratio in naturally occurring organic matter is not greater than 15:1 (Riley and Chester, 1976, p. 12). The strong correlation of chromium with iron in the peroxide plus pyrophosphate extract could result form oxidation of sulfides during the extraction, but interstitial-water data are insufficient to test this hypothesis.

The strongest correlations for data from the Burton site were that of chromium with carbon. Chromium concentrations in the sediment interstitial water increased as total carbon decreased and the C:N ratio in the sediment solids increase.

Table E-13.—*Interstitial water data for Calcasieu River cores collected in May 1986*

[Values are concentrations; micromoles per liter for NH_4; micromoles per gram for NH_4 (adsorbed); millimoles per liter for Cl, Br, HPO_4, AND SO_4; micrograms per liter for Cr, Mn and Fe]

Depth (cm)	pH	NH_4	NH_4ADS	Cl	Br	HPO_4	SO_4	Cr	Mn	Fe
					B-130					
1.0	7.6	0.53	2.52	193	0.28	.	5.890	5.2	1.19	1,480
3.0	7.9	0.98	5.40	229	0.36	0.37	2.010	17.2	0.78	1,220
5.0	7.7	1.43	6.34	222	0.34	0.39	0.920	8.0	0.64	1,280
7.0	7.6	1.66	5.38	220	0.32	0.48	0.410	8.0	0.96	1,290
9.0	7.7	1.89	9.61	218	0.51	0.51	0.360	8.3	1.56	1,160
20.2	7.5	2.57	10.40	222	0.33	0.48	0.001	22.3	5.00	5,630
31.4	.	.	7.70	.	.	.	.	.	.	.
42.8	.	3.12	.	.	.	.	.	15.7	.	.
55.1	.	.	16.80	.	.	.	.	.	.	.
66.3	.	.	11.20	.	.	.	.	.	.	.
					BDI					
1.0	7.5	1.52	1.31	288	0.48	.	5.19	5.5	6.59	4,880
3.0	7.4	2.42	5.07	285	0.79	.	1.12	11.6	7.90	6,130
5.0	7.6	2.84	3.41	291	0.63	.	0.78	8.3	8.38	1,690
7.0	7.7	3.61	2.50	300	0.61	0.66	0.66	11.2	11.10	2,430
9.0	7.6	4.12	.	299	0.58	0.73	0.46	15.6	12.40	540
24.2	7.6	6.70	7.00	340	0.59	0.55	0.33	10.8	16.60	3,630
38.6	.	6.16	5.54	.	.	.	.	14.2	24.10	7,370
50.6	.	6.34	8.59	.	.	.	.	.	15.30	16,600
67.4	.	5.88	8.36	.	.	.	.	14.4	16.80	3,150
81.1	.	4.42	3.90	.	.	.	.	9.3	9.64	3,400
					CITGO					
1.0	.	0.06	0.25	.	.	.	.	1.0	6.16	19,000
3.0	.	.	0.60	.	.	.	.	2.6	1.44	1,750
5.0	.	.	.	.	.	.	.	3.2	1.78	520
7.0	.	.	1.30	.	.	.	.	2.7	1.92	290
9.0	.	0.32	1.39	169	0.14	.	4.98	1.8	2.23	660
16.2	.	.	2.80	.	.	.	.	1.2	2.21	280
28.6	.	.	3.50	.	.	.	.	1.4	2.11	360
14.0	.	.	.	140	0.13	.	0.69	1.6	2.14	3,930
					BURTON					
1.0	7.7	0.28	0.36	250	0.34	.	12.10	5.2	7.31	2,750
3.0	7.3	0.56	1.39	219	0.29	.	8.43	4.5	6.02	3,000
5.0	7.4	0.79	1.56	214	0.28	.	6.87	4.2	6.70	5,620
7.0	.	1.02	2.69	.	.	.	.	3.0	4.51	3,320
9.0	7.4	1.15	2.94	224	0.33	.	4.33	2.4	10.20	3,620
21.4	.	1.80	5.21	.	.	.	.	2.2	7.80	2,380
46.2	7.5	2.06	3.10	165	0.20	.	0.25	2.5	13.50	3,680
58.6	.	1.48	0.84	.	.	.	.	.	.	.

Table E-14.—*Sediment solids data for Calcasieu River cores collected in May 1986*

[Values are concentrations; micrograms per gram dry weight for Cr and Mn; milligrams per gram dry weight for Fe; grams per 100 grams dry weight (percent) for carbon]

Depth (cm)	Total Cr	H_2O_2/HCl Cr	H_2O_2/ P_2O_7 Cr	Total Mn	H_2O_2/HCl Mn	H_2O_2/ P_2O_7 Mn	Total Fe	H_2O_2/HCl Fe	H_2O_2/ P_2O_7 Fe	Carbon	C:N
						B-130					
1.0	33	16.100	3.79	89	100	124	17,000	7,470	3,071	1.25	11.7925
3.0	50	7.820	5.42	130	164	212	22,000	6,329	3,084	1.71	11.4765
5.0	.	.	.	.	.	.	.	.	.	.	.
7.0	.	.	.	.	.	.	.	.	.	.	.
9.0	.	.	.	.	.	.	.	.	.	.	.
20.2	62	17.250	6.46	310	214	158	32,000	11,063	3,987	2.24	10.6667
31.4	.	.	.	.	.	.	.	.	.	.	.
42.8	76	6.095	2.00	290	262	213	36,000	5,458	1,200	2.26	9.3388
55.1	.	.	.	.	.	.	.	.	.	.	.
66.3	.	.	.	.	.	.	.	.	.	.	.
						BDI					
1.0	82	35.535	16.3	650	296	330	34,000	11,287	6,132	4.81	13.1063
3.0	83	40.135	16.8	690	568	405	38,000	12,480	6,406	3.67	12.4830
5.0	.	.	.	.	.	.	.	.	.	.	.
7.0	.	.	.	.	.	.	.	.	.	.	.
9.0	150	44.045	20.6	690	546	288	34,000	10,474	6,762	4.84	12.8042
24.2	.	.	.	.	.	.	.	.	.	.	.
38.6	69	45.770	21.0	670	606	434	27,000	9,513	5,019	3.56	14.5306
50.6	.	.	.	.	.	.	.	.	.	.	.
67.4	.	.	.	.	.	.	.	.	.	.	.
81.1	30	14.490	23.9	130	133	125	8,400	3,557	2,298	1.41	19.3151
						CITGO					
1.0	93	15.525	7.38	190	164	78	17,000	4,319	3,961	11.30	33.3333
3.0	89	22.655	5.92	210	195	36	20,000	3,458	2,748	11.90	33.4270
5.0	42	9.890	5.48	270	187	68	19,000	3,449	2,616	10.80	32.9268
7.0	.	.	.	.	.	.	.	.	.	.	.
9.0	.	.	.	.	.	.	.	.	.	.	.
16.2	.	.	.	.	.	.	.	.	.	.	.
28.6	.	.	.	.	.	.	.	.	.	.	.
41.0	120	10.925	2.90	210	132	88	22,000	3,314	1,634	4.91	26.5405
						BURTON					
1.0	78	4.715	2.53	470	425	239	24,000	5,735	1,936	0.897	13.0000
3.0	97	6.095	2.46	730	495	379	29,000	10,351	2,737	1.160	13.8095
5.0	.	.	.	.	.	.	.	.	.	.	.
7.0	.	.	.	.	.	.	.	.	.	.	.
9.0	.	.	.	.	.	.	.	.	.	.	.
21.4	100	9.085	2.00	900	762	564	33,000	8,836	3,573	1.400	11.7647
46.2	.	.	.	.	.	.	.	.	.	.	.
58.6	58	21.965	7.58	340	499	158	21,000	20,000	4,396	1.680	14.0000

Table E-15.—*Correlation coefficients based on data for sediment cores from the sites B-130, BDI, Citgo, and Burton in the Calcasieu River, Louisiana. Samples were collected in May 1986*

	B-130	BDI	Citgo	Burton
Interstitial-water Fe:Cr	+0.77	-0.07	-0.49	+0.12
Interstitial-water Mn:Cr	+0.73	+0.66	-0.58	-0.47
H_2O_2-HCl extract Fe:Cr	+0.85	+0.84	+0.16	+0.96
H_2O_2-HCl extract Mn:Cr	-0.48	+0.93	+0.52	-0.02
H_2O_2-P_2O_7 extract Fe:Cr	+0.93	-0.77	+0.97	+0.72
H_2O_2-P_2O_7 extract Mn:Cr	-0.22	-0.64	-0.37	-0.72
C/N:Cr	-0.43	-0.20	+0.30	+0.81
Sediment organic carbon: Interstitial- water Cr	+0.84	+0.17	+0.31	-0.95
Adsorbed NH4+: Interstitial-water Fe	+0.58	+0.51	-0.58	-0.28

The chromium and iron concentrations in the extract containing peroxide-plus-hydrochloric acid also were correlated suggesting a possible association of chromium with iron oxides in addition to organic matter. Chromium and manganese concentrations were not correlated in any of the samples from the Burton site.

Interstitial-water analyses indicated that sulfate reduction was occurring near the sediment-water interface at sites B-130 and BDI. The gradual decrease in interstitial-water sulfate concentrations at the Burton site suggests that sulfate reduction occurred in deeper depths in the sediment.

The extracted concentrations of manganese from sediment samples from all four sites averaged 86 percent of the total sediment concentrations. These data imply that most of the manganese in these sediments exists as manganese-oxide coatings.

DISCUSSION

The existence of a single process for the retention of a metal by sediment solids from these environmentally different sites in the Calcasieu River is not expected. In these sediments, it is assumed that more than one mechanism is working at each location to partition chromium into solid phases. The dominant mechanism(s) would be expected to be evidenced by strong statistical correlation.

Because total chromium concentrations in sediment did not differ significantly among the sampling sites, elevated concentrations of chromium in interstitial water at sites B-130 and BDI compared with the concentrations at Citgo and Burton sites cannot be explained by total chromium concentration. The total concentration of a metal in sediment does not distinguish whether the metal is present in sediment coatings and, therefore, whether the metal is readily available to solution. Interstitial-water concentration data and data obtained by treating the sedimentary material with selected extractants are used to determine the conditions that will result in the transfer of metal from solid to solution phases. Correlation coefficients for the interstitial-water data suggest that the increases in concentrations of chromium in interstitial water results from the dissolution of iron oxides and manganese oxides at site B-130 and manganese oxides at site BDI. The peroxide-plus-hydrochloric acid extraction data support the hypothesis that it is the dissolution of iron oxides at site B-130 that increases the concentrations of chromium in the interstitial water because the concentrations of iron and chromium extracted in the laboratory are highly correlated. The laboratory extractions of metals from the sediment taken at site B-130 do not corroborate evidence that the dissolution of manganese oxides adds chromium to the interstitial water because the manganese and chromium concentrations present in either the peroxide-plus-hydrochloric acid extraction solution or the peroxide-plus-pyrophosphate extraction solution are not correlated.

The pattern of correlation coefficients substantiates the importance of manganese oxides at site BDI. At this site, the chromium concentrations in interstitial water are correlated with manganese, and, although both peroxide-plus-hydrochloric acid extractable iron and manganese correlate with the extracted chromium, the correlation is stronger for manganese than for iron.

Statistical evaluation of the data from the Citgo site indicates only one notable correlation. The correlation between iron and chromium concentrations in the peroxide-plus-pyrophosphate extract is statistically significant. Because there are insufficient sulfate data to determine the influence sulfate reduction in these sediments, the contribution of sulfides cannot be evaluated. It is possible that the pyrophosphate solution solubilized some organic compounds from these sediments, which are highly contaminated with petroleum products (C:N approximately 30). Concentrations of chromium in the interstitial water from the Citgo sediment are the lowest among the four sampling sites. The difficulty with which chromium is extracted from Citgo sediments leads to the assumption that the chromium in these sediments is associated with refractory organic matter.

At the Burton site, no positive correlation between iron or manganese concentrations and chromium concentrations in interstitial water were found. The correlation between extractable iron and extractable chromium concentrations is strong, suggesting that iron oxides could play a role not evident from the interstitial-water data. This relation may not be evident in the interstitial-water data if the sediment redox-potential is too oxidizing for iron-oxide dissolution. No positive correlation was found between manganese and chromium concentrations in the sediment. Analysis of the sediment data indicates strong correlations of chromium with organic carbon and the C:N ratio, suggesting that the association of chromium with labile organic matter is important in this sediment. Degradation of the organic matter could release the chromium to solution. This reaction is possible in either oxidizing or reducing conditions. The data support a possible partitioning of chromium with organic matter on the sediment solids. An association between chromium and iron oxides can only be surmised.

Adsorbed ammonium can provide information about the surface properties of sediment solids. This is especially true when adsorbed ammonium data correlates positively with concentrations of iron in interstitial water (Simon and Kennedy, 1987). Dissolution of iron-oxide coatings at sites B-130 and BDI is indicated by the positive correlation between an increase in interstitial-water concentrations of iron and the increase in adsorbed ammonium concentrations with depth in the sediment cores. The fact that concentrations of chromium in interstitial water also increase with depth in the cores is additional evidence that dissolution of iron oxides releases associated chromium. The highly adsorptive nature of iron and manganese oxides makes them ideal substrates for scavenging metals from solution. Dissolution of these oxides under reducing conditions would release associated metals into solution.

SUMMARY

Four phases that partition chromium with sediment solids were identified by statistical analyses of data from four sites in the Calcasieu River. At the location (B-130) upstream from the petrochemical input iron-oxide phases dominated the partitioning of chromium with sediment solids. Iron oxides were important to a lesser degree at the location (Burton) most downstream from the petrochemical input. Data from the sites most affected by petrochemical input, BDI and Citgo, indicated that chromium retention by sediment solids was dominated by manganese oxides (BDI) and refractory organic matter (Citgo). Work with these Calcasieu River sediments suggests that by using extraction with hydrogen peroxide-plus-dilute hydrochloric acid, extraction with hydrogen peroxide-plus-pyrophosphate, and organic carbon and nitrogen analyses of freeze-dried sediment, a distinction can be made among chromium associated with iron oxides, manganese oxides, labile organic matter, and refractory organic matter.

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UPTAKE OF MANMADE ORGANIC COMPOUNDS BY *RANGIA CUNEATA* IN THE LOWER CALCASIEU RIVER, LOUISIANA

By Charles R. Demas[1] and Dennis K. Demcheck[1]

ABSTRACT

Rangia cuneata, a brackish-water clam, was collected from an area of Lake Charles, Louisiana, unaffected by manmade organic compounds and placed in cages at two sites in the lower Calcasieu River affected by these compounds and at one recovery site downstream from the affected area in July and August 1987. Analyses of water and bottom material for volatile organic compounds and acid-base/neutral extractable organic compounds indicated that no chemical contamination of the Lake Charles area has occurred. Elevated concentrations of bromoform, chloroform, and 1,2-dichloroethane in water and hexachlorobenzene and hexachlorobutadiene in bottom material were found at the affected sites in the lower Calcasieu River. Low or undetectable concentrations of organic compounds were present at the recovery site.

Results of tissue analyses of Rangia cuneata from the four study sites were variable. Little or no uptake of organic compounds by Rangia cuneata occurred at the Lake Charles site. Complete mortality of Rangia cuneata occurred at the site on the lower Calcasieu River where the most extensive contamination occurred (probably because of elevated water temperatures). Significant uptake of bromoform, chloroform, 1,2-dichloroethane, hexachlorobenzene, and hexachlorobutadiene by Rangia cuneata occurred at the second affected site. Uptake by Rangia cuneata of hexachlorobutadiene and hexachlorobenzene also occurred at the recovery site, although in smaller amounts, indicating movement of these compounds much farther downstream than indicated by chemical analysis of water and bottom material.

The above results indicate that Rangia cuneata has great potential for use as a monitoring tool in areas where contamination by manmade organic compounds may have occurred. This is especially true in areas where the contamination occurs at concentrations below analytical detection limits in water and bottom material.

INTRODUCTION

The lower Calcasieu River, in southwestern Louisiana, is typical of Gulf Coast estuarine systems that have been seriously affected by the chemical and maritime industries. Previous studies by Steinheimer and others, 1981; DeRouen and Stevenson, 1987; Pereira and others, 1988; Demas, in press; and numerous unpublished reports by the U.S. Environmental Protection Agency (U.S. EPA), (Philip Crocker, U.S. Environmental Protection Agency, written commun., 1988) and Louisiana Department of Environmental Quality (LDEQ), (Michael Schurtz, Louisiana Department of Environmental Quality, written commun., 1985) have documented the presence of manmade organic compounds in water, on suspended sediment, and in bottom material at specific locations in the river.

Volatile organic compounds (VOC) are widespread in their distribution and are present in a wide range of concentrations in the water column. In contrast, acid-base/neutral (ABN) extractable organic compounds, such as hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD), are present at some sites in the lower Calcasieu River at elevated concentrations in bottom material. Concentrations of these compounds usually are below levels of detection in the water column. Both classes of organic compounds have been detected in tissue samples collected from aquatic organisms present in the Calcasieu River (Pereira and others, 1988; Michael Schurtz, Louisiana Department of Environmental Quality, written commun., 1988; unpublished data on file at the Louisiana District Office of the U.S. Geological Survey). Pereira and others (1988) reported that several species of fish and one species of crab had concentrations of HCB and HCBD in equilibrium with concentrations of these compounds in water and attached to suspended sediments but not in equilibrium with concentrations of these compounds in bottom material. Unfortunately, all the

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[1] U.S. Geological Survey, Baton Rouge, La.

organisms sampled are motile, and it was impossible to determine if concentrations of organic compounds detected in their tissue was a result of environmental exposure in the area of capture or a result of exposure in other areas prior to their capture.

This study, which uses *Rangia cuneata* (referred to as *Rangia* throughout the rest of the report), was undertaken to provide additional information on the movement of the organic compounds in the lower Calcasieu River. *Rangia* were collected from an unaffected area of Lake Charles and placed in cages in affected and recovery zones farther downstream for approximately 30 days (fig. E-10). *Rangia*, a brackish-water clam, was selected for study for several reasons: (1) It is endemic in the Calcasieu River; (2) it is present in an unaffected area of the Calcasieu River, and therefore provides a natural control population; (3) its body mass and numbers are large enough to provide specimens adequate for transplanting and chemical analyses; and (4) it is nonmotile in its adult stage. The purpose of this paper is to present the results of an uptake study using *Rangia* in relation to the variable distribution of man-made organic compounds present in the lower Calcasieu River.

MATERIALS AND METHODS

Rangia were collected from a large bed (site 1) in the northwestern corner of Lake Charles (fig. E-10) using a biological dredge scraper. Specimens were cleaned with native water, sorted for size and condition, and placed in a clean, galvanized tub prior to placement in holding cages constructed of rubber-coated wire mesh. Approximately 80 specimens where placed in each cage. Cages were placed on or suspended slightly above the bottom at sites 2 and 3 in the affected area, and at one recovery site, site 4 (fig. E-10). Recovery site refers to an area of the lower Calcasieu River located downstream from the affected area. The recovery area had low concentrations of VOC in water ABN in bottom material compared to the affected area. Cages were left for 35 days at sites 1, 2, and 4; and 41 days at site 3 (because of access problems).

Temperature, pH, dissolved oxygen, specific conductance, salinity, and oxidation-reduction potential were recorded at the surface and bottom of the water column at each site prior to placement of *Rangia* and immediately after their retrieval using an *in situ* monitor. Water and bottom-material samples were collected at each site concurrent with collection or placement of *Rangia* and analyzed for VOC and ABN. Water for VOC analysis was collected using a stainless-steel sewage sampler containing a clean, fired, amber, 40-mL (milliliter) septum vial. VOC analysis was done at the U.S. Geological Survey National Water Quality Laboratory according to methods in Wershaw and others (1983). Detection limits for the analytical procedures are given in table E-16. Water for ABN analysis was collected with a wire-basket sampler containing a 1-liter clean, fired, glass bottle. ABN in bottom material were collected with a stainless-steel petite-ponar sampler and placed in clean, fired, 1-liter glass bottles. ABN in water and bottom material were analyzed at the Tennessee Valley Authority Laboratory according to U.S. EPA method 625 (U.S. Environmental Protection Agency, 1979b). Detection limits for the analytical procedures are given in table E-16. All water and bottom-material samples were stored at 4 °C (degrees Celsius) until analysis.

Two groups of 40 *Rangia* from site 1 were composited and analyzed separately for ABN, and two individual *Rangia* were analyzed for VOC at the beginning of the study. Similarly, 40 *Rangia* from site 1, and 36 *Rangia* from sites 3 and 4 (including one group of duplicates at site 4) were analyzed for ABN, and 4 *Rangia* (including one duplicate at site 4) were analyzed for VOC at sites 1, 3, and 4 at the end of the study. *Rangia* were frozen immediately after collection and shipped on dry ice prior to analyses. All tissue analyses were performed at the Mississippi State University Chemistry Laboratory using methods developed in cooperation with the U.S. Fish and Wildlife Service (L. Lane, Chemistry Laboratory, Mississippi State University, written commun., 1986).

RESULTS

Physical and chemical data collected at the surface and bottom of the water column (table E-17) indicated that dissolved-oxygen (DO) concentrations were biologically nonstressful throughout the study area at times of deployment and recovery of *Rangia*. Physical and chemical characteristics of water at the bottom of the water column had the greatest affect on *Rangia*. DO concentrations ranged from 3.8 mg/L (milligrams per liter) at the bottom at site 1 in July to 5.7 mg/L

Table E-16.—*Detection limits for volatile organic and acid-base/neutral extractable compounds analyzed from the lower Calcasieu River samples*

[All values for water, in micrograms per liter; bottom material, in micrograms per kilogram; and represent lowest levels of detection]

Volatile organic compounds					
Benzene	0.2	Methylene chloride	0.2	1,2-Dichloroethane	0.2
Bromoform	.2	Styrene	.2	1,2-Dichloropropane	.2
Carbon tetrachloride	.2	Tetrachloroethylene	.2	1,3-Dichloropropene	.2
Chlorobenzene	.2	Toluene	.2	1,2-Transdiolethylene	.2
Chloroethane	.2	Trichloroethylene	.2	2-Chloroethyl vinyl ether	.2
Chloromethane	.2	Trichlorofluoromethane	.2	1,2-Dichlorobenzene	.2
Chloroform	.2	Vinyl chloride	.2	1,3-Dichlorobenzene	.2
Dibromochloromethane	.2	1,1-Dichloroethylene	.2	1,4-Dichlorobenzene	.2
Dichlorobromomethane	.2	1,1-Dichloroethane	.2	1,2-Dibromoethylene	.2
Dichlorodifluoromethane	.2	1,1,1-Trichloroethane	.2	1,2-Trans-Dichloroethylene	.2
Ethylbenzene	.2	1,1,2-Trichloroethane	.2	Cis-1,3-Dichloropropene	.2
Methyl bromide	.2	1,1,2,2,-Tetrachloroethane	.2	Trans-1,3-Dichloropropene	.2

Acid-base/neutral extractable organic compounds

	Water	Bottom material		Water	Bottom material
Acenaphthene	5.0	200	4-Chloro-3-methylphenol	30.0	1,200
Acenaphthylene	5.0	200	Chrysene	10.0	400
Anthracene	5.0	200	Di-n-Butyl phthalate	5.0	200
Benzo a anthracene			Di-n-Octylphthalate	10.0	400
1,2-benzanthracene	5.0	530	Diethyl phthalate	5.0	200
Benzo-a-pyrene	10.0	400	Dimethyl phthalate	5.0	200
Benzo-b-fluoranthene	10.0	400	4,6-Dinitro-2-methylphenol	30.0	1,200
Benzo ghi perylene	10.0	400	Fluoranthene	5.0	200
Benzo k fluoranthene	10.0	400	Fluorene	5.0	200
Butyl benzyl phthalate	5.0	200	Hexachlorobenzene	5.0	200
Hexachlorobutadiene	5.0	200	1,4-Dichlorobenzene	5.0	200
Hexachlorocyclopentadiene	5.0	200	Bis (2-chloroethoxy) methane	5.0	200
Hexachloroethane	5.0	200	Bis (2-Chloroethyl)ether	5.0	200
Indeno (1,2,3-CD) pyrene	10.0	400	Bis (2-chloroisopropyl) ether	5.0	200
Isophorone	5.0	200	2-Chloronaphthalene	5.0	200
N-nitrosodi-N-propylamine	5.0	200	2-Chlorophenol	5.0	200
Nitrosodiphenylamine	5.0	200	Bis (2-ethylheyl) phthalate	5.0	200
Naphthalene	5.0	200	2-nitrophenol	5.0	200
Nitrobenzene	5.0	200	2,4-Dichlorophenol	5.0	200
N-nitrosodimethylamine	5.0	200	2,4-Dimethylphenol	5.0	200
Pentachlorophenol	5.0	1,200	2,4-Dinitrophenol	20.0	
Phenanthrene	5.0	200	2,4-Dinitrotoluene	5.0	200
Phenol	5.0	200	2,4,6-Trichlorophenol	20.0	800
Pyrene	5.0	200	2,6-Dinitrotoluene	5.0	200
1,2-Dichlorobenzene	5.0	200	4-Bromophenyl phenyl ether	5.0	200
1,2,4-Trichlorobenzene	5.0	200	4-Chlorophenyl phenyl ether	5.0	200
1,3-Dichlorobenzene	5.0	200	4-Nitrophenol	30.0	1,200

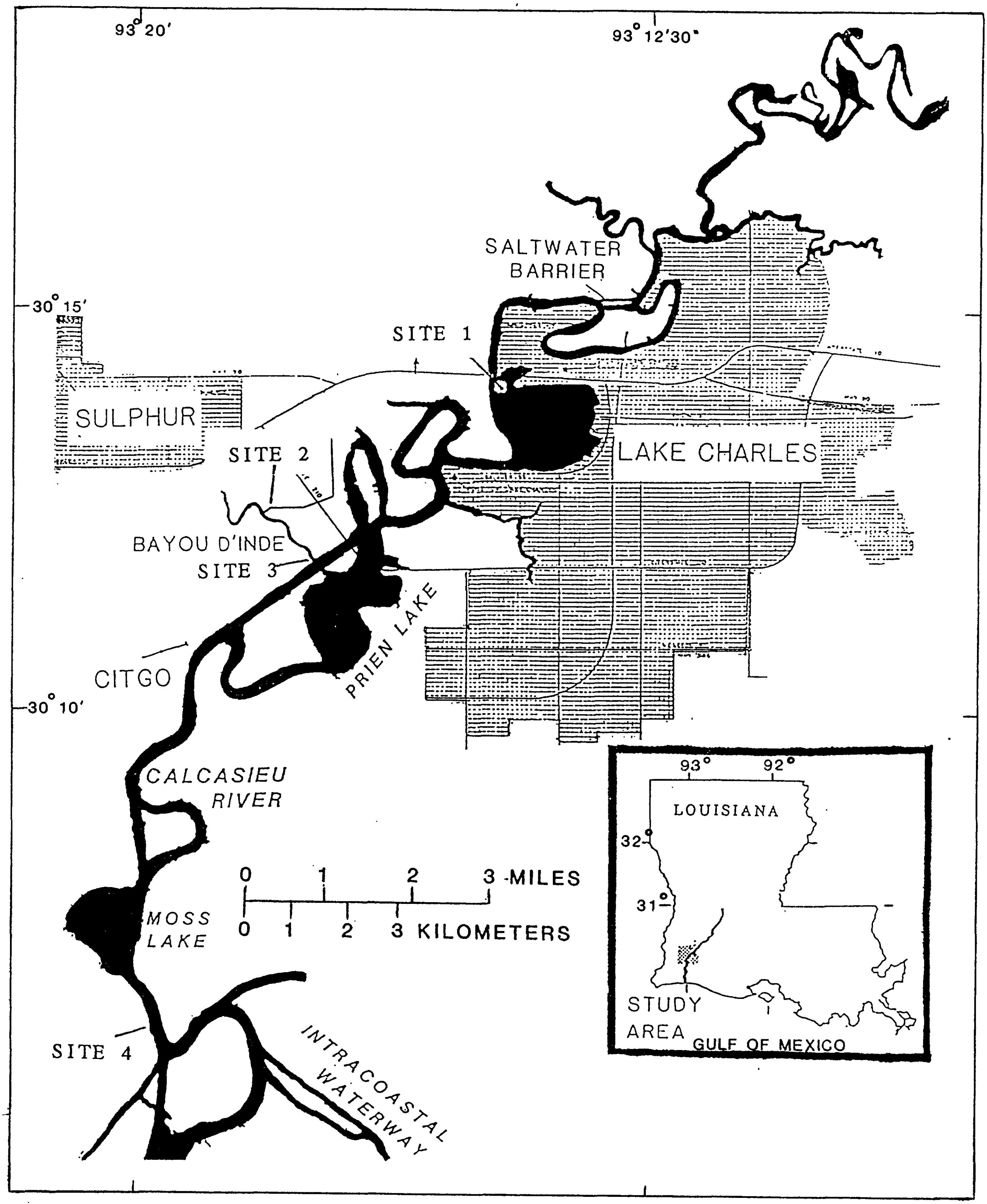

Figure E-10. – Uptake of manmade organic compounds by *Rangia cuneata* in the lower Calcasieu River, Louisiana study area.

Table E-17. —*Physical and chemical field values recorded at four sites in the lower Calcasieu River, Louisiana, July-September 1987*

[°C, degrees Celsius; mg/L, milligrams per liter; μS/cm, microsiemens per centimeter at 25 degrees Celsius; ppt, parts per thousand; mV, millivolts]

Site	Temperature °(C)	pH (units)	Dissolved oxygen (mg/L)	Specific conductance (μS/cm)	Salinity (ppt)	Oxidation-reduction potential (mV)
			July 21, 1987			
1	Surface 28.6	6.6	4.9	1,900	0.5	+157
	Bottom 28.6	6.4	3.8	2,400	.8	+154
2	Surface 35.9	7.3	4.0	8,500	4.4	+156
	Bottom 36.0	7.3	4.1	8,500	4.1	+158
3	Surface 32.7	7.0	4.4	6,480	3.1	+150
	Bottom 31.3	7.0	4.3	6,150	2.9	+149
4	Surface 29.9	7.9	7.1	8,750	4.6	+164
	Bottom 29.6	7.6	4.0	12,600	6.6	+165
			August 25, 1987			
1	Surface 31.0	7.3	5.7	7,720	3.9	+188
2	Surface 41.0	7.5	5.6	22,200	13.2	+168
	Bottom 41.0	7.5	5.4	22,200	13.2	+168
4	Surface 32.2	8.2	6.6	23,000	13.8	+146
	Bottom 31.7	8.0	5.1	24,500	14.8	+157
			September 1, 1987			
3	Surface 33.2	7.8	7.8	17,500	10.0	+163
	Bottom 33.4	7.3	4.4	22,500	13.3	+174

at the bottom at site 1 in August. Specific conductance and salinity increased from the beginning to the end of the study. Salinity ranged from 0.8 ppt (parts per thousand) in July to 3.9 ppt in August at the bottom at site 1 and from 6.6 ppt in July to 14.8 ppt in August at the bottom at site 4. Similar increases in salinity also were observed at sites 2 and 3 during the course of the study. The pH ranged from 6.4 in July at the bottom at site 1 to 8.0 in August at the bottom at site 4. Temperatures recorded at the bottom at sites 1, 3, and 4 ranged from 28.6 °C in July at site 1 to 33.4 °C in August at site 4. Temperatures at the bottom at site 2 ranged from 36.0 °C in July to 41.0 °C in August. The high bottom temperature recorded at site 2 in August is suspected as the major cause for the 100 percent mortality of the *Rangia* deployed at this site.

Water and bottom material were analyzed for VOC and ABN at the detection limits listed in table E-16. Chemical data collected (tables E-18 and E-19) at the beginning of the study verified earlier findings (Pereira and others, 1988; Demas, in press) that sites 1 and 4 represent areas of the lower Calcasieu River that are relatively unaffected by the chemical industries. No VOC or ABN were detected in the water and bottom material collected at site 1 on July 21, 1987. Duplicate tissue analyses (table E-20) performed on *Rangia* collected on the same date also

Table E-18.—*Concentrations of volatile organic compounds in water from the lower Calcasieu River system, Louisiana*

[Concentrations in micrograms per liter; ND, not detected]

Organic[1] Site:[1]	1	2	3	4
Date sampled: 7-21-87				
Dichlorobromomethane	ND	9.1	5.1	ND
Carbon tetrachloride	ND	.20	ND	ND
1,2-Dichloroethane	ND	31	10	0.80
Bromoform	ND	150	41	ND
Chlorodibromomethane	ND	33	16	ND
Chloroform	ND	53	22	1.7
Chloroethane	ND	.60	ND	ND
Methylene chloride	ND	1.2	ND	ND
Tetrachloroethylene	ND	8.2	4.1	ND
1,1-Dichloroethane	ND	.70	.30	ND
1,1,1-Trichloroethane	ND	3.1	1.7	ND
1,1,2-Trichloroethane	ND	7.5	2.9	ND
1,1,2,2-Tetrachloroethane	ND	2.5	ND	ND
1,2-Transdichloroethylene	ND	2.0	.50	ND
Vinyl chloride	ND	1.0	ND	ND
Trichloroethylene	ND	5.3	3.8	1.0
Dates sampled: 8-25 to 9-1-87				
Toluene	[2]1.0	[2].20	ND	ND
Benzene	[2].50	ND	ND	ND
Dichlorobromomethane	ND	3.7	2.5	ND
1,2-Dichloroethane	ND	34	20	3.5
Bromoform	ND	110	160	3.5
Chlorodibromomethane	ND	13	12	ND
Chloroform	ND	25	17	1.9
Tetrachloroethylene	ND	17	6.6	.50
1,1-Dichloroethane	ND	1.1	1.3	ND
1,1-Dichloroethylene	ND	1.6	.50	ND
1,1,1-Trichloroethane	ND	5.1	2.6	ND
1,1,2-Trichloroethane	ND	12	6.0	ND
Vinyl chloride	ND	.80	.40	ND
Trichloroethylene	ND	8.3	3.8	ND

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[1] Refer to table E-16 for complete list of organic compounds analyzed. Only those above the detection limit are listed in this table.

[2] Denotes possible laboratory contamination.

Table E-19. – *Concentrations of acid/base-neutral extractable organic compounds in water and bottom material from the lower Calcasieu River system, Louisiana, and percent recovery rates of laboratory spikes*

[Concentrations in water, in micrograms per liter; bottom material, in micrograms per kilogram; ND, not detected]

Site[1]:	2		3	4	
Organic compound[2]	Water	Bottom material	Bottom material	Bottom material	Percent recovery[3]
Date sampled: 7-21-87					
Acenaphthylene	ND	7,500	ND	ND	--
Fluoranthene	ND	19,000	ND	ND	47
Benzo(a)anthracene	ND	4,100	ND	ND	77
Hexachlorobutadiene	8	34,000	ND	ND	50
Acenapthene	ND	7,700	ND	ND	48
4-Bromodiphenyl ether	ND	6,400	ND	ND	46
Hexachlorobenzene	ND	37,000	16,000	ND	57
1,2,4-Trichlorobenzene	ND	6,700	ND	ND	49
Napthalene	ND	6,800	ND	ND	56
Phenanthrene	ND	18,000	ND	5,900	--
Benzo(b)fluoranthene	ND	21,000	ND	ND	19
Benzo(a)pyrene	ND	22,000	ND	ND	12
Ideno(1,2,3-cd)pyrene	ND	22,000	ND	ND	--
Benzo(ghi)perylene	ND	20,000	ND	ND	--
Dates sampled: 8-25 to 9-1-87					
Hexachlorobenzene	ND	24,000	15,000	ND	6
1,4-Dichlorobenzene	ND	430	ND	ND	45
1,2,4-Trichlorobenzene	ND	19,000	ND	ND	54
Hexachlorobutadiene	ND	27,000	ND	ND	49
4-chlorodiphenyl ether	ND	16,000	ND	ND	46
4-bromodiphenyl ether	ND	12,000	ND	ND	47
Fluoranthene	ND	6,500	ND	ND	46
Pyrene	ND	5,600	ND	ND	--

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[1] Water and bottom material analyzed from site 1 contained no detectable concentrations of organic compounds. (See table E-16.)

[2] Refer to table E-16 for complete list of organic compounds analyzed. Only those above the detection limit are listed in this table.

[3] Dashes in percent recovery column indicates not in quality control.

contained no detectable concentrations of VOC and ABN (pyrene was detected at the lower limit of detection, 10 μg/kg (micrograms per kilogram), in one sample, indicating possible sample contamination). Because no organic compounds were detected in tissue of *Rangia* collected at site 1, this site was a good source of organisms for the study.

Water and bottom material collected at site 2, located in an industrial outfall, contained the highest concentrations of VOC and ABN found during the study. VOC in water (table E-18) were detected in concentrations ranging from 150 μg/L (micrograms per liter) for bromoform to 53 and 31 μg/L for chloroform and 1,2-dichloroethane, respectively. ABN (table E-19) were not detected or were present at very low concentrations in water (HCBD was detected at a concentration of 8 μg/L) at site 2. ABN in bottom material, in contrast, were present at very high

Table E-20.—*Manmade organic compounds in Rangia cuneata from the lower Calcasieu River system, Louisiana, July 21-September 1, 1987*

[Concentrations in micrograms per kilogram, whole body basis; ND, not detected]

Organic compound		Site				
Site:	1			3	4	
Date:	July 21 (replicate)		August 25	September 1	August 25 (replicate)	
Volatiles	1 clam					
Bromoform[1]	ND	ND	ND	350	5	5
Chloroform[2]	5	4	ND	28	18	8
1,2-Dichloroethane[1]	ND	ND	ND	17	ND	ND
Organochlorines[3]	40 clams			36 clams		
Hexachlorobenzene	ND	ND	ND	220	20	
Hexachlorobutadiene	ND	ND	10	580	150	
Octachloronapthalene	ND	ND	ND	ND	ND	
Octachlorostyrene	ND	ND	ND	20	ND	
Polynuclear aromatic hydrocarbons[3]						
Benzopyrene	ND	ND	ND	ND	ND	
Benzoperylene	ND	ND	ND	ND	ND	
Napthalene	ND	ND	ND	ND	ND	
Phenanthrene	ND	ND	ND	ND	ND	
Fluoranthrene	ND	ND	ND	10	10	
Pyrene	10	ND	ND	10	20	
Chrysene	ND	ND	ND	20	10	
Moisture (percent)	90.4	90.5	89.9	88.3	89.4	
Lipid (percent)	.5	.5	.5	.3	.3	

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[1] Lower level of detection is 2 micrograms per kilogram.

[2] Due to variable blank, any value below 15 micrograms per kilogram may not be real.

[3] Lower level of detection is 10 micrograms per kilogram.

concentrations. For example, HCBD and HCB were detected at site 2 in concentrations of 34,000 and 37,000 μg/kg, respectively. Water at site 3, located approximately 1 mile downstream from site 2, also had very high concentrations of VOC; bromoform, chloroform, and 1,2-dichloroethane were detected in concentrations of 41, 22, and 10 μg/L, respectively. HCB was the only ABN detected in water or bottom material at this site; it was detected in bottom material at a concentration of 16,000 μg/kg.

VOC were detected at or near the lower limits of detection in water samples at site 4. Bromoform was not detected at this site, and chloroform and 1,2-dichloroethane were detected in concentrations of 1.7 and 0.8 μg/L, respectively (table E-18). No ABN were detected in water and only phenanthrene was detected in bottom material at site 4, indicating little or no transport of ABN into this area.

Concentrations of most chemical constituents in water and bottom material (tables E-18 and

E-19) collected after *Rangia* specimens had been onsite a minimum of 35 days, were similar to or greater than those concentrations at the beginning of the study. Bromoform and 1,2-dichloroethane concentrations increased at sites 3 and 4. Bromoform concentration increased from 41 μg/L in July to 160 μg/L in September at site 3 and from not detected in July to 3.5 μg/L in August at site 4. At site 2, HCB concentrations decreased from 37,000 to 24,000 μg/kg and HCBD concentrations decreased from 34,000 to 27,000 μg/kg from July to August, respectively.

Mortality was unexpectedly high in the caged *Rangia* at sites 2 and 3. Initial study plans included sampling at 30- and 60-day intervals to determine if ABN concentrations in *Rangia* tissues reached an equilibrium with ABN concentrations in bottom material, and to establish whether VOC concentrations in tissue stabilize or fluctuate with changing VOC concentrations in the water. Unfortunately, mortality at site 2 was 100 percent and 55 percent at site 3, compared to 17 percent at site 4. The high mortality at sites 2 and 3 led us to limit the experiment to the 30-day interval because of the lack of specimens at these sites.

Results of *Rangia* tissue analyses are shown in table E-20. *Rangia* at site 1 showed no uptake of VOC or ABN with the exception of HCBD. HCBD in *Rangia* tissue at site 1 was detected at 10 μg/kg. The lowest limit of detection of HCBD in *Rangia* tissue was 10 μg/kg for this study indicating possible sample contamination during analysis. *Rangia* at site 3, in contrast, contained relatively high concentrations of VOC and ABN. Bromoform, chloroform, and 1,2-dichloroethane were detected in *Rangia* in concentrations of 350, 28, and 17 μg/kg, respectively. HCBD and HCB were detected in *Rangia* in concentrations of 580 and 220 μg/kg, respectively. These relatively high concentrations of VOC and ABN detected at site 3 verified water and bottom-material chemical data that showed significant movement downstream of both classes of compounds from the outfall to the mouth of Bayou d' Inde. *Rangia* at site 4 had detectable concentrations of VOC and ABN. Bromoform and chloroform were detected in *Rangia* tissue at site 4 at concentrations of 5 and 18 μg/kg, respectively. HCBD and HCB were detected in *Rangia* tissue at concentrations of 150 and 20 μg/kg, respectively. It should be noted that because of variable blank concentrations, chloroform concentrations in *Rangia* tissue below 15 μg/kg may be suspect. Also, the lower limit of detection for HCB in *Rangia* tissue was 10 μg/kg for this study.

HCB and HCBD were detected in *Rangia* tissue at site 4, but were not detected in water and bottom material at this site. This indicates that transport of HCBD occurs much farther downstream than indicated by chemical data from water and bottom-material samples. Earlier studies (Pereira and others, 1988; Demas, in press) indicated that ABN would precipitate out of the water column into the bottom material very quickly on exposure to saltwater. Remobilization studies using bottom material from site 2 indicate that HCB and HCBD are bound relatively tightly to bottom material, and small concentrations of these compounds are released to the water column only on exposure to freshwater (Demas and Demcheck, 1989, this Proceedings). Because no freshwater was present in the lower Calcasieu River during the uptake study, there must have been a source of these compounds other than remobilization from the bottom material. Pereira and others (1988) reported microgram-per-kilogram concentrations of HCB and HCBD on suspended sediment and nanogram-per-liter concentrations in water collected at site 2. The low concentrations of HCB and HCBD on suspended sediment and in the water column appear to be the source of these compounds in the *Rangia* collected at site 4.

VOC determinations in *Rangia* were based on an unpublished modification of a U.S. Environmental Protection (1979a) method 624 and all results were interpreted accordingly (L. Lane, Chemistry Laboratory, Mississippi State University, oral commun., 1988). VOC detected in *Rangia* tissue show similar distribution to HCBD and HCB in *Rangia* tissue. Highest concentrations of VOC in *Rangia* tissue were found at site 3. Bromoform concentrations in *Rangia* tissue (350 μg/kg) at this site exceeded concentrations in water (41 and 160 μg/kg) determined at the beginning and end of the study, respectively, indicating that *Rangia* could bioconcentrate this compound. Chloroform and 1,2-dichloroethane, in contrast, were detected in *Rangia* tissue in concentrations similar to concentrations detected in water at site 3. Bromoform, chloroform, and 1,2-dichloroethane also were detected in *Rangia* tissue at concentrations similar to concentrations detected in water at site 4. The lack of apparent bioconcentration of chloroform and 1,2-dichloroethane at site 3 and of bromoform at site 4 may be related, in part, to the low concentrations of bromoform, chloroform, and 1,2-dichloroethane present in the aquatic environment at these sites. Uptake rates by *Rangia* of bromoform, chloroform, and 1,2-dichloroethane may just exceed depuration and metabolic rates when low concentrations are present in the environment; this would account for the low accumulation of bromoform, chloroform, and 1,2-dichloroethane observed in *Rangia* at this site. Similar observations on the affect of compound concentration in the environment and the rate of uptake by aquatic organisms were made by Conner (1984), and Oliver and Niiml (1985). Both studies found that uptake of manmade organic compounds by aquatic organisms increased with increasing concentrations in the environment.

Rangia appears to be a good collector of organic compounds present in the lower Calcasieu River. *Rangia* shows potential for use as a monitoring tool in areas where there is an external source of VOC and ABN but the concentrations are below levels of detection, as shown by tissue data for site 4.

CONCLUSIONS

Rangia cuneata were collected from an unaffected area of Lake Charles and placed in cages at two sites affected by manmade organic compounds and at one recovery site downstream in the lower Calcasieu River for a 35- to 42-day exposure period. VOC and ABN analysis of water and bottom material from the three test sites and the unaffected site showed no chemical contamination at the Lake Charles site, elevated concentrations of VOC (bromoform, chloroform, and 1,2-dichloroethane) in water and ABN (HCB and HCBD) in bottom material at the affected sites, and low concentrations of the same VOC and ABN at the recovery site.

Concentrations of VOC and ABN in *Rangia* tissue was related to concentrations of these compounds in water and bottom material at the four study sites. Little or no uptake of VOC or ABN by *Rangia* occurred at the Lake Charles site. Mortality of *Rangia* was 100 percent at the site with the highest concentrations of contaminants (most probably caused by elevated water temperatures) and significant uptake of VOC and ABN by *Rangia* occurred at the second affected site. Surprisingly, uptake of ABN at the recovery site also was significant, indicating movement of these compounds much farther downstream than indicated by chemical analysis of water and bottom material.

The above results indicate that *Rangia* has great potential for use as a monitoring tool in areas where contamination by some manmade organic compounds have occurred. This is especially true in areas where concentrations of contaminants in water and bottom material are below analytical detection limits.

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(p.321 follows)

ESTIMATION OF VOLATILIZATION-RATE COEFFICIENTS FOR VOLATILE ORGANIC COMPOUNDS IN BAYOU D' INDE, LOUISIANA

By Dennis K. Demcheck,[1] Charles R. Demas,[1] and Philip B. Curwick[2]

ABSTRACT

Synthetic volatile organic compounds were sampled in water from an industrial outfall and downstream from the outfall in Bayou d' Inde, a small tributary to the lower Calcasieu River, Louisiana, on September 17-18, 1987, to determine volatilization-rate coefficients in a field setting. The method used to calculate the rate coefficients was adapted from a method developed for determining desorption coefficients for reaeration studies.

The rate coefficients computed for eight selected volatile organic compounds suggest that production of some volatile organic compounds may be occurring in water from the industrial outfall. In contrast, significant volatilization of these same organic compounds occurred downstream in Bayou d' Inde. Water from the industrial outfall did not mix vertically as it flowed into Bayou d' Inde, indicating the need for accurate time-of-travel information at all depths in tidally affected streams. The study adds to the understanding of processes controlling the fate of toxic substances in the lower Calcasieu River.

INTRODUCTION

The presence of volatile organic compounds (VOC) in the Bayou d' Inde area of the lower Calcasieu River has been extensively documented by the U.S. Geological Survey (Demas and others, 1988; Demas, in press) and by the Louisiana Department of Environmental Quality (LDEQ) (Michael Schurtz, Louisiana Department of Environmental Quality, written commun., 1987). VOC have been found in concentrations exceeding 3,000 μg/L (micrograms per liter) in an industrial outfall that flows from a large chemical plant in the Lake Charles area into Bayou d' Inde. In contrast to heavier synthetic organic compounds detected in the Bayou d' Inde area, VOC tend to be dissolved in the water column and do not preferentially bind with bottom material. Therefore, VOC behave similarly to hydrocarbon gases such as ethylene and propane, and equations used to describe desorption coefficients for ethylene and propane (Kilpatrick and others, 1987) can thus be used to estimate desorption (volatilization) coefficients for VOC found in the environment. The decrease in concentration of VOC in short reaches of Bayou d' Inde suggests that volatilization may be a dominant process involved in the removal of these compounds from the aquatic environment. Estimation of the rate coefficients, however, has not previously been attempted.

This paper describes a study to determine volatilization coefficients of selected VOC in a field setting utilizing techniques developed for reaeration studies. VOC and dye samples were collected on September 17-18, 1987, from an industrial outfall and a 1-mile reach of Bayou d' Inde, a small tributary to the lower Calcasieu River (fig. E-11).

MATERIALS AND METHODS

The volatilization coefficients of selected VOC were measured using a Lagrangian sampling strategy. In this method, a particular parcel of water is followed as it moves downstream, and samples of the same parcel of water are collected at different locations. The field procedure consisted of the simultaneous collection of VOC samples and samples of rhodamine-WT dye injected at a point upstream in the industrial outfall. VOC samples were collected at sampling points when peak dye concentrations were detected. Dye samples were collected in 40-mL (milliliter) vials in stainless-steel sewage samplers. Dye samples from the bottom of the water column were collected with a sewage sampler modified for point sampling. The sampler was rinsed with deionized water between samples. Dye concentrations were measured with a filter fluorometer, according to methods

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[1] U.S. Geological Survey, Baton Rouge, La.
[2] Ecotech, Baton Rouge, La.

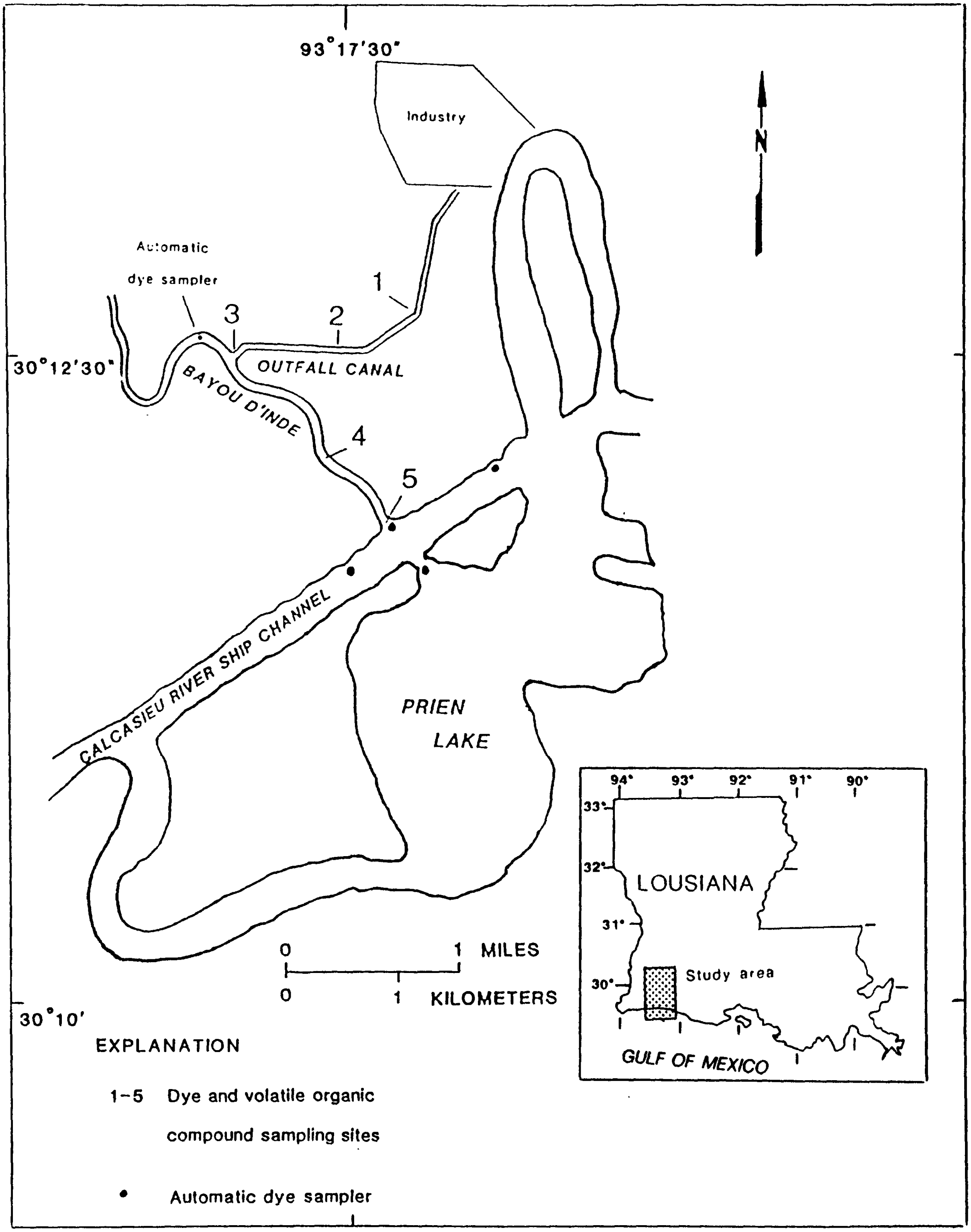

Figure E-11.—Study area, Calcasieu River, Louisiana.

listed in Wilson and others (1986). VOC samples were similarly collected in clean, baked 40-mL vials with Teflon[2] septum caps, placed in stainless-steel sewage samplers. VOC samples were stored at 4 °C (degrees Celsius) and analyzed at the U.S. Geological Survey National Water Quality Laboratory according to methods listed in Wershaw and others (1983).

The dye is assumed to be transported as a conservative solute in the same manner as the VOC. Therefore, the dye acted as a tracer and alerted the field crews when to sample, assuring that the same parcel of water was sampled at each downstream site. Any decrease in peak dye concentration would be the result of dilution, dispersion, or incomplete mixing. Travel times are computed from peak concentration to peak concentration at successive sampling points.

Discharge measurements were made at site 1 (dye-injection point) and at site 4. The measurements indicated the streamflow conditions prevalent during sampling.

The study reach was divided into four sections (fig. E-11). Field personnel used two sets of sewage samplers to ensure that the top and bottom of the water column were sampled simultaneously. Automatic dye samplers were placed at several locations to define movement of the dye cloud during the night and next morning.

The volatilization coefficient K were computed from the equation

$$K = \frac{\ln[(C_v)_u/(C_v)_d]}{(t_d - t_u)}$$

where the subscripts u and d refer to upstream and downstream; $(t_d - t_u)$ refers to travel time, in hours; and (C_v) is the concentration of the VOC, in micrograms per liter. This equation assumes a constant rate of injection of the VOC and steady-state concentration distributions in the study reach.

RESULTS

Movement of the dye cloud, used to compute travel time of the VOC, is shown in figure E-12. Vertical mixing was complete by the time the dye reached site 2, but a pronounced lack of vertical mixing with Bayou d' Inde water was apparent at site 4. Incomplete vertical mixing commonly occurs in this area. Bidirectional flow, caused by tidal fluctuations in this estuarine system, can produce unpredictable circulation patterns. In addition, a temperature gradient often exists in the industrial outfall-Bayou d' Inde area. Industrial cooling water discharged into the outfall canal during the study was 38.1 °C. However, the temperature was 29.3 °C near the bottom of Bayou d' Inde. The discharge at site 1 (dye-injection point) was 358 ft^3/s (cubic feet per second). The basically rectangular channel of the outfall canal has an average depth of about 6 feet. The discharge at site 4 at this time was 356 ft^3/s. Thus, the flow of the outfall canal was producing all of the downstream flow of Bayou d' Inde (average depth, 10 feet) at this point in the tidal cycle. The warmer, less dense outfall canal water overrode the Bayou d'Inde water, producing an almost complete absence of dye at the bottom of site 4. Because travel time was not available to correlate with VOC concentrations at the bottom of Bayou d' Inde, volatilization coefficients were not computed for these sampling points.

An unexpected result of the study was that the dye failed to enter the Calcasieu River Ship Channel during the 24-hour duration of the study. A review of historical dye-tracing studies of circulation patterns (Curwick, 1987) indicated that dye would enter the ship channel and the entrance to Prien Lake, and then move upstream or downstream, depending on the stage in the tidal cycle. A combination of a moderate wind from the southeast and tidal effects, plus the fact that almost all of the dye was being transported near the surface of Bayou d' Inde, caused the dye to move into a shallow (about 2-feet deep) marshy area immediately adjacent to and northeast of the mouth. The dye never reached either of the two automatic dye samplers in the ship channel or the dye sampler at the cross-channel entrance to Prien Lake. Neither was dye detected by the automatic sampler stationed on Bayou d' Inde just upstream from site 3. A previous study (Demas and others, 1988) showed the effects of

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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.

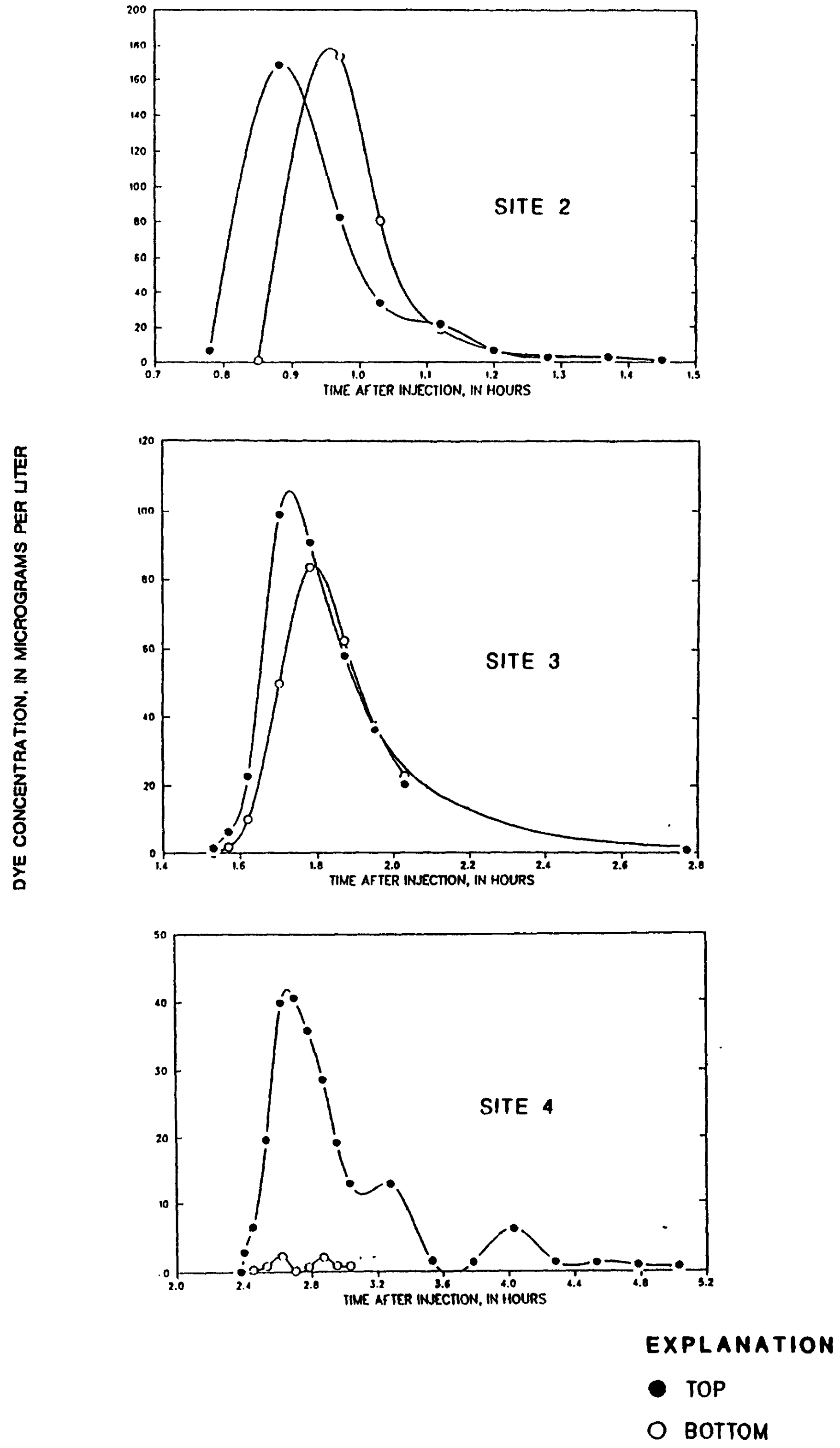

Figure E-12.—Dye concentrations at three sites along the study reach.

Table E-21. – *Concentrations of volatile organic compounds (VOC) detected at five sites in an industrial outfall and Bayou d' Inde, Louisiana, September 17, 1987*

[Concentrations in micrograms per liter; T., top; B., bottom]

Compound	Site 1	2	3	4	5
Bromoform (T.)	73	65	68	42	15
Bromoform (B.)	74	60	52	11	3.9
Chloroform (T.)	120	98	88	65	31
Chloroform (B.)	120	84	82	21	6.5
Chlorodibromomethane (T.)	6.2	5.4	4.1	3.1	1.3
Chlorodibromomethane (B.)	6.0	3.5	3.6	.9	.4
1,2-Dichloroethane (T.)	59	47	42	35	16
1,2-Dichloroethane (B.)	60	36	37	12	4.1
Tetrachloroethylene (T.)	7.1	7.7	8.2	5.8	3.2
Tetrachloroethylene (B.)	8.0	8.2	7.7	2.3	.8
1,1,2,2-Tetrachloroethane (T.)	5.8	6.5	5.5	3.9	1.6
1,1,2,2-Tetrachloroethane (B.)	6.3	4.4	4.7	1.1	.4
1,1,2-Trichloroethane (T.)	7.7	9.0	7.5	6.4	2.9
1,1,2-Trichloroethane (B.)	8.0	6.9	7.1	2.1	.9
Trichloroethylene (T.)	5.4	5.7	5.6	4.2	2.2
Trichloroethylene (B.)	5.8	5.0	5.2	2.7	.6

wind on concentrations of VOC in the water column. In this instance, the wind contributed to changes in the areal distribution of the VOC as well.

Concentrations and the volatilization coefficient, K, of eight VOC are shown in tables E-21 and E-22. Multiplying the concentration by the coefficient equals the initial rate of volatilization of that compound in that reach of stream at that particular time. For example, chloroform in the surface stream reach from site 4 to site 5, beginning with a concentration of 65 μg/L, should volatilize at a rate of 65 μg/L X 0.347 per hour, or 22.6 μg/L per hour.

DISCUSSION

The use of the methods described in this paper is based on the assumption that the removal of VOC is by volatilization only and that no other physical, biological, or chemical processes interfere. In an industrial outfall such as this, the assumption may be somewhat unrealistic.

Table E-22. – *Traveltime and volatilization-rate coefficients for six sections of the study area*

[Coefficients in per hour; T., top; B., bottom; *, negative volatilization; NC, not computed (lack of travel time information)]

Sections:	1-2	2-3	1-3	3-4	4-5	3-5
Compound	Travel time between sections, in hours					
	0.88	0.82	1.70	1.00	2.13	3.13
Bromoform (T.)	0.131	*	0.042	0.480	1.31	0.482
Bromoform (B.)	.237	0.175	.208	NC	NC	NC
Chloroform (T.)	.229	.132	.182	.303	.347	.333
Chloroform (B.)	.404	.030	.143	NC	NC	NC
Chlorodibromomethane (T.)	.156	.337	.224	.280	.407	.281
Chlorodibromomethane (B.)	.610	*	.300	NC	NC	NC
1,2-Dichloroethane (T.)	.257	.138	.200	.182	.367	.303
1,2-Dichloroethane (B.)	.578	*	.284	NC	NC	NC
Tetrachloroethylene (T.)	*	*	*	.346	.279	.300
Tetrachloroethylene (B.)	*	.077	.022	NC	NC	NC
1,1,2,2-Tetrachloroethane (T.)	*	.204	.031	.344	.418	.394
1,1,2,2-Tetrachloroethane (B.)	.406	*	.172	NC	NC	NC
1,1,1,2-Trichloroethane (T.)	*	.223	.016	.159	.371	.303
1,1,2,2-Trichloroethane (B.)	.167	*	.070	NC	NC	NC
Trichloroethylene (T.)	*	.022	*	.288	.303	.298
Trichloroethylene (B.)	.168	*	.064	NC	NC	NC

Hydrocarbons are known to be chemically reactive with halogens such as fluorine and chlorine, which may be found downstream from industrial plants (Stedfast and Draper, 1986). Michael Schurtz (Louisiana Department of Environmental Quality, oral commun., 1987) reveals that industries in the area were permitted to treat effluents with chlorine. Discussions with U.S. Geological Survey National Research Program personnel have raised the possibility that some VOC, such as bromoform, may actually be produced in the canal by a substitution reaction, whereby naturally occurring bromide ions from seawater react with residual chlorine and hydrocarbons to produce halogenated hydrocarbon products. These and other interactions may explain why 14 out of 48 volatilization coefficient calculations for VOC in the outfall canal showed negative volatilization (indicated by asterisks in table E-21). Although variable, none of the coefficients in Bayou d' Inde were negative. The volatilization coefficients for the outfall canal are smaller than the coefficients for Bayou d' Inde, even though temperature and hydraulic conditions predict the reverse. Volatilization coefficients are temperature dependent, and temperatures in the outfall were as much as 6.3 °C higher than temperatures in Bayou d' Inde at the surface. Turbulence in the outfall canal also was greater than in Bayou d'Inde, which would tend to increase volatilization. What is apparently being seen in the coefficients is the net effect of volatilization and production. Volatilization probably is occurring in the outfall canal, but production is offsetting the loss of VOC.

A second assumption inherent in this study is that there was a constant input of VOC into the system. VOC were not sampled continuously at site 1. U.S. Geological Survey and Louisiana Department of Environmental Quality data (Michael Schurtz, Louisiana Department of Environmental Quality, written commun., 1988) over the last 2 years, however, document that VOC, such as bromoform, chloroform, and 1,2-dichloroethane, are always present.

Volatilization coefficients in Bayou d' Inde range from 0.159 per hour for 1,1,2-trichloroethane to 1.31 per hour for bromoform. Although the coefficients vary substantially, a logical assumption is that volatilization is affecting the fates of VOC after they move downstream from the chemical reactions that are probably occurring in the industrial outfall canal.

CONCLUSIONS

This study demonstrates the applicability of using time-of-travel dye data in conjunction with VOC sampling to determine VOC volatilization coefficients in a field setting. The rate coefficients indicate that VOC are being produced as well as being lost in the industrial outfall; losses are presumably the result of volatilization in Bayou d' Inde. The paper also shows the importance of accurate time-of-travel data, which can be difficult to obtain in tidally affected systems. Further study could confirm VOC production in the industrial outfall and refine the rate coefficients.

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ABIOTIC PHOTOLYSIS IN THE CALCASIEU RIVER, LOUISIANA

By Marvin C. Goldberg[1], Kirkwood M. Cunningham[1] and Anne C. Sigleo[1]

ABSTRACT

Direct and indirect abiotic photolysis processes can occur in the Calcasieu River, Louisiana. The river was sampled at Bayou d' Inde, which is located at the outfall of an industrial plant. From the sampling point, the channel flows to the Calcasieu Ship Channel located opposite the entrance to Prien Lake. Indirect photolysis was determined by measuring the steady-state hydroxyl radical $[\cdot OH]_{ss}$ *concentration in water from the sampling point. The hydroxyl radical concentration* $[\cdot OH]_{ss}$ *was found to be* 3×10^{-15} *mole per liter, which is one order of magnitude greater than is present in most aquatic waters. The magnitude of the* $\cdot OH$ *concentration indicates that a comparatively large amount of indirect photolysis occurs at the sampling point. This is attributed to the presence of a large number of organic molecules that can act as sensitizers. On the basis of the measured* $[\cdot OH]_{ss}$ *concentration, the calculated half-lives of selected organic functional groups subject to oxidation by* $\cdot OH$ *in the Calcasieu River ranges from 2 to 30 hours. Direct photolysis also is expected to occur in the river. Laboratory studies measured the photolytic dechlorination of octachlorostyrene, octachloronapthalene, and hexachlorobenzene, all of which are present in the Calcasieu River. The quantum yield of octachlorostyrene was* 8.6×10^{-5}, *of octachloronapthalene was* 2.2×10^{-2}, *and of hexachlorobenzene was* 2×10^{-2}. *It is estimated that these molecules would photolyze in the river with half-lives of 4 to 8 hours.*

INTRODUCTION

Aquatic abiotic photolysis reactions are of two kinds, direct and indirect. This work gives examples of each of these types of reactions that take place in the Calcasieu River, La. Indirect reactions are more prevalent because in this process high-energy sunlight is absorbed by a molecule that is capable of transferring that energy to many other types of molecules, whereas the direct-photolysis process requires that the reactant molecule not only be capable of absorbing the sunlight, but also be capable of undergoing a structural change within itself as a consequence of the light absorption. In the indirect-photolysis process, the molecules that are capable of absorbing sunlight energy and transferring it to other molecules are called sensitizers. Generally, when a sensitizer transfers its energy to another molecule, it raises the energy level of the acceptor molecule to an excited energy state where it has a high probability of producing a radical. Most radicals have high energy and react in very fast timeframes with other nearby molecules. The absolute concentrations of these radicals are low, but are important when considering that they are continuously supplied to the system as the steady-state concentration is rapidly reached.

The purpose of this study was to evaluate the extent of photolysis that takes place in the Calcasieu River, and to give examples of direct photolytic reactions that are of significance in this aquatic system. A further purpose of this study was to evaluate the effect of the indirect reactions by measuring the level of $\cdot$OH radical that is present in the river and to estimate the lifetimes of organic materials in the river subjected to reaction with this oxidizing radical.

INDIRECT PHOTOLYSIS

In oxygenated systems, the major radical intermediates that are formed are (Mill and Mabey, 1985):

e^-	The hydrated electron
$RO_2^{\cdot}$	An organic peroxide
$\cdot OH$	The hydroxyl radical
$^1O_2$	Singlet oxygen

The first product listed, the hydrated electron (e^-), reacts with oxygen with a rate constant of 10^{10} L/mol-s (liters per mole per second) to form the superoxide anion (Anbar and others, 1973):

$$e^- + O_2 \rightarrow O_2^- \qquad (1)$$

The second and third products listed have been considered of such general nature in

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

photolysis reactions in aquatic environments that their presence has been considered as an "indicator" of photolytic reactions. We have chosen to measure the third radical type, the hydroxyl radical [·OH], which is produced by many types of sensitizers. The production of [·OH] in water is a three step process where, initially, an organic sensitizer is excited by light to a positive ion and the superoxide ion. The superoxide ion, which also is produced by the hydrated electron, in turn, reacts in water to produce hydrogen peroxide, which reacts with light to produce ·OH (reactions 2-4):

$$\text{Organic} + h\nu + O_2 \rightarrow \text{Organic}^+ + O_2^- \quad (2)$$

$$2O_2^- + 2H^+ \rightarrow H_2O_2 \quad (3)$$

$$H_2O_2 + h\nu \rightarrow 2\,\cdot OH \quad (4)$$

A good indicator of the extent of photolytic reaction in an aquatic environment is a measurement of the steady-state concentration of the hydroxyl radical $[\cdot OH]_{ss}$.

A reliable method of measuring ·OH is given by Haag and Hoigne (1985). They introduced rate equation 5:

$$-\frac{d[M]}{dt} = k_M[M][\cdot OH]_{ss} \quad (5)$$

This is the rate equation for the reaction between the probe molecule M, which is an ·OH scavenger, and the steady-state concentration in moles per liter of the hydroxyl radical $[\cdot OH]_{ss}$, with a known rate constant of k_M in some time period, dt. Because $[\cdot OH]_{ss}$ is constant, integration of 5 yields the equation:

$$[\cdot OH]_{ss} = \frac{\ln\left(\frac{M_o}{M}\right)}{K_M \Delta t} \quad (6)$$

where M is the concentration after time t of n-butyl chloride, the probe molecule, and M_o is the initial concentration of n-butyl chloride. The steady-state concentration of the hydroxyl radical is [·OH]ss and Δt is the time of reaction. The rationale for the accuracy of this measurement was given by Haag and Hoigne (1985). The rate constant, k_M, for n-butyl chloride was found experimentally to be 3×10^9 L/mol-s.

Experimental Procedure

Calcasieu River water was collected from Bayou d' Inde at the location indicated in figure. E-13. This water was shipped to the U.S. Geological Survey Laboratory in Denver, Colo., where it was irradiated in a Rayonet[2] "sunlight simulation" irradiator having a maximum energy from 300 to 400 nm (nanometers). Irradiation times were 4 hours. Several samples were run and all the data were merged to minimize statistical differences in sample collection, handling, and analyses. Hydrogen peroxide was added to bring the measured concentration of [·OH] into the range of analytical detection. Sample analyses involved fitting a least-squares line through the ensemblage of data and extrapolating to the y-intercept to find the $[\cdot OH]_{ss}$ concentration at zero-added hydrogen peroxide concentration.

Results

The [·OH]ss concentration in water collected from the Calcasieu River as a function of decreasing hydrogen peroxide is shown in figure E-14. The extrapolated value of [·OH]ss concentration at zero concentration of added hydrogen peroxide is 3.5×10^{-15} mol/L (moles per liter). As a comparison, the Platte River water upstream from the city of Denver has [·OH]ss in the order of 10^{-16} mol/L; the Arkansas River drainage along an iron-rich stream has [·OH]ss concentration as high as 10^{-14} mol/L and Lake Greifensee in Switzerland has [·OH]ss concentrations on the order of 10^{-16} mol/L. Mill and Mabey (1985) found that most waters tested had [·OH]ss on the order of 10^{-17} mol/L. Even though the practice of measuring the [·OH]ss concentration is relatively new, it can be stated that most waters probably fall in the range of 10^{-16} to 10^{-17} mol/L. Concentrations on the order of 10^{-15} mol/L indicate a large amount of photolytic activity. In the case of the Calcasieu River, this is undoubtedly caused by the large number of organic molecules present (Pereira and others, 1988) at the sample-collection location that are able to absorb high-energy sunlight, which is then converted by reactions 2,3,4 to ·OH.

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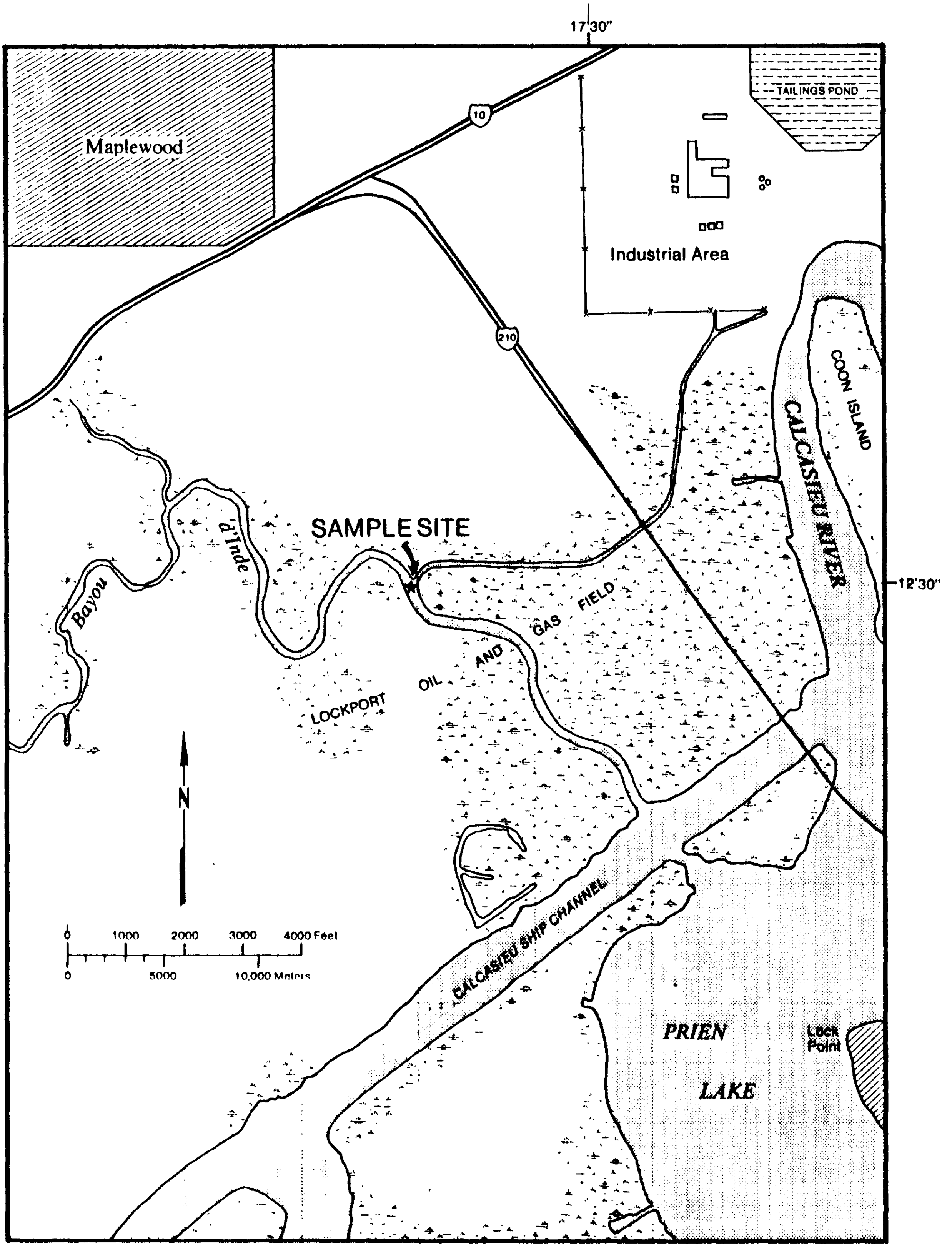
[2] The use of trade names in this paper is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.



Location Map Adapted from U S G S 7½ Minute Quadrangle - WESTLAKE, Louisiana

Figure E-13.—Location of the sampling point at Bayou d' Inde, Louisiana.

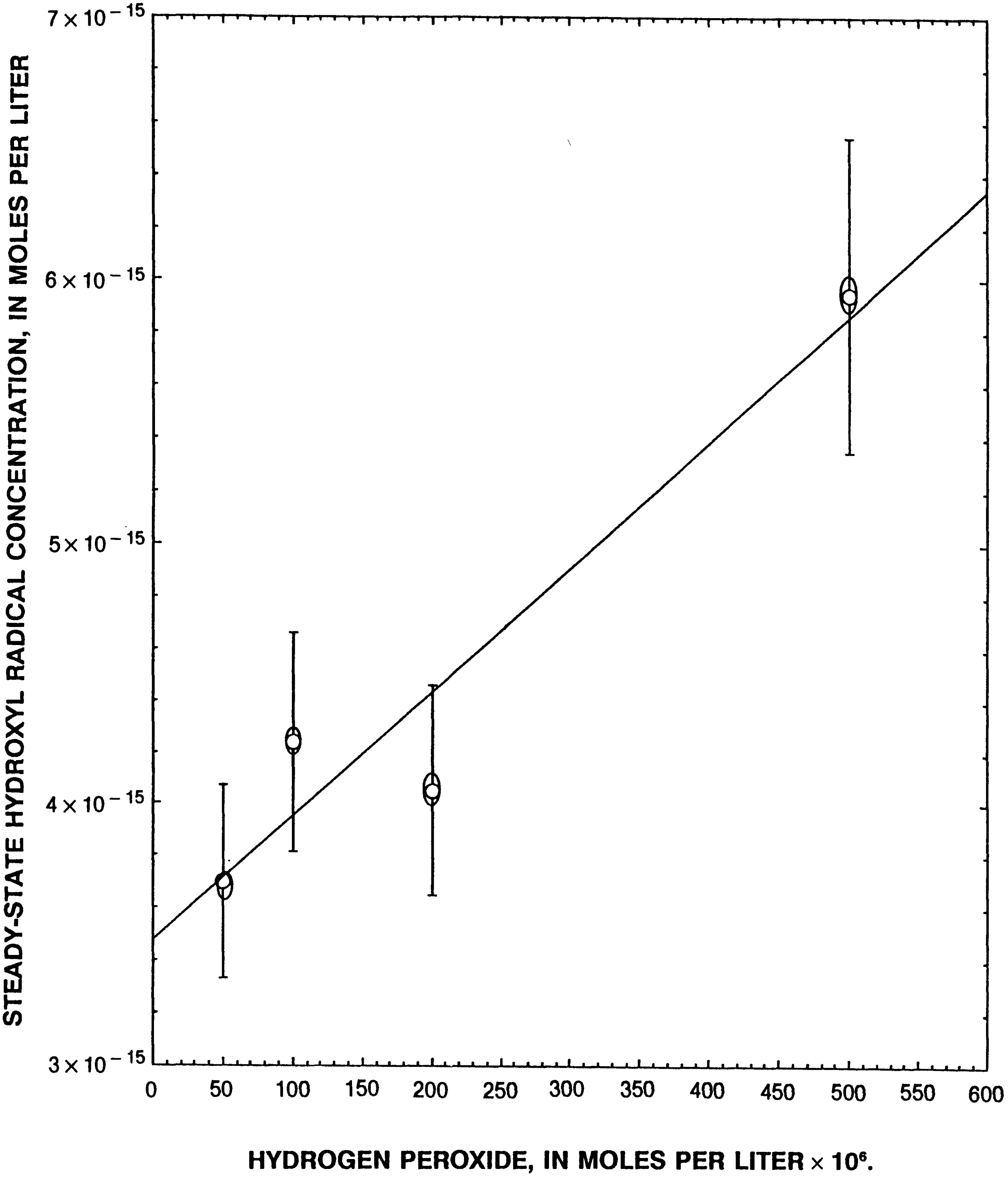


Figure E-14. – The steady-state hydroxyl radical concentration in the Calcasieu River, Louisiana.

Using the standard rate equation:

$$-\frac{d[C]}{dt} = k_{ox}\, n\, [C][ox] \qquad (7)$$

where ox is the oxidizer ($\cdot$OH), t is time, k is the rate constant for the reaction and C is the concentration of the material being oxidized, the rate of oxidation can be stated in terms of a first order rate equation. This equation, when integrated, takes the form:

$$\ln\left(\frac{C_o}{C_t}\right) = \sum nk'_{ox}t \qquad (8)$$

where n is the number of reactive sites in material C, k′ is a pseudo first order rate constant

and (9)

$$t_{1/2} = \frac{\ln 2}{\sum nk'_{ox}}$$

Some typical half-lives for organic oxidation by $\cdot$OH radicals at concentration of $\cdot$OH found in the Calcasieu River, based on rate constants in Anbar and others (1973), are given in table E-23.

DIRECT PHOTOLYSIS

Highly chlorinated aromatic hydrocarbons (HCAH) are pollutants of concern in aquatic environments because of their persistence (Hutzinger, 1982) and toxicity (Lai, 1984). Because common degradation pathways (microbial attack, volatilization, and so on) tend to be slow for these compounds, sunlight photolysis may play an important role. In recent years, a number of studies (Mill and Mabey, 1985; Cesareo and others, 1986; Choudry and others, 1986) have outlined the basic phenomena of the photolytic degradation of HCAH, as well as plausible mechanisms of the degradation reactions. In organic solvent-water mixtures, reductive dechlorination reactions appear to be most important in aromatic chlorides (Ar-Cl):

$$\text{Ar-Cl} + h\nu \rightarrow \text{Ar-Cl}^* \rightarrow \text{Ar}\cdot + \text{Cl} \qquad (10)$$

$$\text{Ar}\cdot + \text{RH} \rightarrow \text{ArH} + \text{R}\cdot \qquad (11)$$

It can be speculated that reactions 10 and 11 will also be the most important for highly insoluble HCAH in aquatic systems, because they are found preferentially in the organic-rich environments of colliodal particles, in surfactant films, or on the surface of mineral particulates.

In this work, we have determined the disappearance quantum yield of several HCAH compounds, some of which have been detected at elevated concentrations in the sediments of Bayou d' Inde, an estuarine environment impacted by petrochemical and agrochemical industries (Pereira and others, 1988). Typical concentrations found in bottom and suspended sediments, respectively, in micrograms per gram were: hexachlorobenzene (HCB) (7544,33.7), octachlorostyrene (OCS) (56.0,5.6), and octachloronapthalene (OCN) (12.0,0.81).

Experimental Procedures

All HCAH compounds were obtained as standard reference materials from the U.S. Environmental Protection Agency or from a commercial supplier. They were photolyzed in 50:50 acetonitrile:water solutions at 2 to 4 micromolar concentrations in quartz bulbs under

Table E-23.—*Half-lives in Calcasieu River water of representative organic reactive groups*

Reactive group	Half-life, in hours
Olefin (ethylene)	30
Alcohol (butyl alcohol)	30
Aldehyde (butyraldehyde	16
Aromatic amine (phenyl alanine)	8
Benzyl (benzyl alcohol)	6
Phenol (phenol)	6
Hydroquinone (hydroquinone)	3
Hydroperoxide (ROOH)	2

clear midday sunlight or in a thermostated Pyrex cell under 300 to 400 nm lamp light in a well-type irradiator. The lamp spectrum was obtained from the manufacturer and the sunlight spectral distribution was available from the literature (Dulin and Mill, 1982).

Determination of incident light flux for the irradiator was performed using phenylglycolic acid (Defoin and others, 1986). For sunlight, the variable quantum yield p-nitroacetophenone/pyridine actinometer (light flux measuring compound) of Dulin and Mill (1982) was used, with pyridine concentration adjusted to give an actinometer half-life approximately equal to that of the HCAH compound. In sunlight experiments, the actinometer was set outside under the same conditions and for the same time as used for the HCAH compound.

Remaining HCAH or actinometer concentration as a function of photolysis time was determined by high pressure liquid chromatography (C-18 column, 50:50 acetonitrile:water mobile phase).

Results

Because the amount of photo-induced chemical reaction that occurs in a direct photolysis reaction is directly proportional to the amount of light absorbed by the photoactive compound, comparisons of the spectral overlap of lamp or sunlight spectra with that of HCAH absorption spectra are shown in figures E-15 and E-16, respectively. The degree of spectral overlap decreases in the order OCN > OCS > HCB. Curves for dichlorobiphenyl, tetrachlorobiphenyl, and biphenyl are also shown on these plots, although the overlap with either sunlight or lamp spectra were negligible for these compounds, or they were otherwise found to be non-photoactive under these experimental conditions.

The wavelength-averaged disappearance quantum yields for HCB, OCN, and OCS were calculated from figure E-17 (and comparable data for the UV lamp photolyses in figure E-17), using the expressions below from Dulin and Mill (1982)

$$d[C]/dt = 2.303[C]r\Phi\Sigma L_{\lambda}\varepsilon_{\lambda} = kpE[C] \quad (12)$$

$$\Phi_{c}E = \Phi_{a}(1/S)(\Sigma L_{\lambda}\varepsilon_{\lambda})a/(\Sigma L_{\lambda}\varepsilon_{\lambda})c \quad (13)$$

where [C] is the concentration of the compound (HCAH or actinometer) that is disappearing, r is a reaction parameter characteristic of the photolysis cell; Φ_{cE} and Φ_a are disappearance quantum yields for the HCAH compound and actinometer, respectively; $L\lambda$ is the incident light flux at wavelength λ; ε_λ is the absorptivity of the photoactive compound at wavelength λ; and S is the slope of a plot of $\ln([C]_0/[C]t)$ for the actinometer compound versus the same quantity for the HCAH compound, when both are exposed to the same integrated light flux. Equations 12 and 13 apply only to optically dilute (maximum absorbance less than .05) solutions.

Plots of equation 12 for the sunlight photolyses of HCB, OCN, and OCS are shown in figure E-18. The indicated slopes are linear least-squares fits and are equal to the parameter S in equation 13. On the basis of these slopes and the known values of actinometer quantum yield, the disappearance quantum yields from sunlight photolysis in table E-24 were calculated. Comparable plots for photolysis with the UV lamp are shown in figure E-18, and the resulting quantum yields also reported in table E-24. The quantum yield of HCB should be regarded as of marginal significance, given the poor overlap of this compound with both sun and lamplight. No photoproduct peaks were observed in any of the photolytes.

DISCUSSION

The agreement between sunlight and lamplight-derived quantum yields in table E-24 is quite good except for HCB. The results for Φ, combined with the estimated values for r and for Σ L <F128Ml ε_λ in equation 13, show that OCN and OCS will photodegrade in unclouded, midday, midsummer sunlight with a half-life of about 4 to 8 hours. From this data, a qualitative estimate can be made of how fast such compounds might degrade in the environment of Bayou d' Inde in midsummer. In this location, the contaminated sediments lie under about 2 meters of estuarine water with a suspended-solids concentration of about 10 to 15 ppm (parts per million), and a total dissolved organic carbon concentration of about 5 ppm, some of which will absorb sunlight. Considering just the former contributor to sunlight loss with water depth, the approximate empirical expression of Miller and

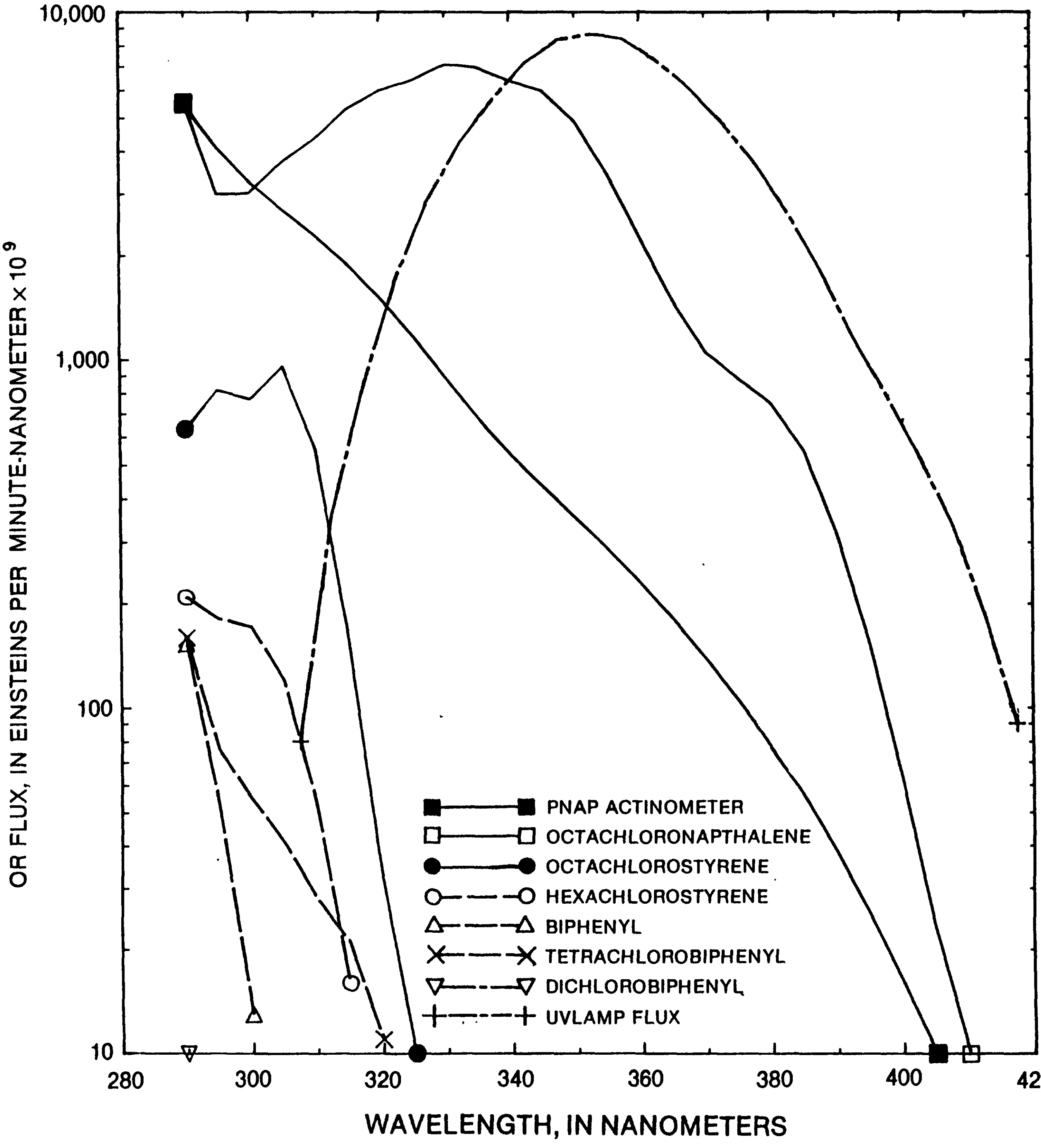


Figure E-15.—Comparison of the UV lamp flux spectrum impinging on the photolysis cell, in Einsteins per minute per nanometer, with the molar absorptivity of octachloronapthalene, octachlorostyrene, hexachlorobenzene, biphenyl, dichlorobiphenyl, tetrachloribyphenyl, and the actinometer in units of liter per mole per centimeter.

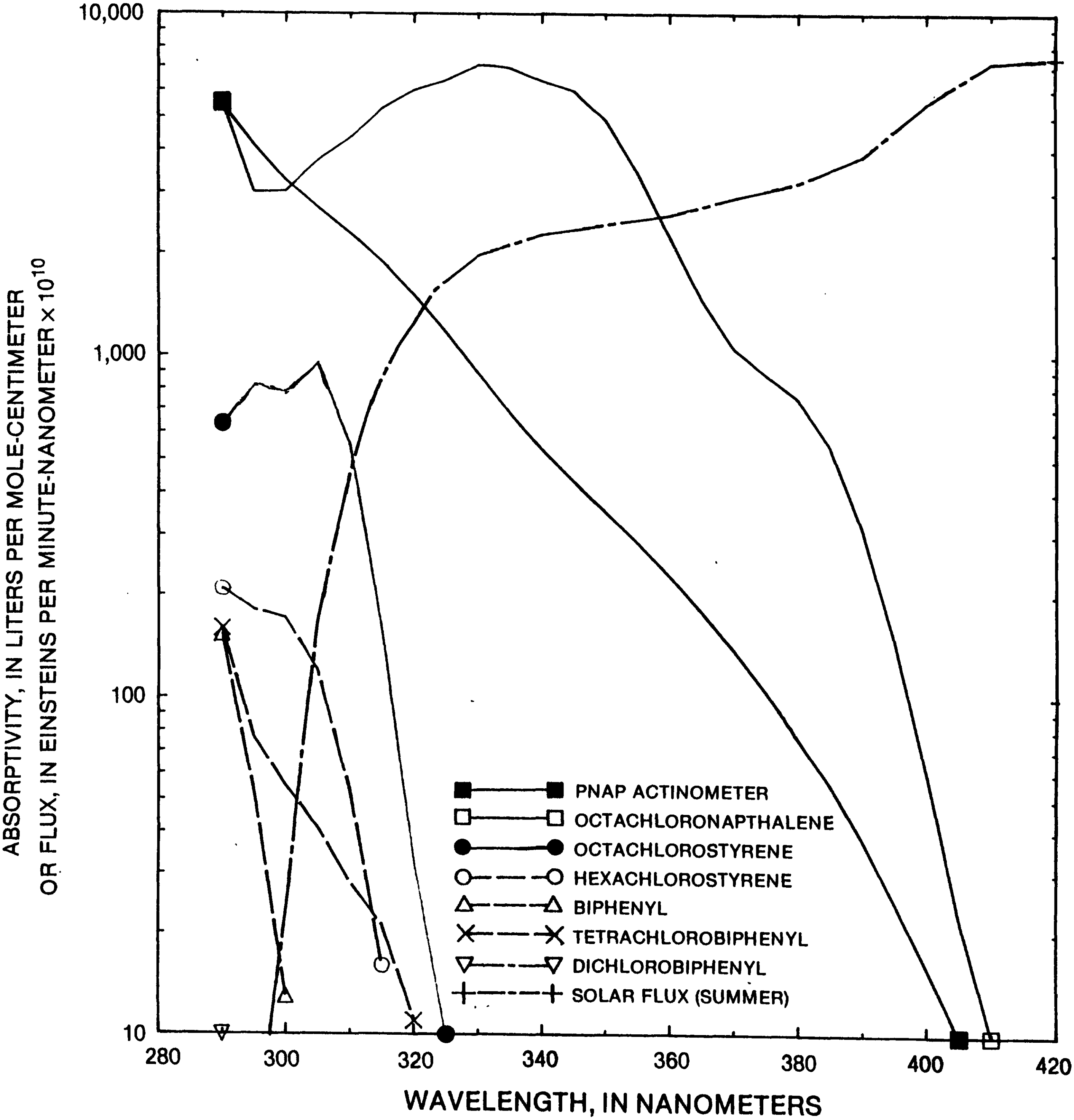


Figure E-16. – Comparison of midday summer sunlight flux spectrum, in Einsteins per minute per nanometer, with the molar absorptivity of octachloronapthalene, octachlorostyrene, hexachlorobenzene, biphenyl, dichlorobiphenyl, tetrachlorobiphenyl, and the actinometer in units of liters per mole per centimeter.

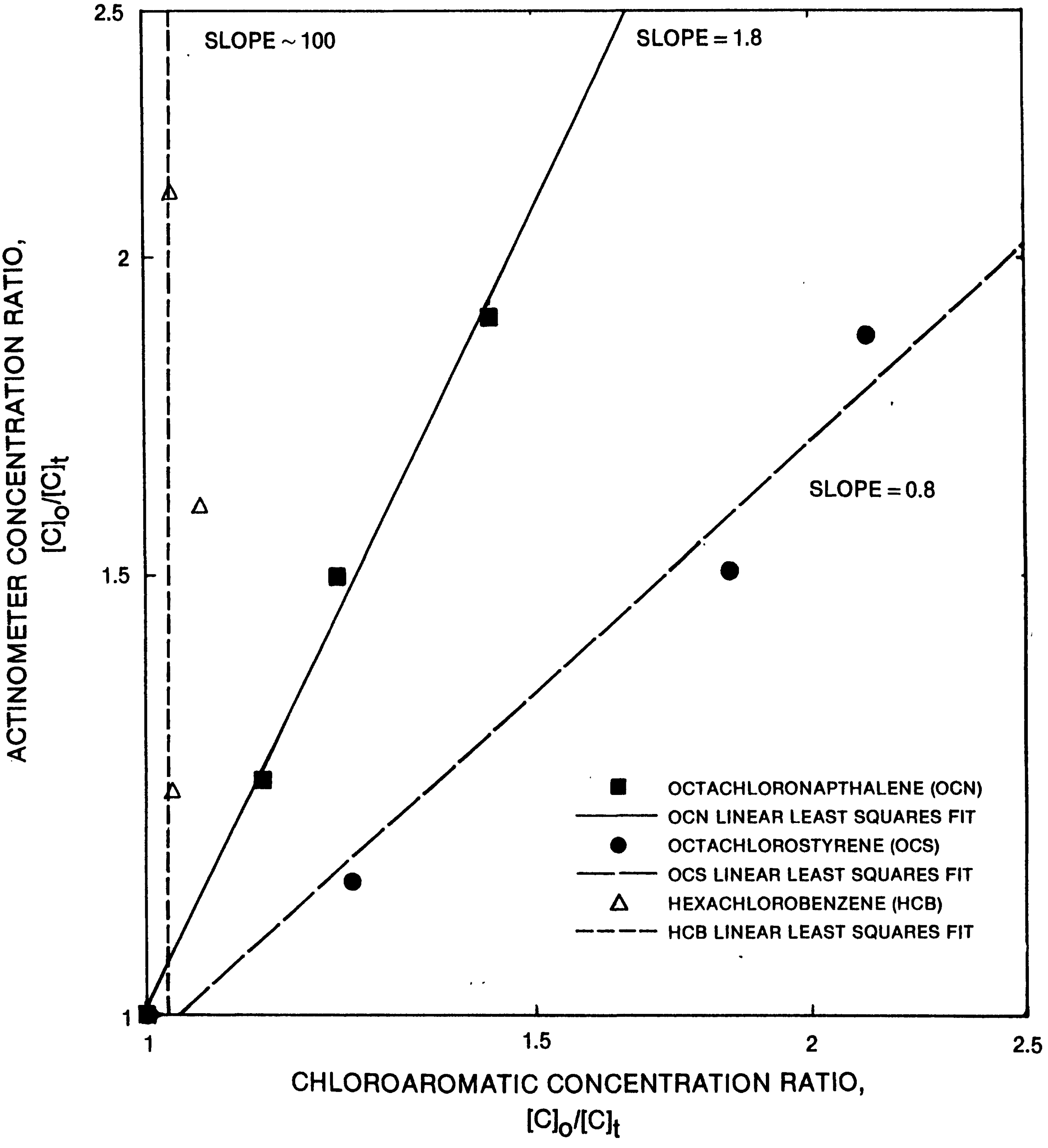


Figure E-17. – Paranitroacetophenone actinometer concentration ratio $[C_o]/[C_t]$ as a function of the concentration ratio $[C_o]/[C_t]$ for octachloronapthalene, octachlorostyrene, and hexachlorobenzene for sunlight irradiation.

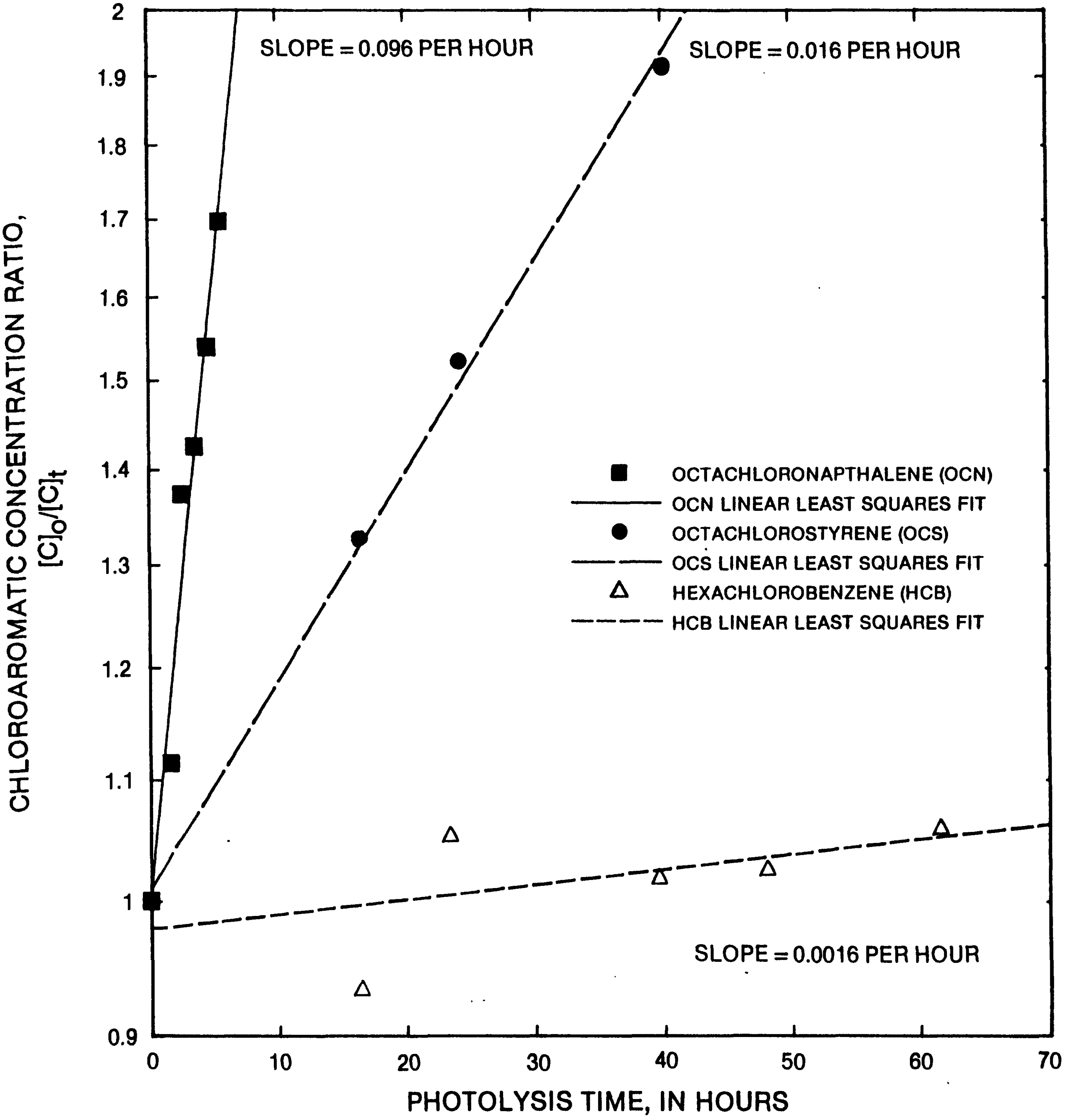


Figure E-18.—The concentration ratio $[C_o]/[C_t]$ for octachloronapthalene, octachlorostyrene, and hexachlorobenzene as a function of UV-lamp photolysis time.

Table E-24.—*Disappearance quantum yields*[1] *for octachloronapthalene, octachlorostyrene, and hexachlorobenzene*

Compound	Sunlight photolysis x 10^3	Lamp photolysis x 10^3	Average x 10^3
Octachloronapthalene	0.098	0.074	0.086
Octachlorostyrene	21	22	22
Hexachlorobenzene	2	20	11

[1] Quantum yield is the ratio of moles of product formed to moles of photons absorbed by the reactant molecules. The ratio is unitless.

Zepp (1979) can be used to estimate the relative UV flux reaching the bottom sediments:

$$\ln(I_o/I) = K_{atten}DC_{s,} \qquad (14)$$

where I_o = Solar UV flux incident on the water surface:

D = depth to light absorbing bottom sediment (approximately 180 centimeters);

C_s = concentration of suspended sediment in milligrams per liter (approximately 10 milligrams per liter);

K_{atten} = attenuation constant, approximately .0026 liters per milligram-centimeter.

Using this expression, I/I_o is approximately equal to 10^{-5}, suggesting that photochemical change even at the surface of the bottom sediment may be very slow (a matter of years) unless these sediments are resuspended. By contrast, the photolysis rate for the HCAH in the suspended sediments will be faster than that in the bottom sediments because they will be much more likely to come into contact the with UV part of the sunlight spectrum. However, the data in Pereira and others (1988) show that the fraction of HCAH in the suspended sediment is very small and the rate of transfer between suspended and bed sediment HCAH is very low. Therefore, the photolytic decay of the total pool of HCAH through the photolysis of HCAH in the suspended sediment fraction also will be very slow.

CONCLUSIONS

Indirect abiotic photolysis takes place in the Calcasieu River, La. Comparison of the steady-state $[\cdot OH]_{ss}$ hydroxyl radical concentration in this river with other aquatic systems leads to the conclusion that the river, at the sampling point, is more photoactive than normal aquatic waters. Due to the nature of oxidizing radicals, which are produced by indirect photolysis, there must be a broad and extensive effect on the organic constituents of the river among the organic reactive groups that react with these radicals. For reactions with $\cdot OH$, the half-lives for the organic reactive groups listed in the discussion ranged from 2 to 30 hours. Because the $[\cdot OH]_{ss}$ radical concentration was measured at an industrial outfall, the results at this location may overly emphasize the photolytic reactions in the parts of the river that are less concentrated in organic molecules, nevertheless, there are significant and measurable indirect photolytic reactions taking place in this system.

Direct photolysis is a factor in the dechlorination of some types of chlorinated hydrocarbons and the laboratory tests conducted on octachloronapthalene, octachlorstyrene, and hexachlorobenzene indicate that, under optimal conditions, these materials are expected to photodegrade in the Calcasieu River with half-lives of 4 to 8 hours.

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SITE DESCRIPTION AND SUMMARY OF RESEARCH ACTIVITIES ON THE MOVEMENT AND FATE OF CHLORINATED SOLVENTS IN GROUND WATER AT PICATINNY ARSENAL, NEW JERSEY

By Thomas E. Imbrigiotta[1] and Mary Martin[1]

ABSTRACT

The U.S. Geological Survey is conducting an interdisciplinary research study of ground-water contamination by chlorinated solvents and other contaminants at Picatinny Arsenal, New Jersey. This paper summarizes the hydrogeology, extent of ground-water contamination, and the research activities that are ongoing at the Building 24 site at Picatinny Arsenal. The ground-water contamination is primarily within the 50-foot thickness of unconfined glacial sediments and extends from Building 24 to Green Pond Brook, the ground-water discharge point.

Laboratory and field studies were used to study the effect of soil moisture on trichloroethylene-vapor sorption to the unsaturated zone soil. A mathematical transport model is being developed to test hypotheses on air-phase transport and in situ *microbial degradation of chlorinated solvents in the unsaturated zone.*

Similar areal and vertical distributions of organic and inorganic compounds suggest that both types of compounds are transported in the ground-water system from near the water table at Building 24, downgradient and downward to near the base of the unconfined aquifer, and then upward where they discharge to Green Pond Brook. Trace-metal distributions and areas of enrichment were determined in core samples at various locations in the plume. Elevated dissolved organic carbon concentrations near Building 24 were explored using a new isolation technique and analysis with carbon-13 nuclear-magnetic-resonance spectroscopy.

Microbial populations in soil from the unsaturated zone were determined to range from 0.5 to 6 million organisms per gram of soil. Soil microcosms are being used to determine trichloroethylene biotransformation rates for aerobic unsaturated and aerobic saturated conditions and for anaerobic saturated conditions in the presence of a supplementary carbon source. Preliminary areal and cross-sectional solute-transport models were constructed to define the horizontal movement of selected contaminants in the unconfined sediments and the vertical movement of these contaminants within and between aquifers at the site.

INTRODUCTION

Contamination of ground water by chlorinated solvents is a major, widespread problem because these compounds are used in many different processes including metal degreasing, dry cleaning, organic synthesis, and fumigation, and because these compounds are relatively soluble compared to other synthetic organic contaminants. The movement and fate of chlorinated solvents transported in aquifer systems need to be investigated.

The U.S. Geological Survey is conducting an interdisciplinary research study of ground-water contamination by chlorinated solvents and other contaminants at Picatinny Arsenal in north-central New Jersey. The objectives of the study are to (1) improve the understanding of the chemical, physical, and biological processes that affect the movement and fate of these contaminants, particularly trichloroethylene, in the subsurface; (2) determine the relative importance of these processes; and (3) develop predictive models of contaminant transport. The study is being conducted at two sites, near Buildings 24 and 95, where the ground water has been affected by effluent from metal-plating, degreasing, and etching operations (fig. F-1). Research has progressed further at the Building 24 site than at the Building 95 site, and only the Building 24 site and its associated research activities are discussed here.

Picatinny Arsenal is located in north-central New Jersey. The arsenal employs approximately 6,400 people in research and development of

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

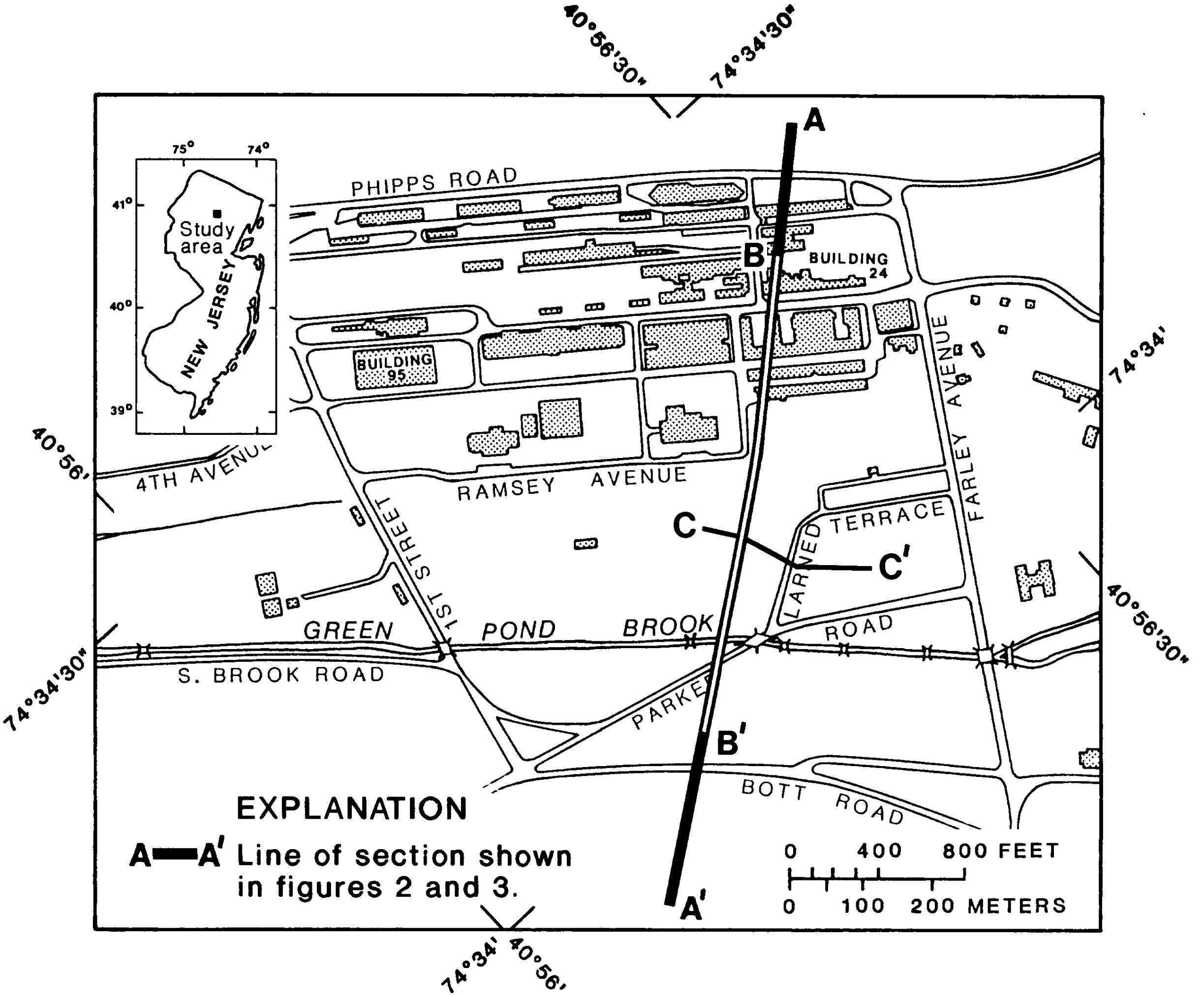

Figure F–1.—Location of Building 24 study area at Picatinny Arsenal.

munitions and weapons. From 1960 to 1981, a metal-plating wastewater-treatment system in Building 24 discharged tens of thousands of liters of wastewater daily into two unlined lagoons. The metal-plating wastewater contained trace metals, such as cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), vanadium (V), and zinc (Zn), and other ions used in plating solutions, such as sodium, potassium, sulfate, chloride, and cyanide (Fusillo, Ehlke, and Martin, 1987). From 1973 to 1985, a metal-degreaser overflow system discharged pure chlorinated solvents into a dry well through an open-ended overflow pipe. The discharge from the overflow system contained primarily trichloroethylene (TCE) and later (after 1983) 1,1,1-trichloroethane (TCA) (Fusillo, Ehlke, Martin, and Sargent, 1987). The overflow discharge may have also contained some tetrachlorethylene (PCE) and cis-1,2-dichloroethylene (cis-DCE). The infiltration of wastewater from the lagoons and chlorinated solvents from the dry well has contaminated the ground water downgradient from Building 24. The contaminant plume extends from Building 24 to Green Pond Brook, a distance of about 1,650 feet (Fusillo, Ehlke, Martin, and Sargent, 1987).

The purpose of this paper is to present (1) a description of the Picatinny site, including the generalized hydrogeology and known extent of ground-water contamination of the aquifer system; and (2) a summary of the significant findings for each of the research activities that are ongoing at the Picatinny site.

HYDROGEOLOGY

Picatinny Arsenal is located in a glaciated valley between two northeast-to-southwest trending bedrock ridges that rise about 200 to 300 feet above the glacial sediments. At the contamination site, as much as 250 feet of unstratified and stratified drift overlies a U-shaped weathered bedrock surface. A generalized hydrogeologic

CHAPTER F – CHLORINATED SOLVENTS IN GROUND WATER AT PICATINNY ARSENAL, NEW JERSEY

(p. 343 follows)

section (A-A′ in fig. F-2) across the valley near the contaminant plume shows an approximately 50-foot-thick unconfined aquifer in the area between Building 24 and Green Pond Brook. In this area, the unconfined aquifer is underlain by about 60 feet of confining sediments. Near the lateral limits of the glacial sediments, the confining sediments are present in numerous discontinuous layers, and the thickness of the unconfined sediments is areally variable. The unconfined sediments range in grain size from gravel and coarse sand to fine clay and have an estimated average horizontal hydraulic conductivity of 60 ft/d (feet per day), on the basis of aquifer-test and grain-size analyses. The confining sediments are composed of interbedded fine sand, silt, and clay that have a combined estimated vertical hydraulic conductivity of 0.6 ft/d.

Beneath the confining sediments, the confined aquifer is approximately 60-feet thick and is composed of predominately fine to coarse sands, that contain some finer (silt and clay) and coarser (gravel, pebbles, cobbles, and boulders) sediments. The confined aquifer has an estimated horizontal hydraulic conductivity of 120 ft/d, on the basis of aquifer-test and grain-size analyses. Bedrock in the study area consists mainly of dolomite. The bedrock is separated from the overlying unconsolidated sediments by a zone of weathered bedrock of variable thickness. The weathered bedrock is less permeable than the

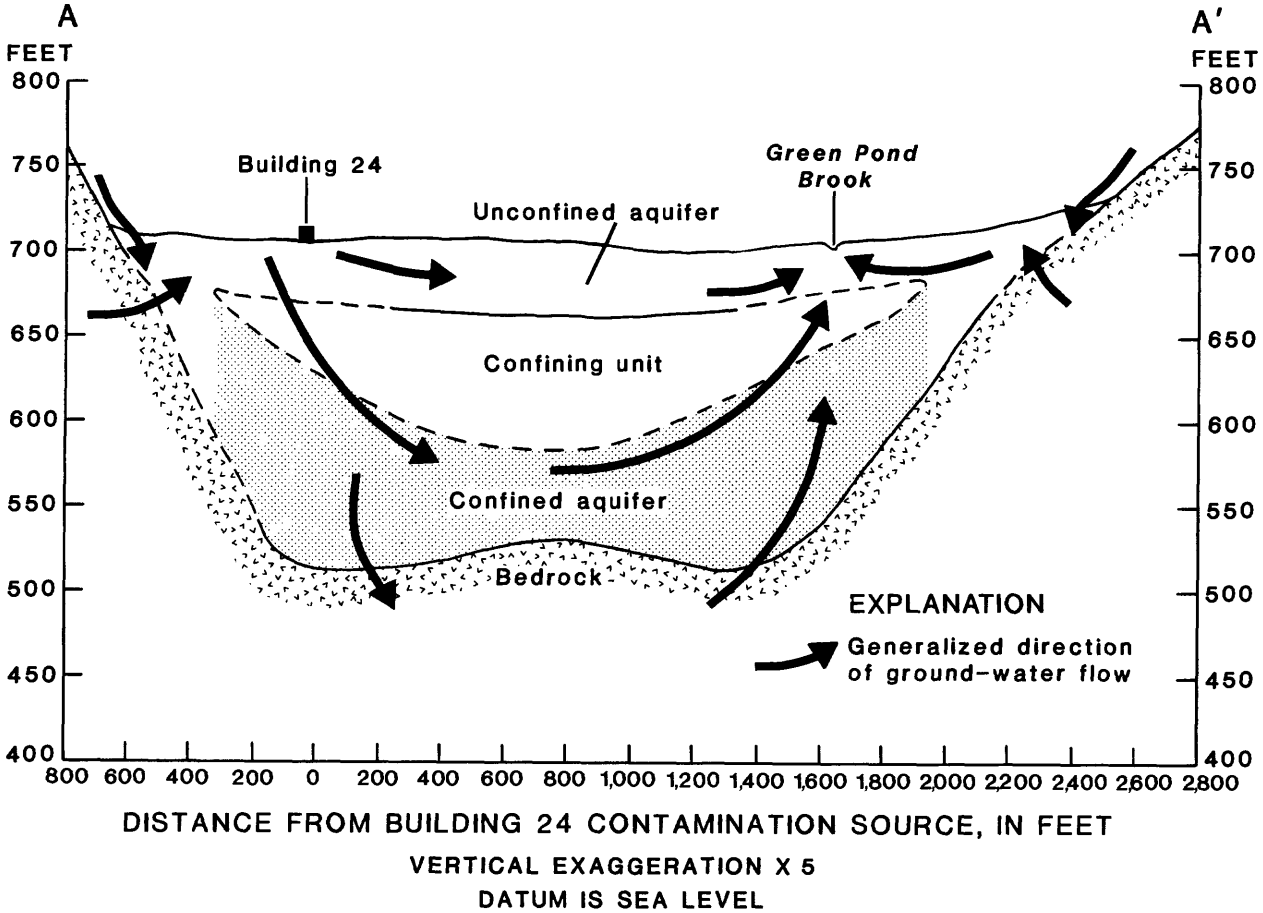

Figure F–2.– Generalized hydrogeologic section A-A′ showing direction of ground-water flow (modified from Fusillo, Ehlke, and Martin, 1987, fig. 3). Location of section shown in figure F–1.

overlying sediments and the underlying fractured dolomite and is a leaky confining unit between the overlying and underlying aquifers.

Ground water in the unconfined aquifer in the study area flows from the northern limit of the glacial sediments to Green Pond Brook primarily in a southeasterly direction (fig. F-1) with a slight downvalley component of flow to the southwest. Near Building 24, vertical flow is downward through confining sediments to the confined aquifers, and then upward near Green Pond Brook where it discharges (fig. F-2). Horizontal gradients in the confined aquifers also are toward the stream but have a downvalley component of flow that is slightly larger than that in the unconfined aquifer. The ground-water flow system is presented in detail in another paper (Martin, 1989, this Proceedings).

GROUND-WATER CONTAMINATION

Ground-water contamination near Building 24 has previously been discussed by Sargent and others, (1986), Fusillo, Ehlke, and Martin (1987), and Fusillo, Ehlke, Martin, and Sargent (1987). The study by Fusillo, Ehlke, Martin, and Sargent (1987) involved the use of a drive-point sampling device to define the three-dimensional extent of chemical constituents in the unconfined aquifer. TCE, the primary organic contaminant, was found at a maximum concentration of 44,000 μg/L (micrograms per liter) at a site about 3 feet downgradient from a dry well at Building 24. The ground-water contamination is primarily contained within the 50-foot thickness of unconfined glacial sediments and extends from Building 24 to Green Pond Brook, the ground-water discharge point. The vertical distribution of TCE along the hydrogeologic section B-B′, the approximate center of the plume as determined by the drive-point sampling, is shown in figure F-3. Although not as widely distributed, other organic compounds were detected in the drive-point sampling; maximum levels were 200 μg/L for PCE, 380 μg/L for cis-DCE, 50 μg/L for TCA, and 30 μg/L for vinyl chloride. Elevated concentrations of trace metals also were found; maximum levels were 65 μg/L for Cd, 48 μg/L for Cr, 70 μg/L for Cu, 190 μg/L for Pb, and 54 μg/L for V. A detailed synopsis of the ground-water chemistry in the study area is presented in another paper (Imbrigiotta and others, 1989, this Proceedings).

RESEARCH ACTIVITIES

Four major areas of research at Picatinny Arsenal are:

(1) Chlorinated solvents in the unsaturated zone
(2) Chemistry of contaminated ground water
(3) Microbial transformations of chlorinated solvents, and
(4) Distribution and movement of chlorinated solvents in ground water.

Work on each of these topics has been done by a number of researchers. A brief summary of the current research findings on each subject is given in the following sections.

Chlorinated Solvents in the Unsaturated Zone

Laboratory and field studies were used to determine the distribution of TCE vapors in the unsaturated zone above the main axis of the contaminant plume. Gas samples were collected from two or three depths at each of six locations within the 5- to 15-foot-thick unsaturated zone. Laboratory experiments have confirmed the hypothesis that soil moisture, up to saturation soil-moisture content, strongly suppresses TCE vapor sorption to soil. Measurement of the moisture content of soil samples collected from the unsaturated zone, in conjunction with laboratory-generated water-vapor isotherms for the same soil samples, indicates that the distribution of TCE between vapor and soil can be predicted from a batch water-soil isotherm and the compound's Henry's Law constant. TCE vapor-soil partition coefficients were measured in the field and normalized for soil organic-carbon content. These values will be compared with previously reported partition coefficients for water-soil systems.

A multiconstituent, multiphase mathematical transport model is being developed to test hypotheses on air-phase transport and *in situ* microbial biotransformation of chlorinated solvents in the unsaturated zone. Laboratory column experiments are planned to evaluate the complex interrelation between the simultaneous diffusive transport of organic and inorganic gases and microbial biotransformation. These experiments will be used to test, under controlled conditions, assumptions incorporated in the mathematical transport model.

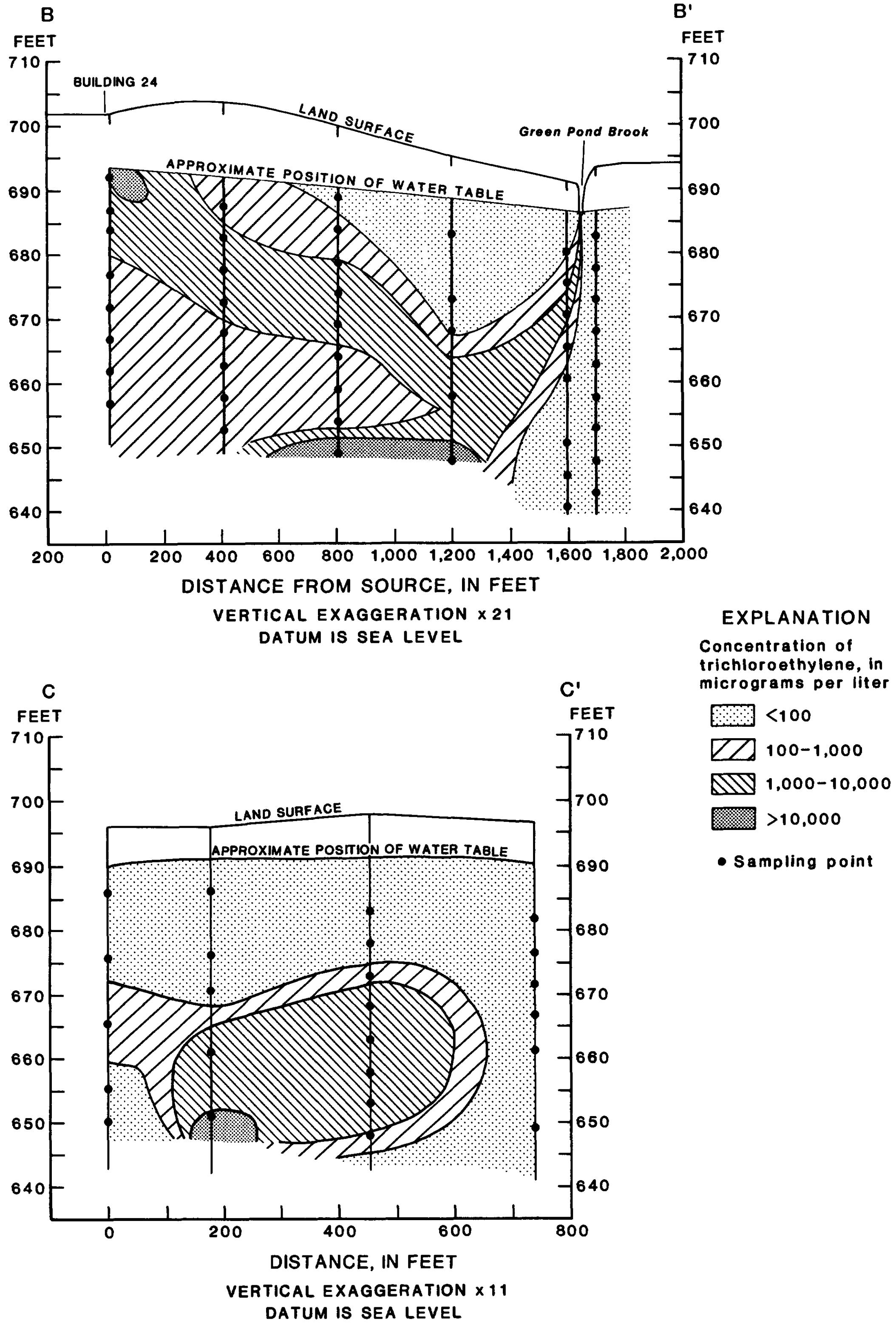

Figure F–3.—Vertical distribution of trichloroethylene along hydrogeologic sections B-B′ and C-C′ on the basis of drive-point sampling data for 1986 (section B-B′ from Fusillo, Ehlke, Martin, and Sargent, 1987, fig. D–3). Location of sections shown in figure F–1.

Preliminary results of sampling nests of vapor probes near Building 24 have shown a more complex vapor distribution than anticipated. Additional sampling for chlorinated hydrocarbons, organic degradation products, and inorganic gases will be necessary to characterize further the vapor plume in the unsaturated zone. These data will aid in formulating hypotheses to be tested by the vapor transport model and in the design of the column experiments.

Field experiments are planned to evaluate *in situ* transport characteristics needed for the unsaturated zone transport model. These characteristics include air-filled porosity, permeability, and effective diffusion coefficients. Temperature profiles measured with thermistors nested in the unsaturated and shallow saturated zones will be used to study energy flux and dynamics of the soil mixing zone.

Chemistry of Contaminated Ground Water

The chemistry of ground water in the unconfined aquifer downgradient from Building 24 was defined by the results of the drive-point sampling summarized by Fusillo, Ehlke, Martin, and Sargent (1987) and the results of sampling 27 new wells in 1987. Comparison of water quality in a well immediately downgradient from the source area with background water quality in an area unaffected by the plume indicated that water from the near-source well has much lower dissolved oxygen concentration and a specific conductance value and sodium, potassium, chloride, sulfate, and alkalinity concentrations two to four times the background levels. Water from the near-source well had detectable concentrations of cyanide (0.04 mg/L) (milligrams per liter), Cr (11 μg/L), and Cu (53 μg/L) and high concentrations of dissolved organic carbon (DOC) (16 mg/L), TCE (greater than 160 μg/L), PCE (49 μg/L), cis-DCE (42 μg/L), and vinyl chloride (20 μg/L), whereas the uncontaminated water contained none of these elements or compounds in concentrations greater than detection limits.

The areal and vertical distributions of organic and inorganic compounds in the unconfined aquifer are similar, indicating that organic and inorganic compounds originate from sources near Building 24 and are transported downgradient along similar flow paths. The plume extends from Building 24 to Green Pond Brook--a distance of about 1,700 feet.

Acid-extractable organic compounds, base/neutral-extractable organic compounds, pesticides, and polychlorinated biphenyls were not detected in samples from wells along the center of the plume, indicating that the high DOC concentrations near the source is not due to the presence of these priority pollutants. Cyanide, a major component of several plating process solutions, was present above detection levels as far as 900 feet downgradient from Building 24.

The distribution of trace metals in aquifer sediment samples collected at locations downgradient of the wastewater lagoons at Building 24 has been determined. Core samples collected nearest to Building 24 have maximum total trace-metal concentrations above background levels for Cr (59 μg/L), Cu (35 μg/L), Ni (26 μg/L), Pb (17 μg/L), V (76 μg/L), and Zn (120 μg/L). Maximum concentrations are at depths of 13 to 14 feet below land surface in most core samples, and below this depth the concentrations are at background concentrations, which range from 7 μg/L for Pb to 41 μg/L for V. One sample collected 1,200 feet downgradient from Building 24 has greater concentrations of Cr, Cu, Ni, Pb, V, Zn, cerium, and cobalt than core samples near Building 24. It is uncertain if the enrichment in downgradient areas is the result of discharges from Building 24 or from somewhere else. The effect of aquifer sediment surface coatings on retention and retardation of trace metals currently is being investigated.

DOC fractions were quantified for a water sample immediately downgradient from the metal-degreaser overflow dry well by using an isolation procedure that separates the dissolved organic material from the particulate and colloidal organic material and also separates the dissolved phase into hydrophobic and hydrophillic fractions. The ground-water sample contains 16 percent of the soluble organic material in the hydrophillic fraction and 84 percent in the hydrophobic fraction. The fractions were analyzed by carbon-13 nuclear-magnetic-resonance spectroscopy to identify the types of carbon bonding in the DOC molecular structure. The Picatinny hydrophobic fraction, which corresponds to a conventional fulvic-acid fraction, has more carboxylate and ketonic carbons and less aromatic carbons than most aquatic fulvic acids. Knowledge of the structure, number, and type of functional groups in the DOC molecules will help determine their role in TCE and trace-metal transport and retention.

Microbial Transformation of Chlorinated Solvents

The microbial transformation of TCE in the unconfined aquifer has been indicated by the detection of cis-DCE and vinyl chloride downgradient from Building 24. Biotransformation of TCE may occur aerobically or anaerobically in the unsaturated and saturated zones. Results of analyses of 16 core samples from the unsaturated zone showed microbial populations of 0.5 to 6 million microorganisms per gram of soil. Preliminary laboratory microcosm experiments attempting to simulate aerobic unsaturated zone conditions have shown little or no biotransformation taking place. However, a fairly stable population of about 40 million microorganisms per gram of soil was observed in these soil microcosms. Bacterial inactivity near the contaminant source is hypothesized to be the result of toxicity, lack of essential nutrients, inappropriate incubation conditions, or experimental error. Biotransformation rates in the aerobic saturated zone currently are being investigated in similar laboratory microcosm experiments.

The effect of supplementary carbon sources on microbial biotransformation of TCE and TCA also is being investigated. Soil microcosms were set up to simulate anaerobic saturated zone conditions, and a suite of alkylbenzene compounds were added as supplementary carbon sources. Preliminary results indicate that loss of TCE from biotransformation was two times greater in the microcosms without alkylbenzenes compared to microcosms with alkylbenzenes.

Distribution and Movement of Chlorinated Solvents in Ground Water

Existing hydrogeologic data were used to develop a preliminary quasi-three-dimensional flow model for the area. Initial calibration of this model has refined initial estimates of the hydraulic characteristics and the initial approximations to the upper recharge boundary. A more detailed three-dimensional flow model is being developed to incorporate additional hydrogeologic data and an areally and temporally variable ground-water recharge boundary on the basis of precipitation and topography. The flow system defined by the three-dimensional flow model is being used to define the boundary conditions of two smaller-scale two-dimensional solute-transport models. Preliminary areal and cross-sectional solute-transport models were constructed to define the horizontal movement of selected contaminants in the unconfined sediments and the vertical movement of these contaminants within and between several aquifers at the site. The preliminary solute-transport models will be modified to include areal- and time-dependent decay terms to represent losses of solute through vaporization and microbiological decay.

The calibrated solute-transport models will be used to (1) quantify factors that control the movement of chlorinated solvents in ground water, (2) determine the relative significance of these factors, and (3) test various hypotheses relating these factors to the fate of chlorinated solvents. These factors include various aspects of the hydrogeology, the system's geochemical behavior, biotransformation, and human activity. The solute-transport-modeling research activities are a focal point at which the results and hypotheses of the separate research activities are analyzed together to provide a complete and consistent definition of the system.

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PRELIMINARY RESULTS OF A STUDY OF THE CHEMISTRY OF GROUND WATER AT THE BUILDING 24 RESEARCH SITE, PICATINNY ARSENAL, NEW JERSEY

By Thomas E. Imbrigiotta[1], Mary Martin[1], B. Pierre Sargent[1], and Lois M. Voronin[1]

ABSTRACT

The water in bedrock and confined aquifers underlying the Building 24 site at Picatinny Arsenal, New Jersey, is similar in chemical composition; the waters are calcium bicarbonate types, have specific conductances of 214 to 245 microsiemens per centimeter at 25 degrees Celsius, and near-zero dissolved oxygen, dissolved organic carbon, and trace-metal concentrations. The water chemistry of the unconfined aquifer differs greatly, depending on whether the wells sampled are within or outside of the contaminant plume. Uncontaminated water from a well in the unconfined aquifer is a sodium chloride bicarbonate type. The uncontaminated water has a specific conductance of 334 microsiemens per centimeter, a dissolved oxygen concentration of 8.9 milligrams per liter, near-detection-limit concentrations of dissolved organic carbon and trace metals, and below-detection-limit concentrations of all purgeable organic compounds. Water from a well immediately downgradient from the Building 24 source area is a sodium chloride type. This water has high specific conductance (739 microsiemens per centimeter), low dissolved oxygen concentration (0.4 milligrams per liter), sodium, potassium, chloride, sulfate, and alkalinity concentrations that are two to four times greater than concentrations in the uncontaminated water, high dissolved organic carbon concentrations (16 milligrams per liter), cyanide, chromium, and copper concentrations above detection limits, and high concentrations of trichloroethylene (greater than 160 micrograms per liter), tetrachloroethylene (49 micrograms per liter), and cis-1,2-dichloroethylene (42 micrograms per liter).

The areal and vertical distributions of trichloroethylene and sulfate in the unconfined aquifer are similar, indicating that organic and inorganic compounds are derived from sources in the Building 24 area, and that both tend to be transported along the same flow paths to Green Pond Brook. Other observations are that (1) high dissolved organic carbon and trace-metal concentrations are present only within 500 feet of the Building 24 source area, (2) high dissolved organic carbon concentrations near the source are not caused by priority pollutants, (3) cyanide is present above detection limits as far as 900 feet downgradient from the source, (4) silica concentrations (6 to 8 milligrams per liter) are about one-half the background concentrations where high dissolved organic carbon concentrations are present near the source, and (5) elevated magnesium concentrations are present downgradient from the source near the discharge point of the ground-water system.

INTRODUCTION

Ground water downgradient from Building 24 at Picatinny Arsenal, N.J., has been contaminated over the past 30 years by discharges from metal-plating operations in Building 24 (Fusillo, Ehlke, and Martin, 1987). From 1960 to 1981, a metal-plating wastewater-treatment system discharged tens of thousands of liters of wastewater daily into two unlined lagoons just north of the building (fig. F-4). The metal-plating wastewater contained trace metals, such as cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), vanadium (V), and zinc (Zn), and other ions used in plating solutions, such as sodium, potassium, sulfate, chloride, and cyanide. From 1973 to 1985, a metal-degreasing-unit overflow system allowed chlorinated solvents to discharge into a dry well through an open-ended overflow pipe (fig. F-4). The metal-degreaser overflow contained primarily trichloroethylene (TCE) and 1,1,1,-trichloroethane (TCA). In addition, tetrachlorethylene (PCE), cis-1,2-dichloroethylene (cis-DCE), and vinyl chloride (VC) also have been found in the ground-water system near Building 24.

Picatinny Arsenal is located in a glaciated valley between two northeast-to-southwest trending bedrock ridges that rise about 200 to 300 feet

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

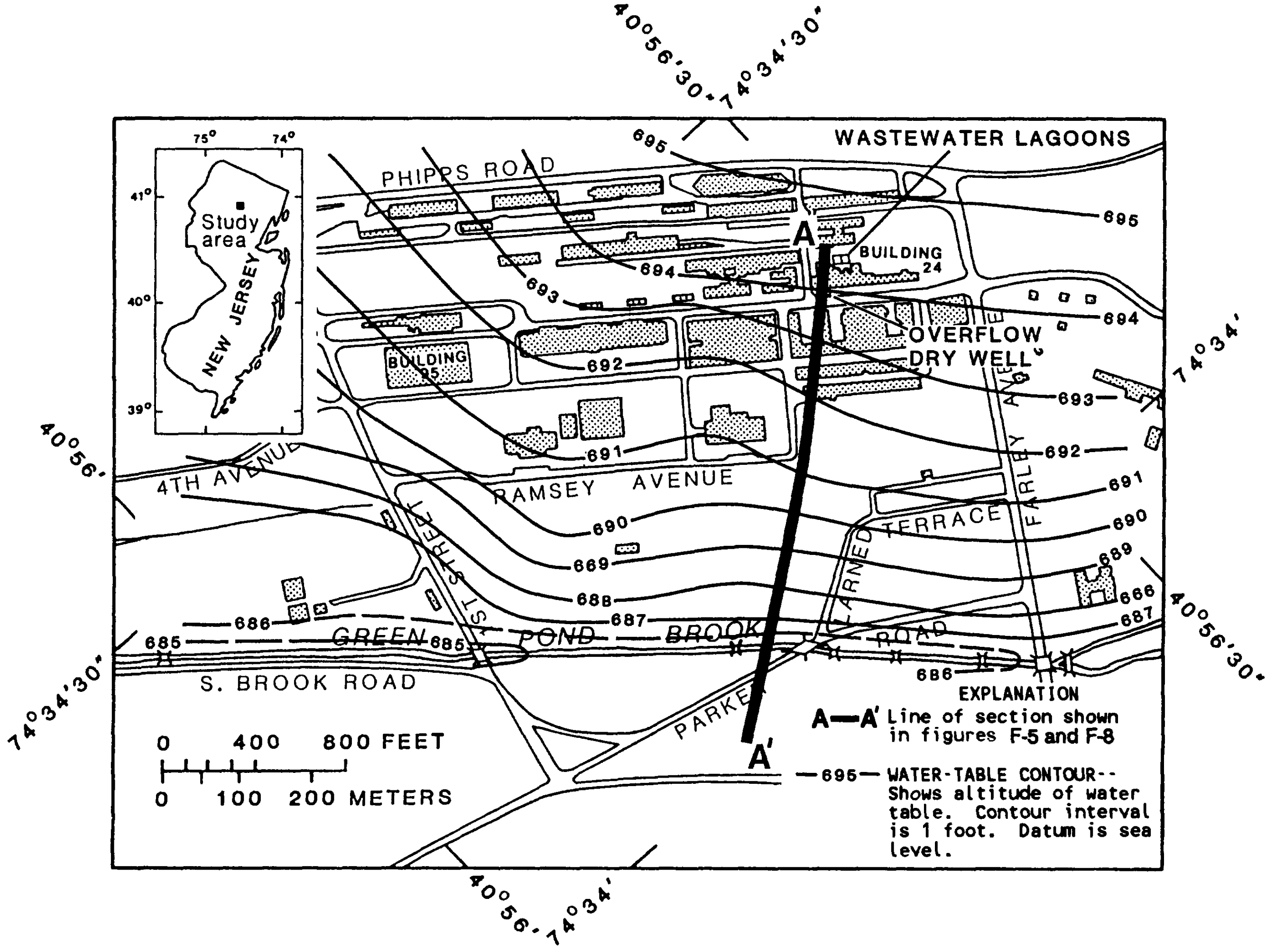


Figure F–4.—Location of Building 24 study area at Picatinny Arsenal and altitude of the water table, June 1987.

above the glacial sediments. At the contaminated site, as much as 250 feet of unstratified and stratified drift overlies a U-shaped weathered bedrock surface. In the area between Building 24 and Green Pond Brook, about 50 feet of unconfined glacial sediments overlie a 60-foot-thick confining unit, which in turn overlies approximately 50 feet of confined glacial sediments; these confined sediments overlie dolomite bedrock.

The general flow pattern in the unconfined aquifer is from the limit of the glacial sediments southeastward to Green Pond Brook. Figure F-4 shows water-table altitudes in the unconfined aquifer. Near Building 24, vertical flow is downward through the confining sediments to the confined aquifers, and then upward near Green Pond Brook where it discharges. Horizontal gradients in the confined aquifers also are toward the stream.

The objectives of the ground-water chemistry study at the Building 24 site are to (1) determine, in detail, the chemical composition of the contaminated ground water; (2) examine the chemical processes that affect the movement of contaminants within the aquifer, including sorption/desorption, partitioning, volatilization, ion exchange, dissolution/precipitation, and oxidation/reduction; and (3) examine the interactions between contaminants and the aquifer matrix and its surface coatings. To date, most of the effort has been to detail the chemical composition of ground water at the Building 24 site.

The purpose of this paper is to present the results of the most recent ground-water sampling and analysis and to discuss plans for accomplishing the second and third objectives.

Ground-water contamination in the vicinity of Building 24 was established previously by Sargent and others (1986), Fusillo, Ehlke, and Martin (1987), and Fusillo, Ehlke, Martin, and Sargent (1987). The study by Fusillo, Ehlke, Martin, and Sargent (1987) involved the use of drive-point sampling devices to define the three-dimensional extent of chemical constituents in the unconfined aquifer. TCE, the primary organic contaminant, was found at a maximum concentration of 44,000 μg/L (micrograms per liter) at a site about 3 feet downgradient from the Building 24 dry well. The vertical distribution of TCE along the approximate center of the plume, as determined by the drive-point sampling, is shown in figure F-5. Although not as widely distributed, other organic compounds were detected in the drive-point sampling; maximum levels were 200 μg/L for PCE, 380 μg/L for cis-DCE, 50 μg/L for TCA, and 30 μg/L for VC. Elevated concentrations of trace metals also were found; maximum levels were 65 μg/L for Cd, 48 μg/L for Cr, 70 μg/L for Cu, 190 μg/L for Pb, and 54 μg/L for V.

METHODS

Thirty-three new wells were installed during July-October 1987. Twenty-seven 2-inch diameter stainless-steel wells that ranged in depth from 16 to 56 feet were installed by hollow-stem auger in the unconfined aquifer to define further the ground-water chemistry of the Building 24 plume. The location of these wells (fig. F-6) were based on the drive-point sampling results. In addition, six 4-inch diameter steel wells that ranged in depth from 95 to 265 feet also were installed by mud-rotary drilling to define further the lithology and water chemistry of the confined and bedrock aquifers.

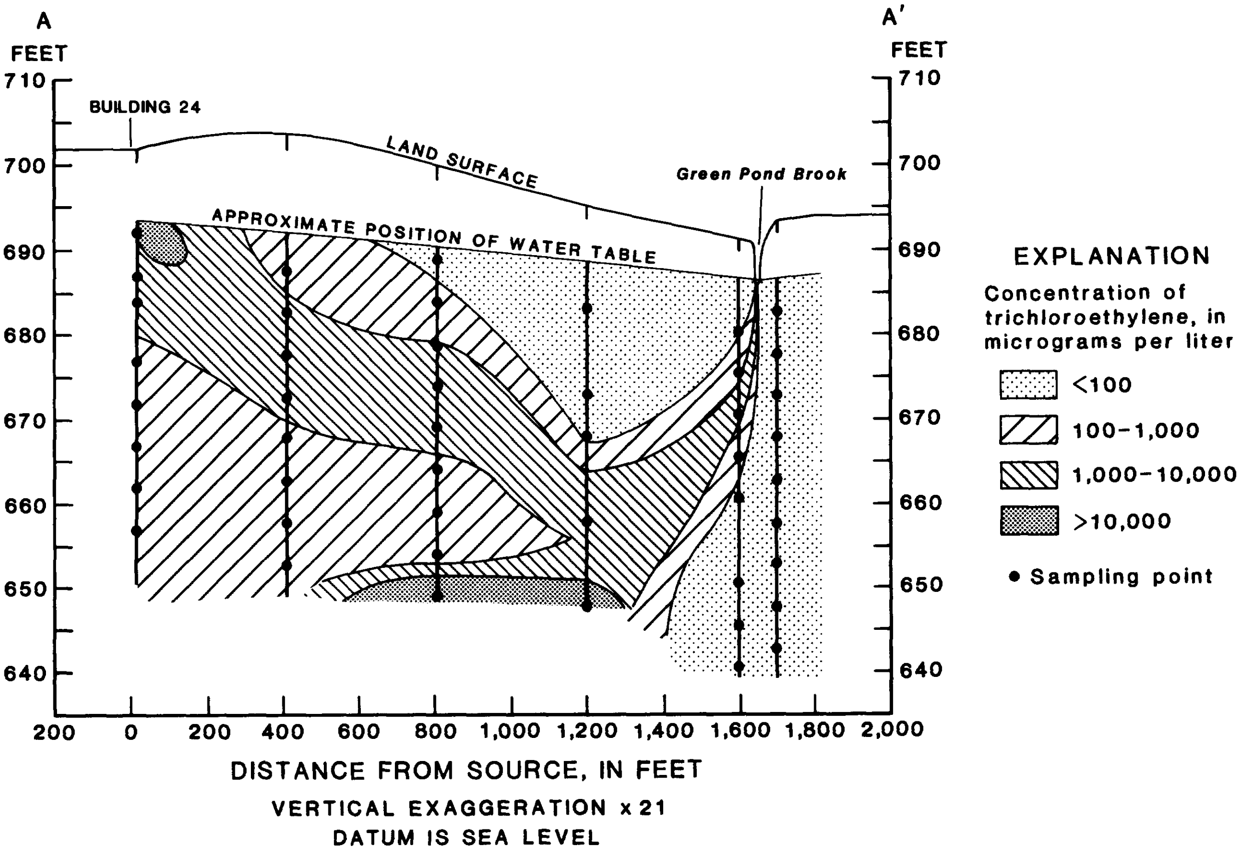


Figure F-5. – Vertical distribution of trichloroethylene along section A-A' through approximate center of the plume based on 1986 drive-point sampling data (from Fusillo, Ehlke, Martin, and Sargent, 1987, fig D-3). Location of section shown in figure F-4.

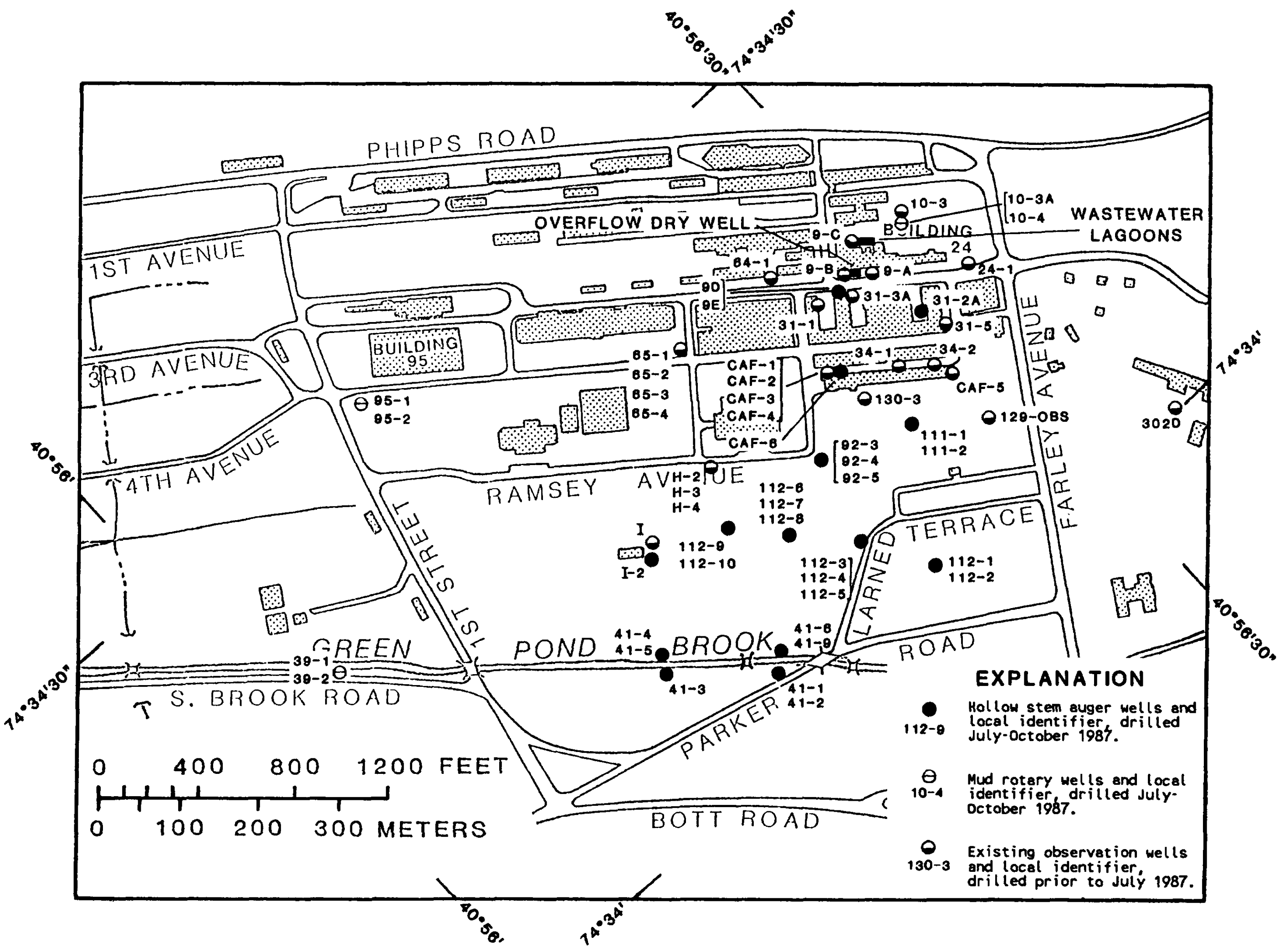


Figure F-6.—Location of wells sampled in October-November 1987.

Four wells completed in bedrock, 6 completed in the confined aquifer, and 55 wells completed in the unconfined aquifer were sampled in October-November 1987 (fig. F-6). All samples were analyzed for field properties and constituents (temperature, specific conductance, pH, alkalinity, and dissolved oxygen), major cations and anions, nutrients, cyanide, silica, dissolved organic carbon (DOC), trace metals, and purgeable organic compounds. In addition, samples from 11 wells were analyzed for acid-extractable organic compounds, base/neutral-extractable organic compounds, pesticides, and polychlorinated biphenyls. Iron and manganese were not measured during this sampling survey. All analyses were done using U.S. Geological Survey and U.S. Environmental Protection Agency protocols (Longbottom and Lichtenberg, 1982; Fishman and Friedman, 1985; Wershaw and others, 1987).

GROUND-WATER CHEMISTRY

The chemistry of ground water in the study area was determined by examining water-quality results for selected wells in each aquifer. Well CAF-1 taps the bedrock aquifer about 400 feet downgradient from the plume source; well CAF-3 taps the confined aquifer at the same site; well 41-2 taps the unconfined aquifer outside the plume; and well 9-E taps the unconfined aquifer in the plume, about 80 feet from Building 24. The locations of these wells are shown in figure F-6. The chemical analyses of water from these four wells are shown in table F-1.

Table F–1.—*Chemical analyses from selected wells at Picatinny Arsenal, New Jersey, sampled in October 1987*

[All measurements in milligrams per liter unless specified.
DOC, dissolved organic carbon; cis-DCE, cis-1,2-dichloroethylene;
PCE, tetrachloroethylene; TCE, trichloroethylene;
mg/L, milligrams per liter; µg/L, micrograms per liter;
°C, degrees Celsius; $CaCO_3$, calcium carbonate;
<, less than; >, greater than
µS/cm, microsiemens per centimeter at 25 degrees Celsius]

Chemical constituent or property	Bedrock well CAF–1	Confined well CAF–3	Unconfined wells	
			Uncontaminated 41–2	Contaminated 9–E
Depth (feet)	268	128	21	19
Temperature (°C)	12.5	14.5	12.0	19.0
pH (units)	7.2	8.0	6.6	7.2
Specific conductance (µS/cm)	214	245	334	739
Dissolved oxygen	.2	.3	8.9	.4
Field alkalinity (mg/L as $CaCO_3$)	97	104	68	153
Chloride	2.0	9.7	48	120
Sulfate	9.4	17	19	42
Fluoride	.2	.2	.1	.3
Calcium	23	26	17	25
Magnesium	8.2	9.7	7.3	3.6
Sodium	3.5	5.1	34	120
Potassium	2.6	.8	1.2	5.0
Silica	15	11	12	6.5
DOC	.5	.6	.8	16
Cyanide	<.01	<.01	<.01	.04
Chromium (µg/L)	<6	<6	7	11
Copper (µg/L)	<8	<8	<8	53
TCE (µg/L)	<1	396	<1	>160
PCE (µg/L)	<1	25	<1	49
cis-DCE (µg/L)	<1	<1	<1	42

Water from the bedrock and confined wells is similar chemically. Water from both wells has near-zero dissolved-oxygen concentrations (indicating probable reducing conditions), calcium bicarbonate-type water and specific conductances of 214 to 245 µS/cm (microsiemens per centimeter) at 25 °C (degrees Celsius). Water from the confined well has slightly greater concentrations of most major cations and anions and consequently a slightly greater specific conductance than water from the bedrock well (table F-1). DOC and trace-metal concentrations are near or below detection limits in water from both wells. The only major difference between water from the two wells is that water from the well in the confined aquifer contains TCE and PCE, whereas water from the bedrock well does not. Movement of TCE into the confined aquifer probably is caused by a production well that induced contaminated water from the unconfined aquifer to flow down through the leaky confining unit.

The chemistry of the ground water from wells in the unconfined aquifer is highly dependent on the locations of the wells in relation to the Building 24 contaminant plume. For example, well 41-2 is located on the southern side of Green Pond Brook in an area unaffected by the plume, whereas well 9-E is located immediately downgradient from the Building 24 source area.

Water from well 41-2 contains 8.9 mg/L (milligrams per liter) of dissolved oxygen (indicating oxidizing conditions) and has a higher specific conductance (334 μS/cm) than does water in the two deeper aquifers (table F-1). This higher specific conductance is caused primarily by greater sodium and chloride concentrations in the unconfined aquifer compared to the deeper aquifers. In fact, water from well 41-2 (like many of the other wells in the unconfined aquifer) is a sodium chloride bicarbonate type. DOC (0.8 mg/L) and trace-metal concentrations (less than 8 μg/L) are below or near detection limits and are similar to concentrations in ground water from the two deeper aquifers (table F-1). No purgeable organic compounds were detected in water from well 41-2. Water from this unconfined well is considered to represent background water quality.

Water from well 9-E has a low dissolved oxygen concentration (0.4 mg/L), indicating probable reducing conditions. The water has a high specific conductance (739 μS/cm), which is more than twice the specific conductance of water from well 41-2 outside the plume. Sodium, potassium, chloride, sulfate, and alkalinity concentrations are two to four times greater than concentrations in water from well 41-2. Water from well 9-E is a sodium chloride type. Water from well 9-E also has a high DOC concentration (16 mg/L), and cyanide (0.04 mg/L), Cr (11 μg/L), and Cu (53 μg/L) concentrations above detection limits. In addition, high TCE (greater than 160 μg/L), PCE (49 μg/L), and cis-DCE (42 μg/L) concentrations are found in the sample from well 9-E. However, concentrations of silica (6.5 mg/L) and magnesium (3.6 mg/L) are lower in water from this well than in water from the uncontaminated well 41-2 (table F-1).

AREAL AND VERTICAL DISTRIBUTION OF CONTAMINANTS IN THE BUILDING 24 PLUME

The areal distributions of TCE and sulfate, which are representative of an organic and an inorganic compound, respectively, are shown in figure F-7. On the basis of data collected from wells in October-November 1987, the areal distributions of these two compounds are similar, indicating that both organic and inorganic compounds are derived from sources near Building 24 and are transported downgradient along similar flow paths in the ground-water system. The area of affected ground water extends approximately 1,650 feet downgradient from Building 24 to Green Pond Brook, the ground-water discharge point. At Green Pond Brook, the plume is estimated to be about 750 feet wide on the basis of the 10 μg/L-TCE concentration contour (fig. F-7).

The vertical distribution of chemical constituents was examined along the approximate center of the plume (section A-A′, fig. F-4). Plots of the vertical distribution of TCE and sulfate on the basis of 1987 well-sampling data are shown in figure F-8. The organic and inorganic constituents have similar vertical distributions. Both plumes extend from near the water table at Building 24, downward to a depth of approximately 50 feet at a site 1,200 feet downgradient from Building 24, and then sharply upward toward Green Pond Brook. The upward discharge into Green Pond Brook is indicated by several constituents that were detected at maximum concentrations at depths of 56 feet at well 112-7 (about 450 feet from Green Pond Brook), and 21 feet at well 41-9 (about 30 feet from Green Pond Brook).

The TCE distribution defined in figure F-8 is similar to that described in Fusillo, Ehlke, Martin, and Sargent (1987) on the basis of drive-point sampling (fig. F-5). This shows that the drive-point sampling technique yields valid and useful results that can be confirmed by conventional well installation and sampling methods. It should be noted that concentrations of TCE obtained by use of drive-point sampling in 1986 were uniformly greater than TCE concentrations

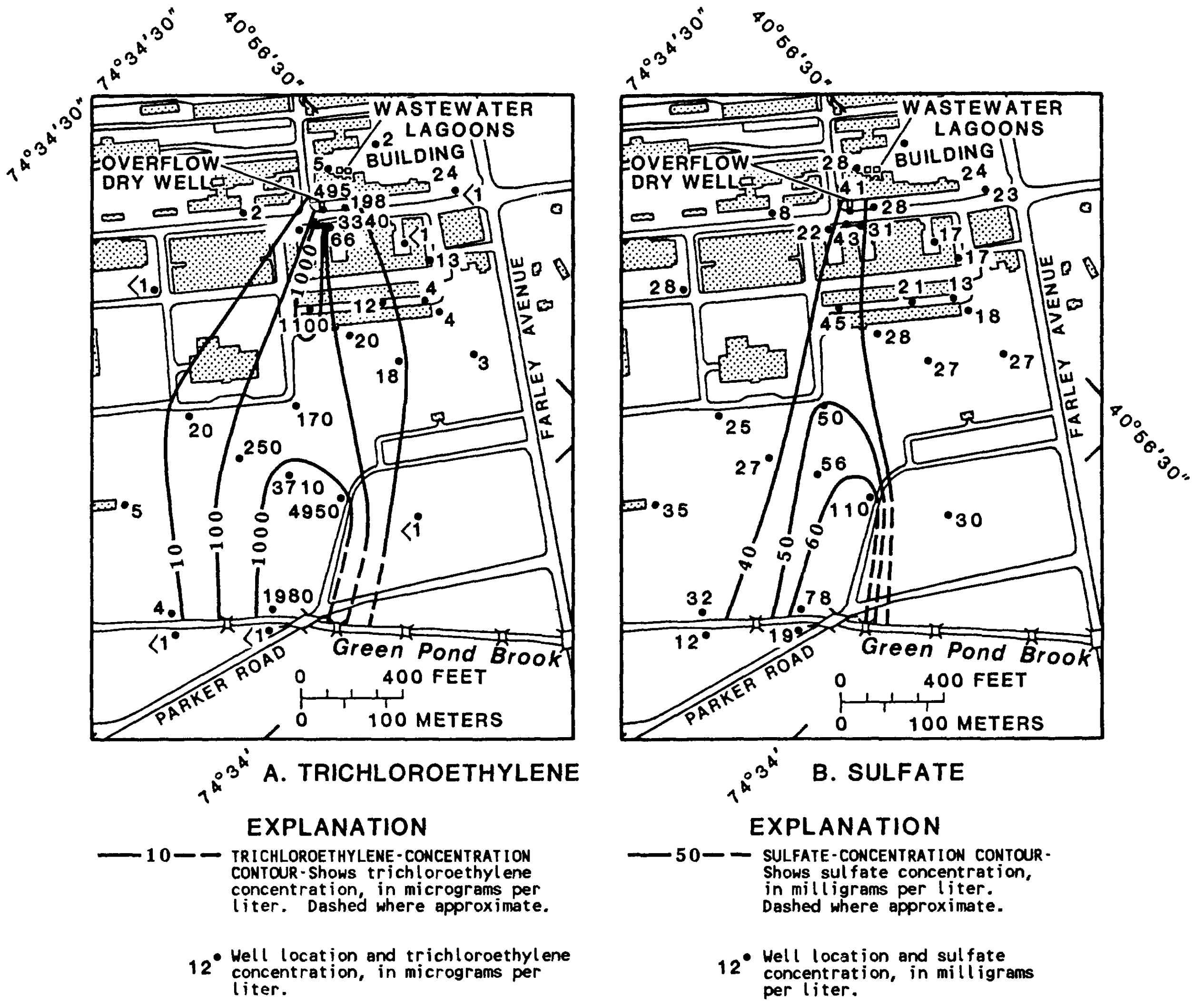


Figure F–7.—Areal distribution of (A) trichloroethylene and (B) sulfate downgradient of Building 24 based on 1987 well-sampling data. Values represent maximum concentrations detected at each site.

detected in wells screened at similar depths in 1987. This difference may be the result of a real decline in TCE concentrations over the course of the year, or dilution of the TCE concentrations found in the well samples, which were integrated over a 5-foot screened interval relative to the TCE concentrations found in the drive-point samples, that were integrated over only a 1-foot screened interval.

Although not shown, other chemical constituents were plotted along the cross section of the plume. The following observations were made:

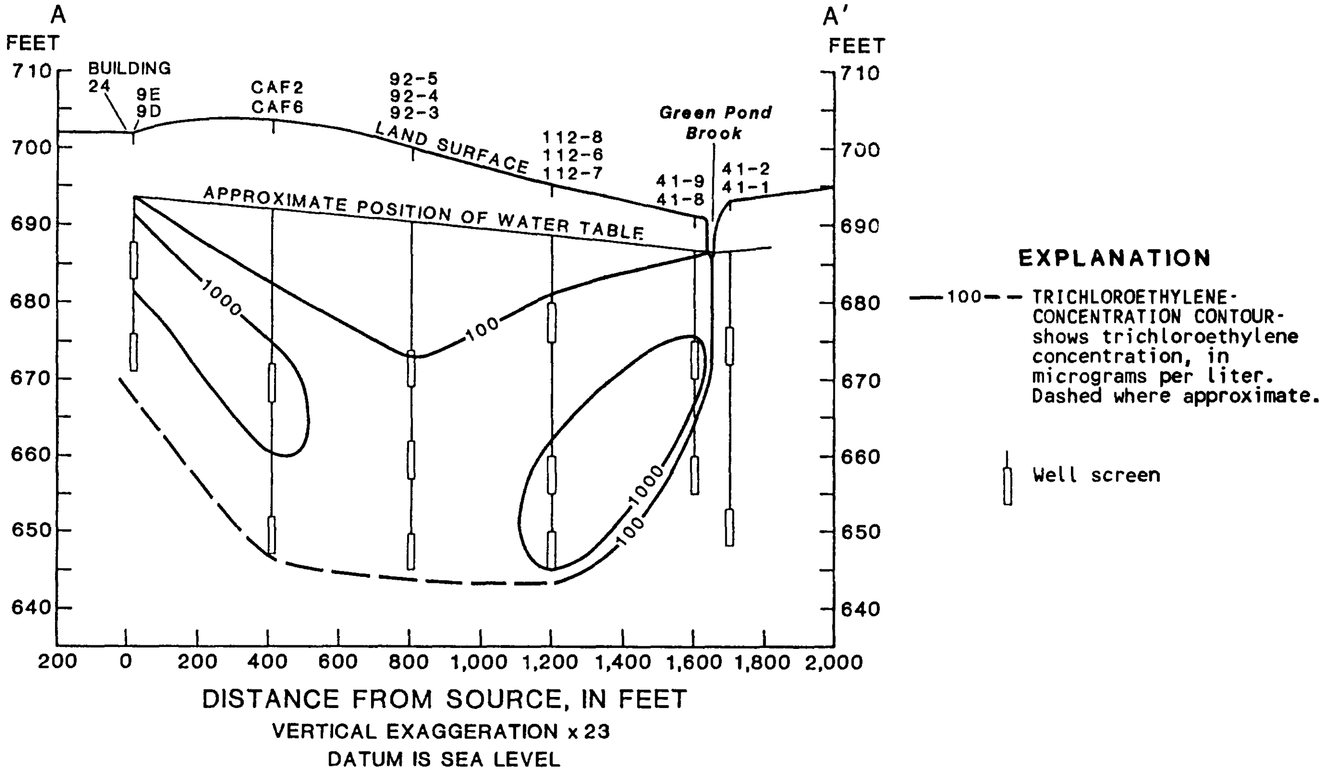
(1) High DOC concentrations and trace-metal concentrations above the detection limit are found only within 500 feet of the Building 24 source area.

(2) Samples from five wells along the cross section were among those analyzed for acid-extractable organics, base/neutral-extractable organics, pesticides, and polychlorinated biphenyls. None of these compounds was detected in any of the wells in the plume. Thus, the high DOC concentrations found at or near Building 24 do not consist of priority-pollutant organics.

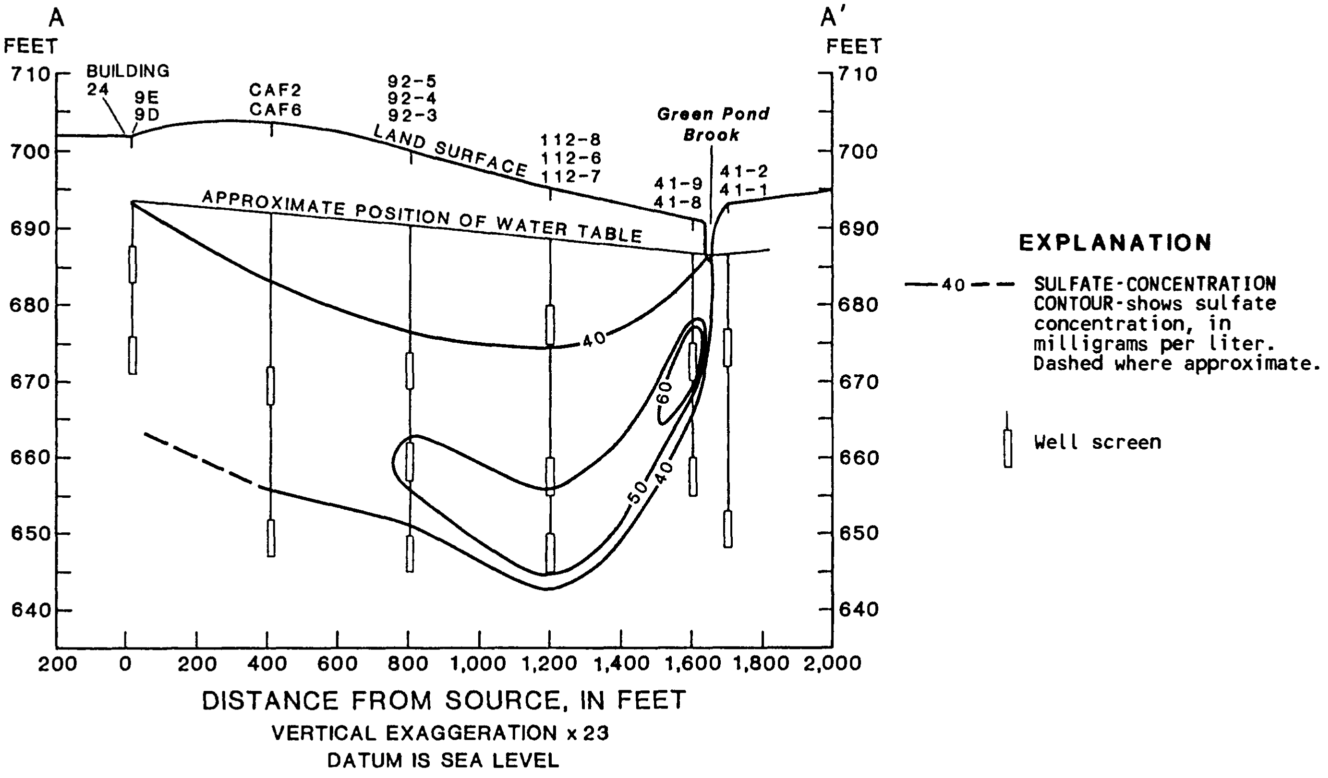
(3) Cyanide, a major component of several plating process solutions, is found above detection levels as far as 800 feet downgradient from Building 24.

(4) Silica concentrations (6 to 8 mg/L) are about one-half the background concentration where DOC and trace-metal concentrations are high near the source of the plume.

(5) Magnesium concentrations are 3.6 mg/L or less near the source but are greater farther downgradient near Green Pond Brook.



A. TRICHLOROETHYLENE



B. SULFATE

Figure F–8.—Vertical distribution of (A) trichloroethylene and (B) sulfate along section A-A′ through approximate center of the plume based on 1987 well-sampling data. Location of section shown in figure F-4.

RESEARCH PLANS

Planned research activities at the Building 24 study site at Picatinny Arsenal relating to ground-water chemistry will primarily focus on the following topics:

(1) Sorption processes and their effect on contaminant transport through the ground-water system will be quantified. A preliminary estimate will be made by analysis of aquifer sediments for organic carbon content and use of partition coefficients from the literature. Laboratory column studies will be used to simulate sorption processes occurring in the field. Adsorption/desorption of TCE and selected inorganic contaminants will be tested in these experiments in short-term and long-term column studies. Soil partition coefficients will be calculated.

(2) Trace metals and their retention by surface coatings in the aquifer system will be investigated. Sequential extractions of various phases on the surface of aquifer sediments will be conducted to determine how trace metals are being retained in the aquifer and to determine their potential for remobilization.

(3) The high DOC concentrations found only in the immediate vicinity of Building 24 will be investigated. The structure and composition of the DOC will be determined through use of tangential-flow filtration and carbon-13 nuclear-magnetic-resonance spectroscopy. An experiment in which aquifer sediments are leached with TCE may be done to determine if soil organic matter can be displaced into solution to produce the observed high DOC concentrations.

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DISTRIBUTION OF TRICHLOROETHENE IN SOIL GAS ABOVE CONTAMINATED GROUND WATER AT PICATINNY ARSENAL, NEW JERSEY

By James A. Smith[1], James A. Kammer[2], Cary T. Chiou[2], and Daniel E. Kile[2]

ABSTRACT

The distribution of trichloroethene vapor in soil gas has been studied above a contaminant plume at Picatinny Arsenal in Morris County, New Jersey. Laboratory studies indicate that trichloroethene vapor sorption to soil is suppressed by moisture but only up to saturation soil moisture content (the moisture content corresponding to 100 percent relative humidity). Above saturation moisture content, trichloroethene vapor sorption can be approximated by a conventional soil-water isotherm. A statistical comparison of field moisture content to saturation moisture content for six soil samples collected from the vadose zone at Picatinny Arsenal indicate that the field moisture content of the vadose-zone soil is above saturation moisture content at a 0.05 probability significance level.

Gas samples from the vadose zone were collected from two or three depths at each of six locations above the main axis of the ground-water solute plume. In general, trichloroethene-vapor concentrations decreased with horizontal distance downgradient from the contaminant source and vertical distance above the water table. The concentration of trichloroethene in all vapor samples collected from depths within 0.75 meter of land surface was less than the analytical quantitation limit of 40 nanograms per liter. The highest trichloroethene concentration (7,300 nanograms per liter) was measured in gas samples collected approximately 0.3 meter above the water table near the source of contamination.

INTRODUCTION

From 1960 to 1981, wastewater from metal-plating operations was discharged into two unlined filtration pits adjacent to Building 24 (fig. F-9) at Picatinny Arsenal in Morris County, N.J. As a result, the unconfined, sand and gravel aquifer that underlies the site has been contaminated with several chlorinated organic compounds. The major component of the organic contamination is trichloroethene, although cis-1,2-dichloroethene (DCE) and tetrachloroethene (PCE) also have been identified in some water samples. Details of the ground-water contamination have been reported by Fusillo and others (1987). This paper discusses the effects of soil-moisture content on the sorption of trichloroethene (TCE) vapor to vadose-zone soil above the ground-water solute plume at Picatinny Arsenal. As a corollary to this objective, the concentrations of TCE in soil gas and underlying shallow ground-water samples (collected during February and March 1988) along the main axis of the plume also are reported.

EXPERIMENTAL SECTION

Soil samples used in this study were collected from the vadose zone at the locations labeled alphabetically in figure F-9. The samples were collected using either a motor-driven hollow-stem auger or a split-spoon sampler manually driven to the desired depth. Ground-water samples were collected at sites 1 to 6 (fig. F-9) using permanently installed stainless-steel probes and a peristaltic pump fitted with Teflon[3] tubing. The depth of the water table below land surface at the site ranges from 1.5 to 3.7 meters; the ground-water samples were collected 1 to 2 meters below the water table. Soil-gas samples were collected from the vadose zone at sites 1 to 6 (fig. F-9) according to methods described by Kammer and Smith (1989). These samples were collected from depths ranging from 0.46 to 2.7 meters below land surface.

Three types of sorption isotherms were generated in the laboratory: a single-vapor isotherm, a dual-vapor isotherm, and a water isotherm. Single-vapor isotherms were used to

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

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

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

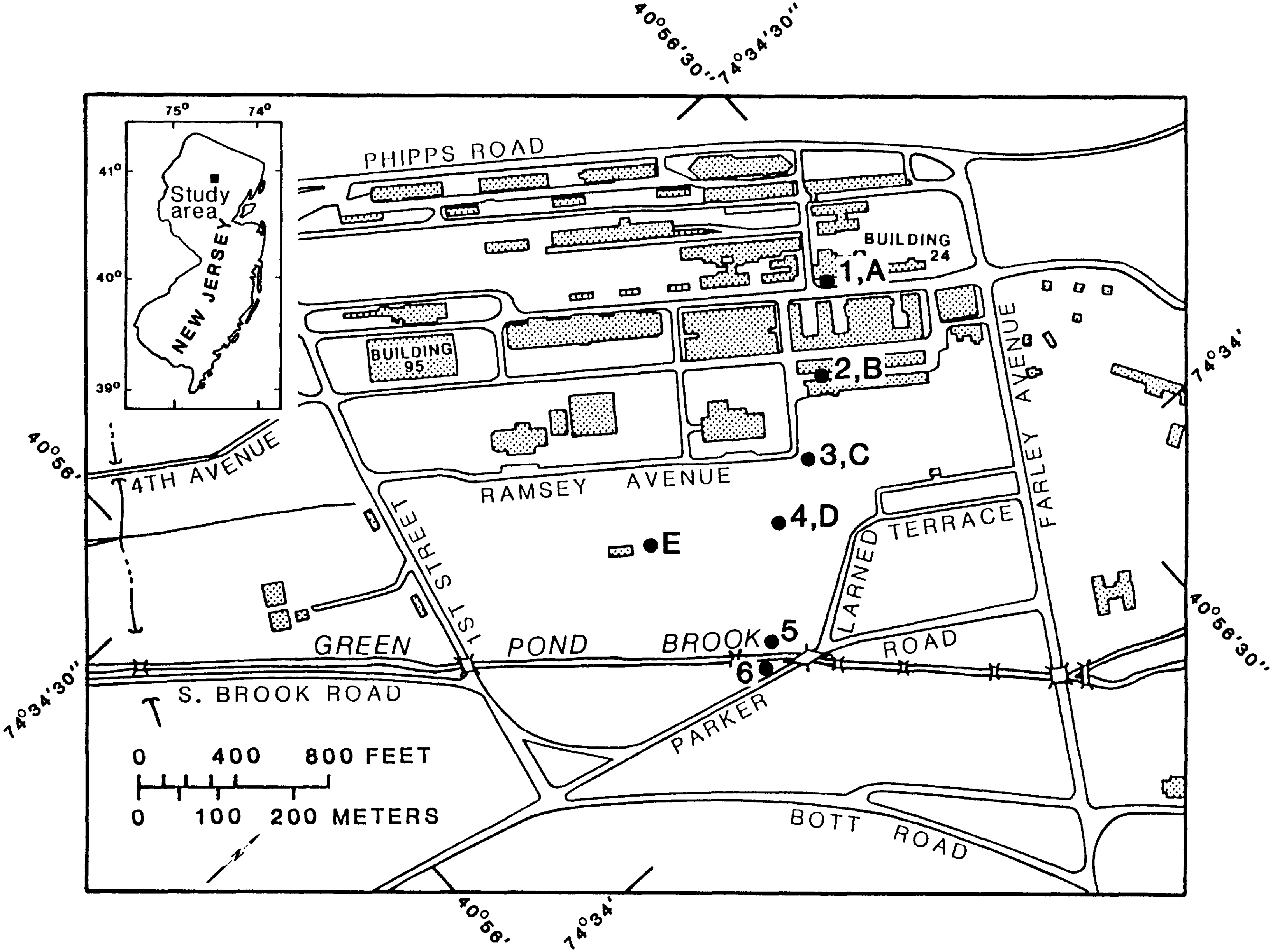

Figure F–9.—Study area showing soil sampling sites (labeled alphabetically) and ground-water and soil-gas sampling sites (labeled numerically).

describe the sorption of TCE or water vapor onto vadose-zone soil. These isotherms were generated using a static sorption chamber described by Chiou and others (1988). A dual-vapor isotherm was used to quantify the sorption of TCE vapor to vadose-zone soil at 40 percent relative humidity (R.H.). The experimental methods employed to produce the dual-vapor isotherm are described by Chiou and Shoup (1985). Sorption of TCE from water to soil (a water isotherm) was quantified by the conventional batch-equilibration method. Known masses of soil, water, and TCE were combined in 25 mL (milliliter) centrifuge tubes and shaken at constant temperature for 24 hours. The tubes were centrifuged at 8000 x g (1 g = 9.81 meters per second^2) for 45 minutes, and the resultant supernatant was extracted with hexane. The extract was then analyzed by direct-injection gas chromatography. The concentration of TCE on the soil in each centrifuge tube was determined by difference.

Soil-gas samples were analyzed for the presence of TCE by discharging the sample collected from the field onto an adsorbent trap. TCE subsequently was desorbed from the trap onto a capillary gas-chromatography column. The concentration of TCE was quantified by a calibrated Hall electrolytic-conductivity detector. Details of the analytical procedure are provided elsewhere in this Proceedings (Kammer and Smith, 1989). The concentration of TCE in ground-water samples was measured using purge-and-trap concentration with capillary gas-chromatography/mass-spectrometry, followed by comparison of mass spectra with authentic standards (Wershaw and others, 1982).

Soil samples collected for moisture-content analysis were transported to the laboratory in 1.9-liter glass jars in an ice-filled cooler. Upon return to the laboratory, the samples were passed through a 2-mm (millimeter) sieve, and 20 to 30 grams of each sieved sample were placed in a preweighed evaporation dish. The dishes containing the samples were then heated to a constant weight at a temperature of 105±5 °C (degrees Celsius) in an oven. The percent moisture content was calculated based on the dry weight of the soil sample.

RESULTS AND DISCUSSION

It has been hypothesized that natural soil functions as a dual sorbent for the uptake of nonionic organic compounds (Chiou and others, 1988; Smith and others, 1988). The mineral surfaces of the soil function as a conventional solid adsorbent and the soil organic matter functions as a partition medium. Adsorption is a surface phenomenon that involves formation of either a physical or a chemical bond between the organic compound and a site on the sediment particle's surface. For a partition process, the organic compound distributes itself between water and the soil organic matter by molecular forces common to solution, similar to the distribution between water and an organic solvent such as n-octanol. The soil-moisture content determines whether the dominant uptake process is adsorption or partition (Chiou and Shoup, 1985; Smith and others, 1988). The predominance of a partition interaction with organic matter in water-saturated soil is caused by the suppression of mineral adsorption by a much stronger competitive adsorption of water on the soil's mineral surfaces.

Figure F-10 presents two TCE vapor-soil isotherms (0 and 40 percent R.H.) and one TCE water-soil isotherm (100 percent R.H.) for surficial soil collected from site B (fig. F-9). The soil sample has an organic-carbon content of 4.02 percent, and is 60 percent sand, 26.5 percent silt, and 13.5 percent clay. The predominant clay mineral is dioctahedral chlorite. The dependent variable in the figure is soil uptake, in milligrams of TCE per gram of soil. The independent variable for the 0 and 40 percent R.H. isotherms is the vapor pressure of TCE, P, normalized by saturation vapor pressure, P°. The independent variable for the 100 percent R.H. isotherm is the aqueous concentration of TCE, C, normalized by its aqueous solubility, S. The data normalization facilitates comparison of vapor-soil isotherms and water-soil isotherms.

The isotherms in figure F-10 illustrate that as R.H. increases, the soil uptake of TCE decreases and the isotherm shapes become more linear. At 0 percent R.H., soil uptake of TCE appears to be caused by adsorption onto mineral surfaces, as evidenced by the similarity of the isotherm's

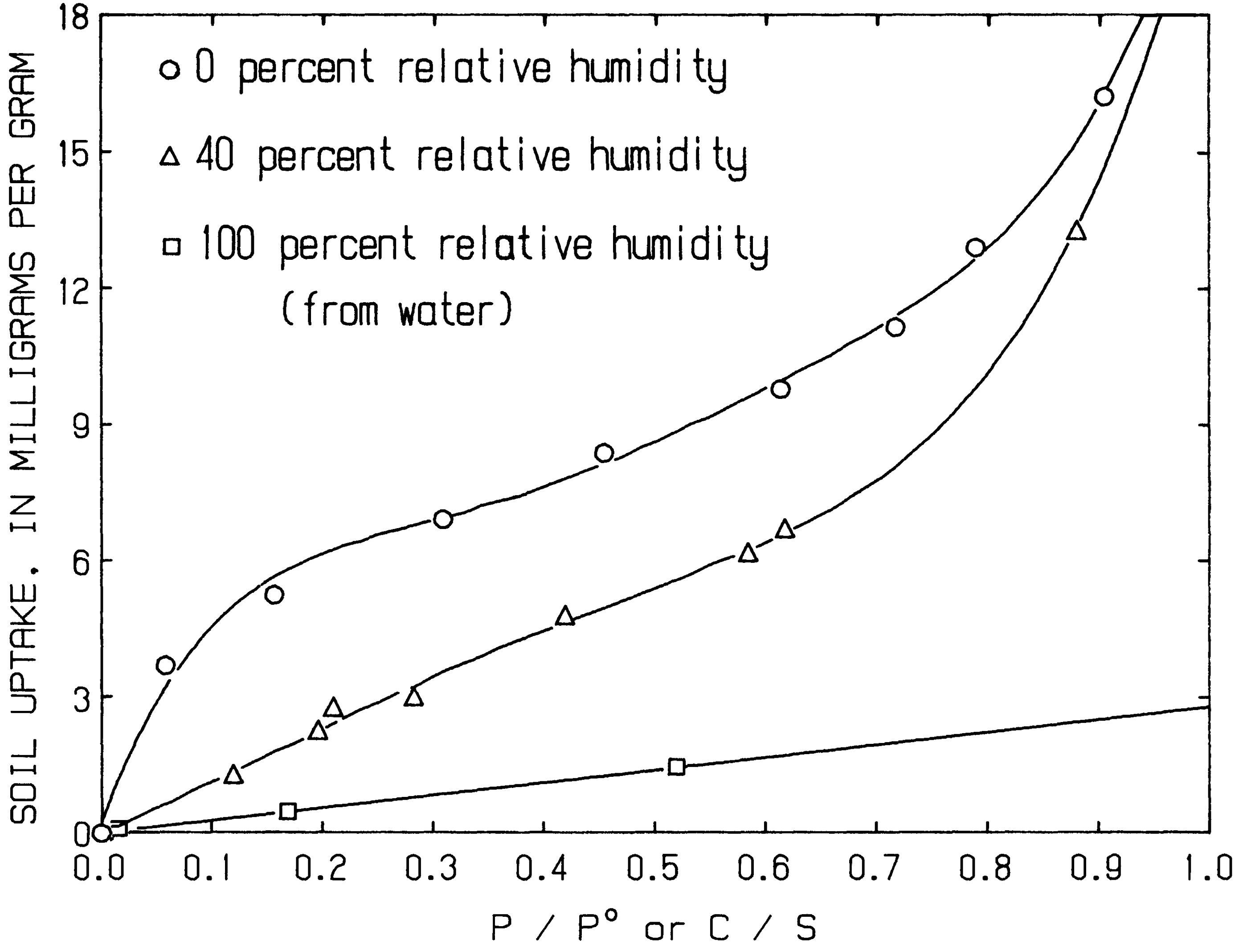

Figure F-10.—Soil uptake of trichloroethene vapor as a function of the vapor's partial pressure (P) normalized to saturation vapor pressure (P°) at 0 and 40 percent relative humidity and soil uptake of trichloroethene from water as a function of its aqueous concentration (C) normalized to its aqueous solubility (S).

shape to that of a conventional Brunauer type-II adsorption isotherm. At higher R.H., the strong dipole interaction of water with the soil mineral surface interferes with TCE adsorption. At 100 percent R.H., TCE uptake by soil is limited to partition into the soil organic matter. The data of figure F-10 agree with data presented by Spencer and others (1969) and Spencer and Cliath (1970), who showed that the vapor densities of dieldrin and lindane decreased when the soil moisture content was decreased below saturation (for example, below a moisture content corresponding to 100 percent R.H.). Likewise, Chiou and Shoup (1985) demonstrated similar moisture-content effects for the vapor sorption of benzene, m-dichlorobenzene, and 1,2,4-trichlorobenzene to soil.

The isotherms of figure F-10 begin to provide insight into the behavior of volatile organic compounds diffusing upward into the vadose zone from a contaminated, water-table aquifer. Near the water table, the mineral surfaces of the soil are likely to be saturated with water, and vapor sorption can be predicted by the 100 percent R.H. isotherm (Smith and others, 1988). By contrast, soil within a few millimeters of land surface will be in equilibrium with the ambient, above-ground air (Smith and others, 1988). For these soils, the 40 percent R.H. isotherm may be a better predictor of vapor uptake by soil.

The experimental results reported in table F-2 and figure F-11 provide additional information about the sorptive behavior of TCE throughout the vadose zone above the contaminant plume at Picatinny Arsenal. Table F-2 compares the field moisture content and the saturation moisture content of six soil samples collected from the vadose zone over a 9-month period. The saturation moisture content for each soil was determined by extrapolating a laboratory-generated water vapor isotherm for the soil to the soil moisture content corresponding to $P/P^{\circ} = 1.0$. Because the vapor phase is saturated with water vapor at $P/P^{\circ} = 1.0$ and in equilibrium with the soil, the soil is also saturated with water vapor. Examples of water-vapor isotherms for two of the soils in table F-2 are shown in figure F-11. At $P/P^{\circ} = 1.0$, the moisture content of the shallow soil is approximately 60 mg/g (milligram per gram), or 6 percent; the moisture content of the deeper soil is approximately 10 mg/g, or 1 percent. The difference between the saturation moisture contents of these two soil samples is likely caused by differences in the surface area per unit weight of the soil. The soil used for the upper isotherm in figure F-11, for example, has a higher clay and silt content than the soil used for the lower isotherm in the figure.

As evidenced by the data in table F-2, the field moisture content of each soil sample is greater than its corresponding saturation moisture content. Application of the nonparametric sign test to the data in table F-2 confirm that the moisture content of vadose-zone soil above the contaminant plume is greater than saturation moisture content at a 95 percent confidence level. This result, in combination with the observed suppression of TCE sorption by moisture (fig. F-10), suggests that there is sufficient moisture present in the vadose zone to limit TCE uptake to partition into the soil organic matter. Therefore, equilibrium TCE sorption can likely be approximated from a conventional water isotherm (for example, a 100 percent R.H. isotherm) if the Henry's Law constant of the organic contaminant is known.

Table F–2.—*Comparison of field and saturation moisture contents of six soil samples collected from the vadose zone*

Collection date	Location	Depth, meters	Field moisture content, percent	Saturation moisture content, percent
3/4/87	B	0.0–0.01	32	6
3/4/87	B	.5–.8	5.1	1
7/30/87	E	.6–.9	12	1
8/3/87	D	.9–1.2	4.5	.5
8/6/87	A	.3–.6	14	1
12/3/87	C	1.7–2.0	5.7	.6

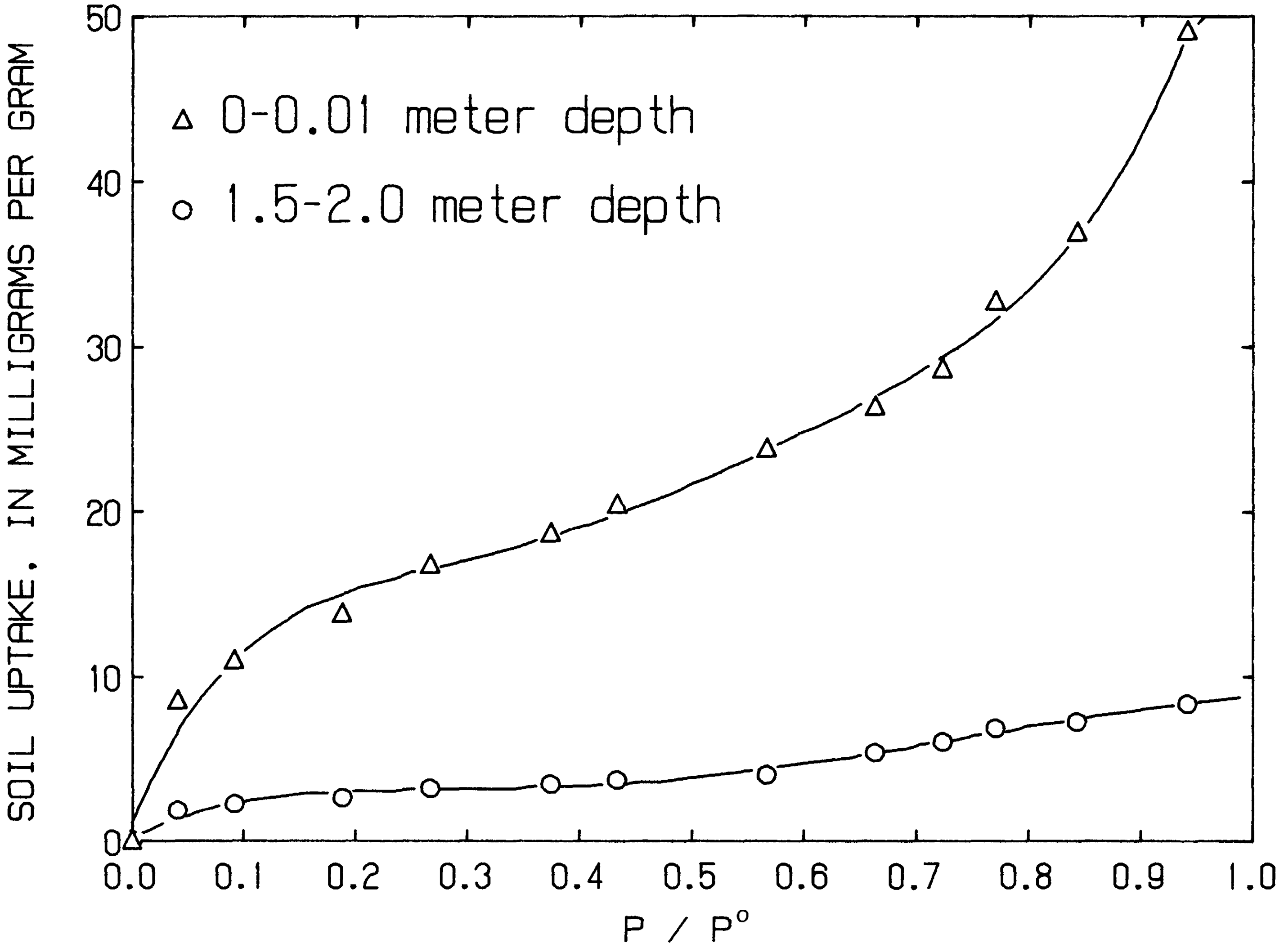

Figure F–11.—Water vapor uptake by two soils collected from site B as a function of the vapor's partial pressure (P) normalized to saturation vapor pressure (P°).

It is noteworthy to compare the upper isotherms in figures F-10 and F-11, which quantify sorption of TCE and water vapor to the same soil sample. The isotherms indicate that water vapor sorbs strongly to the soil relative to TCE. This observation lends further support to the hypothesis that soil moisture interferes with TCE adsorption onto soil mineral surfaces.

The objective of future research at Picatinny Arsenal will focus on the measurement of TCE vapor-soil partition coefficients in the field. Soil gas and adjacent soil will be sampled and analyzed for the presence and concentration of TCE. The ratio of the concentration of TCE on the soil to its concentration in the soil gas will be normalized by the soil organic carbon content and the saturation vapor pressure of TCE. These values will then be compared to previously reported TCE water-soil partition coefficients that have been normalized by soil organic-carbon content and the aqueous solubility of TCE.

In preparation for the measurement of TCE vapor-soil partition coefficients in the field, a reconaissance of the concentration of TCE in the soil gas from the vadose zone and underlying shallow ground water has been conducted. Results of soil-gas sampling and analyses have shown that TCE is the predominant gas-phase contaminant in the study area. Soil-gas samples were collected at two or three depths at each of six locations along the main axis of the contaminant plume (fig. F-9). The TCE concentration in five gas samples was 1,000 ng/L (nanograms per liter) or greater. The maximum TCE concentration (7,300 ng/L) was observed in gas samples collected approximately 0.3 meter above the water table near the source of contamination. DCE and PCE also were detected in selected gas samples at maximum concentrations of 130 ng/L.

The vertical concentration variation of TCE in soil gas at sites 1, 2, and 3 is plotted in figure F-12. The concentration decrease with distance above the water table appears to be linear in accord with a diffusive-transport model. However, extrapolation of the lines in figure F-12 to the vertical axis indicates that the TCE vapor concentration goes to zero at 0.3 to 0.6 meter below land surface. In fact, TCE was not detected in any soil-gas sample collected within 0.75 meter of land surface. The nondetectable level of TCE in this upper soil zone may be attributable to increased contaminant sorption to soil caused by high soil organic-carbon contents near land surface. Another possible explanation includes increased microbial activity (and, therefore, increased contaminant biodegradation) near land surface. It has been established that the size of bacterial populations are typically related to the organic carbon content of natural soil and, in general, the size of the population decreases with depth (Alexander, 1961). Temperature variations throughout the vadose zone may also be contributing to advective transport of TCE. This latter hypothesis, however, does not adequately explain the vertical contaminant distribution at site 1, which is covered by asphalt pavement that presumably prevents any significant mixing of near-surface soil gas with above-land-surface air.

The two plots in figure F-13 represent the vapor concentration of TCE in soil gas (0.3 to 0.6 meter above the water table) and the aqueous concentration of TCE in underlying shallow ground water (1 to 2 meters below the water table) as functions of sample location. In general, changes in the concentration of TCE in the shallow ground water closely parallel changes in the concentration of TCE in the soil gas. Normalization of the concentrations of TCE in soil gas and ground water to vapor and aqueous saturation concentrations indicates a substantial disequilibrium between the aqueous and gaseous phases. This observation, in combination with the vapor concentration gradients illustrated in figure F-12, indicates that TCE volatilization is a significant attenuation mechanism with respect to the ground-water solute plume.

DCE and PCE were also detected in selected soil-gas and water samples. However, because of the paucity of detections, no meaningful association can be made between the concentrations of these two compounds in soil gas and their concentrations in ground water. Nevertheless, if DCE or PCE were detected in soil gas at a given site, the same compound was also detected in the shallow ground water at that site.

SUMMARY

This paper investigates the effect of soil moisture on the sorption of TCE vapor to vadose-zone soil and reports on the distribution of TCE vapor in soil gas above a contaminated, water-table aquifer at Picatinny Arsenal, N.J. Measurement of the moisture content of soil samples collected from the vadose zone, in conjunction

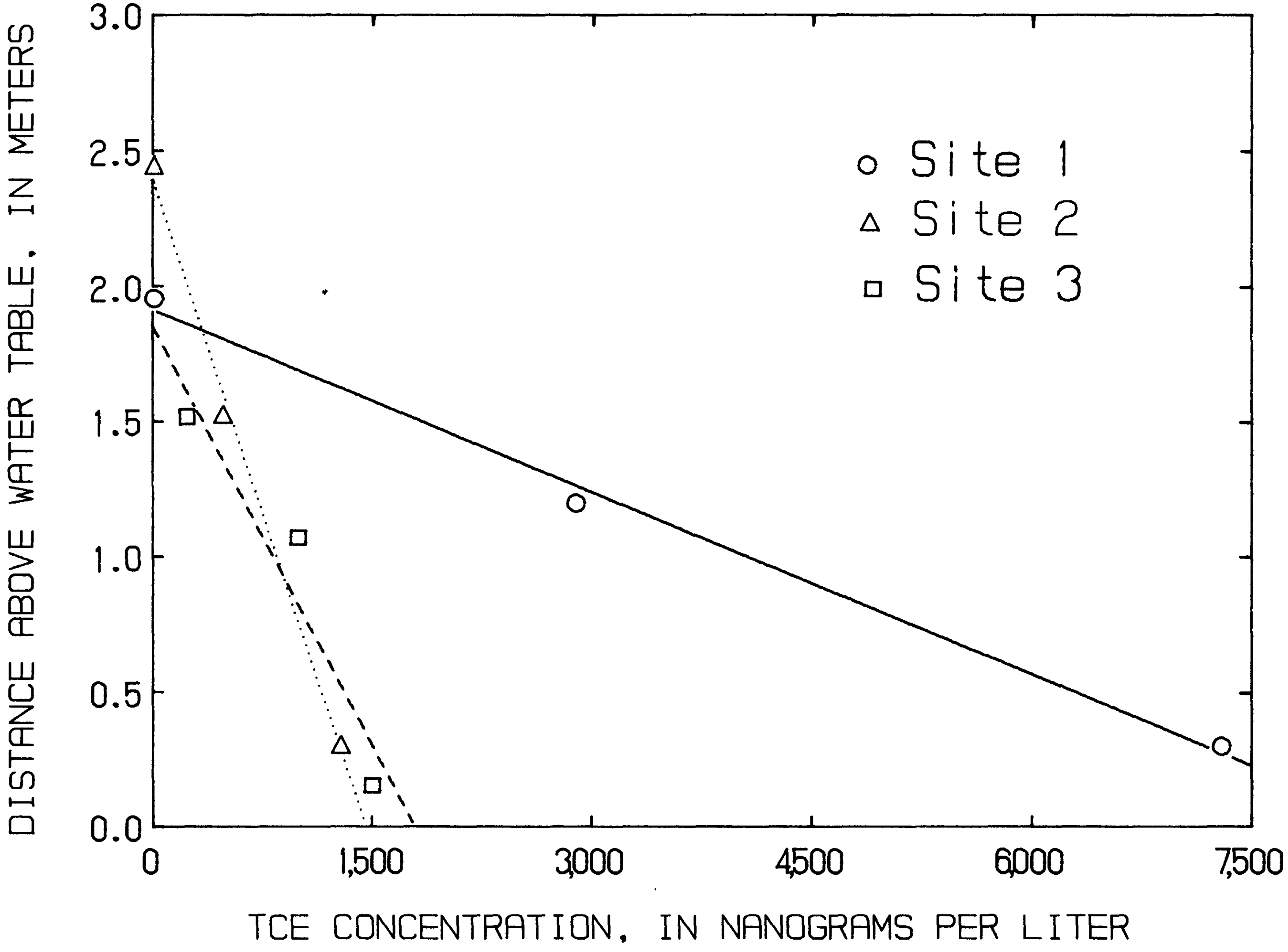

Figure F-12.—Depth profile of trichloroethene (TCE) in soil-gas samples collected from sites 1, 2, and 3.

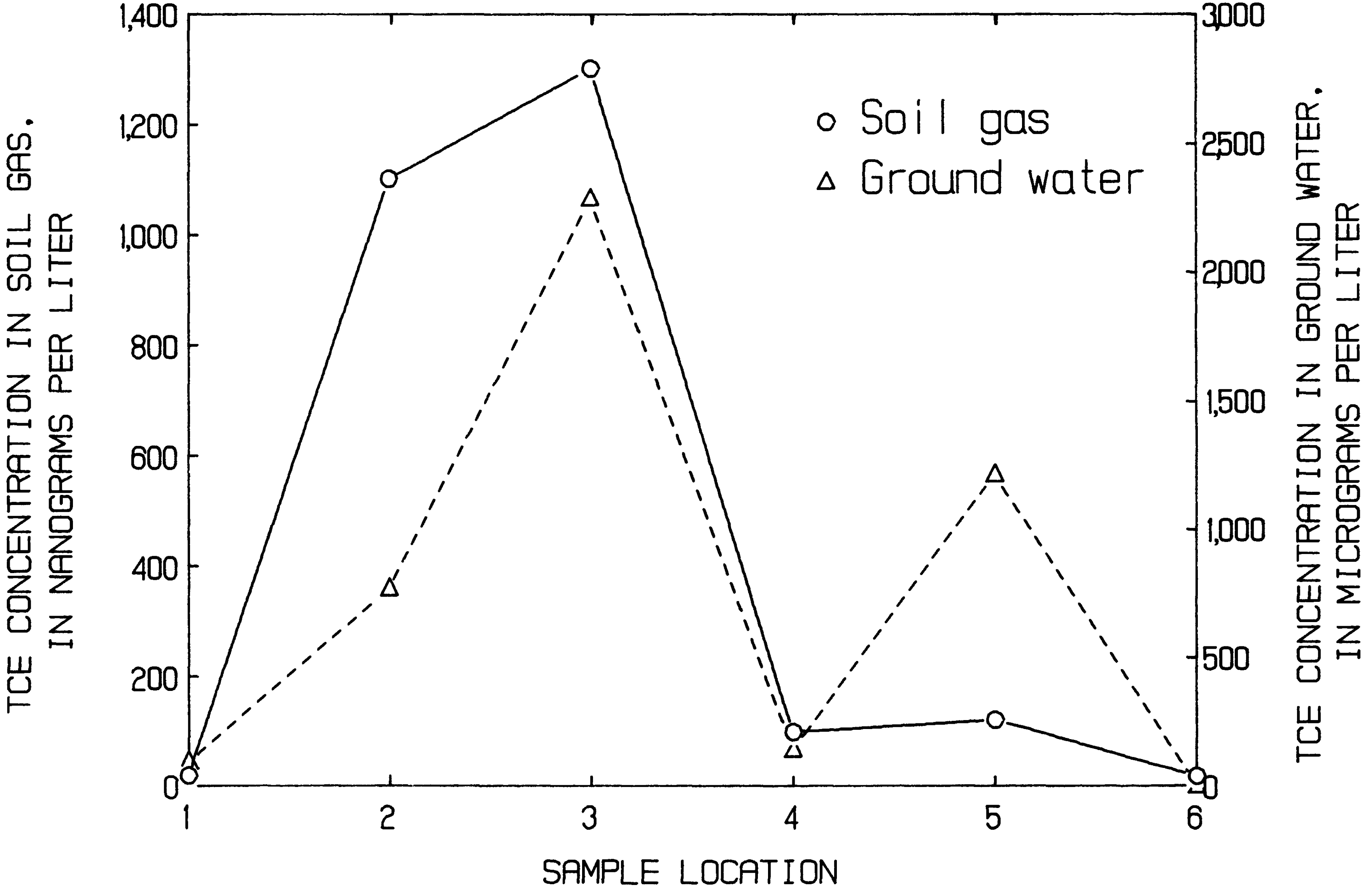

Figure F-13.—Relation between the concentration of trichloroethene (TCE) in soil gas and underlying shallow ground water at six sampling locations.

with laboratory-generated water-vapor isotherms for the same soil samples, indicates that the equilibrium distribution of TCE between vapor and soil can be predicted by a conventional water-soil isotherm and the compound's Henry's Law constant. In general, the concentration of trichloroethene in soil gas collected from the vadose zone at Picatinny Arsenal decreased with horizontal distance downgradient from the contaminant source and vertical distance above the water table. The highest TCE concentration (7,300 ng/L) was measured in gas samples collected approximately 0.3 meter above the water table near the source of contamination. Changes in the concentrations of TCE in the vadose-zone soil gas parallel changes in its concentration in the underlying shallow ground water.

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MICROBIOLOGICAL TRANSFORMATION OF TRICHLOROETHYLENE IN SOIL AT PICATINNY ARSENAL, NEW JERSEY

By Theodore Ehlke[1]

ABSTRACT

Shallow ground water at Picatinny Arsenal in north-central New Jersey has been contaminated with trichloroethylene as a result of metal-plating and degreasing operations in Building 24. The presence of dichloroethylene and vinyl chloride in ground water near Building 24 indicates that biotransformation of trichloroethylene may be occurring under anaerobic conditions at the site. Preliminary results of soil microcosm studies indicate that biotransformation of trichloroethylene in the unsaturated zone under aerobic conditions is negligible. The biotransformation of trichloroethylene in the upper part of the saturated zone in the presence of methane is being investigated.

INTRODUCTION

The U.S. Geological Survey is investigating ground-water contamination at Picatinny Arsenal in north-central New Jersey. Shallow ground water has been contaminated with chlorinated solvents, principally trichloroethylene (TCE) as a result of metal-plating and degreasing operations in Building 24. The suspected TCE contamination source is an overflow pit adjacent to Building 24 (fig. F-14). Additionally, a fuel-oil spill has been identified near Building 31. A network of observation wells was sampled periodically for selected chemical constituents and physical characteristics to identify the extent of the contaminated area (Harte and others, 1986).

Data from a contaminated well located adjacent to Building 24 and an uncontaminated well located near Green Pond Brook are shown in table F-3 (B.P. Sargent, U.S. Geological Survey, written commun., 1988). The data indicate that ground water near the suspected contamination source has a lower pH and contains higher concentrations of chromium, cadmium, sodium, methane, carbon tetrachloride, benzene, trichloroethane, dissolved organic carbon, vinyl chloride, 1,2-dichloroethylene, trichloroethylene, and tetrachloroethylene than background ambient ground water. Dichloroethylene and vinyl chloride, which are degradation products of tetra- and trichloroethylene, are not known to have been used at the site. For this reason, the presence of dichloroethylene and vinyl chloride in ground water near Building 24 suggests possible biotransformation of TCE. Vinyl chloride and dichloroethylene are formed during reductive dehalogenation of TCE under anaerobic conditions (Bouwer and McCarty, 1983).

The U.S. Geological Survey study of microbial transformations of chlorinated solvents at Picatinny Arsenal has the following objectives:

(1) Determination of whether biotransformation of TCE is occurring at Picatinny Arsenal

(2) Determination of the rate at which TCE biotransformation is occurring in the unsaturated and saturated zones of the aquifer

(3) Investigation of the effect of oxygen, alternative degradable organic compounds, trace element, nutrient, and TCE concentration on the concentration on the rate of TCE biotransformation, and

(4) Evaluation of methods for enhancing the biotransformation of TCE and the applicability of biotransformation processes as part of a program for contaminated sites.

This paper describes the experimental approach and preliminary results that relate to the first and second objectives.

APPROACH

Soil and water samples were collected adjacent to Building 24 for microbiological study. A 2.5-inch-diameter split-spoon coring device with sterile plastic liner was used to collect soil samples. The collection procedure was to drill to slightly above the water table using a portable

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

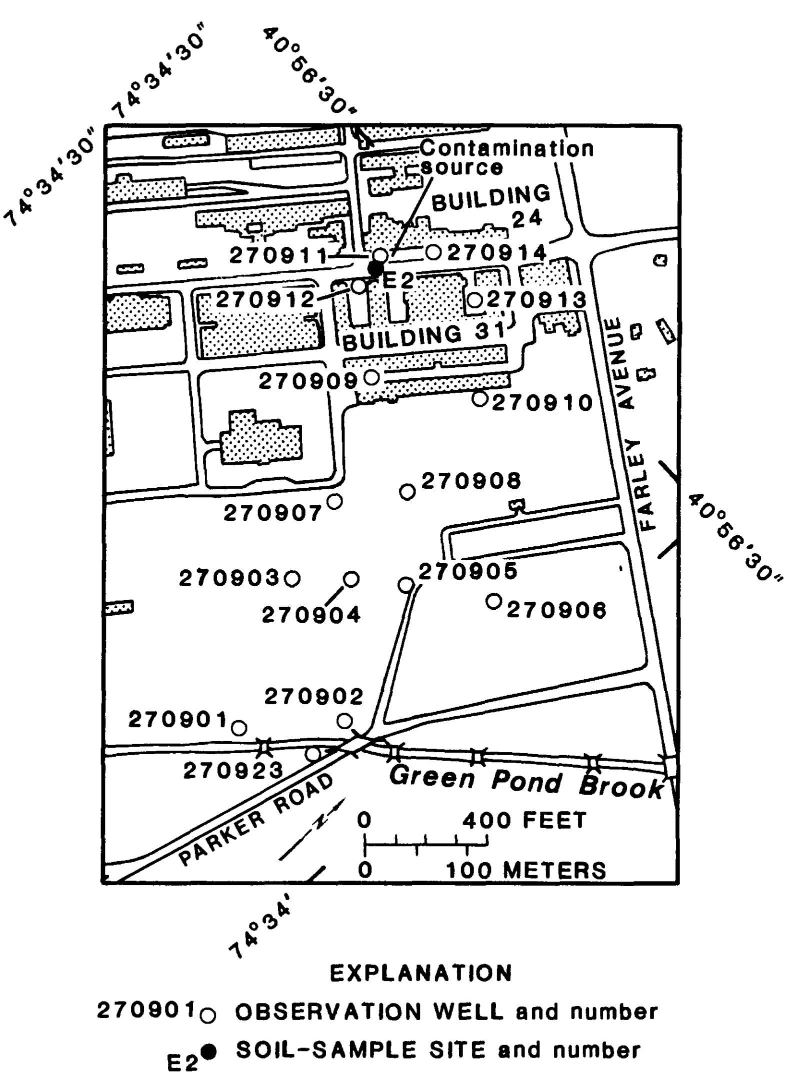

Figure F–14. – Observation wells and soil-sample site at Picatinny Arsenal, N.J.

3-inch-diameter auger and to remove the drill pipe from the borehole. Next, the coring device was driven to the desired depth, removed, and the core material extracted. Finally, 2-inch-long sections at each end of the core were aseptically removed, and the remainder was placed in a sterile container for further processing. Soil cores were collected in this manner from a depth of 8 to 10 feet. After drilling to the water table, water samples were collected from the borehole using a peristaltic pump. The depth to water generally was slightly less than 10 feet.

Soil samples were wet-sieved onsite using a sterilized stainless-steel 2-mm (millimeter) sieve, and native water. The less-than-2-mm fraction was transferred to sterile 1-quart glass jars with Teflon[2]-lined metal caps. Sieving was necessary because of the coarse nature of the soil. Sieved soil samples were chilled enroute to the laboratory and were refrigerated there at 5 °C (degrees Celsius) until processing was completed.

The water samples were stored without headspace in sterile 1-liter amber glass bottles that were chilled in an ice chest while enroute to the laboratory and refrigerated thereafter (at 5 °C) until processing was completed. Chemical constituents and physical characteristics were determined by standard techniques (Skougstad and others, 1979; U.S. Environmental Protection Agency, 1979).

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

Table F-3. – *Chemical and physical properties of water from contaminated and uncontaminated wells at Picatinny Arsenal*

[mg/L, milligrams per liter; μS/cm, microsiemens per centimeter at 25 degrees Celsius; μg/L, micrograms per liter]

Constituent property	Well 270911 (contaminated)	Well 270901 (uncontaminated)
Calcium, mg/L	2.3 - 20	4.3 - 52
Magnesium, mg/L	.2 - 3.3	1.0 - 25
Sodium, mg/L	77 - 130	8.5 - 50
Potassium, mg/L	1.1 - 2.8	.9 - 3.4
Sulfate, mg/L	32 - 58	9.2 - 42
Chloride, mg/L	20 - 110	1.1 - 82
Nitrate, mg/L as nitrogen	.1 - 6.3	.1
pH, units	6.4 - 7.4	7.8 - 8.3
Water temperature, Celsius	19.5 - 26.0	17.0 - 20.5
Specific conductance, μS/cm	273 - 620	160 - 649
Methane, μg/L	2.0 - 150	2.0
Tetrachloroethylene, μg/L	2 - 100	.2 - 1.0
1,1,2-trichloroethylene, μg/L	150 - 44,000	1 - 83
1,2-dichloroethylene, μ/L	1 - 100	1 - 8.5
Vinyl chloride, μg/L	<1 - 100	.2 - 1.0
Dissolved organic carbon, mg/L	1.1 - 48	.6 - 1.7
1,1,1-trichloroethane, μg/L	1 - 100	1
Benzene, μg/L	1 - 100	.2 - 1.0
Carbon tetrachloride, μg/L	1 - 100	.2 - 1.0
Aluminum, μg/L	10 - 680	-
Iron, μg/L	52 - 1,600	7 - 3,000
Chromium, μg/L	1 - 48	1
Cadmium, μg/L	1 - 65	1 - 3

Initial microbiological evaluation of soil samples collected from the unsaturated zone near Building 24 followed a procedure outlined in figure F-15. In the laboratory, the less-than-2-mm fraction of soil was thoroughly mixed and placed in a 1.5-inch-diameter by 24-inch-long glass tube. Air saturated with water vapor was passed through for 24 hours to partially dry the soil, then 50-mL (milliliter) serum bottles were filled with 25 grams of soil. Controls were similarly treated but were autoclaved for 30 minutes on 2 successive days. The serum bottles were spiked with 250 μL (microliters) of sterile TCE solution (200 mg/L (milligrams per liter)), then were capped with Teflon-lined butyl seals and aluminum crimp caps. The bottles were incubated inverted at 20 °C, in darkness. After 1, 7, 14, and 28 days, duplicate serum bottles (termed soil microcosms) were assayed for TCE concentration using gas chromatography. The number of aerobic heterotrophic bacteria (biomass) was determined by spread-plating aliquots of the soil on the surface of a low-nutrient medium, soil extract agar, using a procedure described by Ghiorse and Balkwill, (1985).

RESULTS

The results of microbiological evaluation of soil samples collected near Building 24 are shown in table F-4 and figure F-16. A fairly stable population of about $3.4x10^7$ to $5.1x10^7$ microorganisms per gram of soil was observed in live soil microcosms. Autoclaved microcosms remained sterile throughout this same period. The concentration of TCE in the headspace of soil

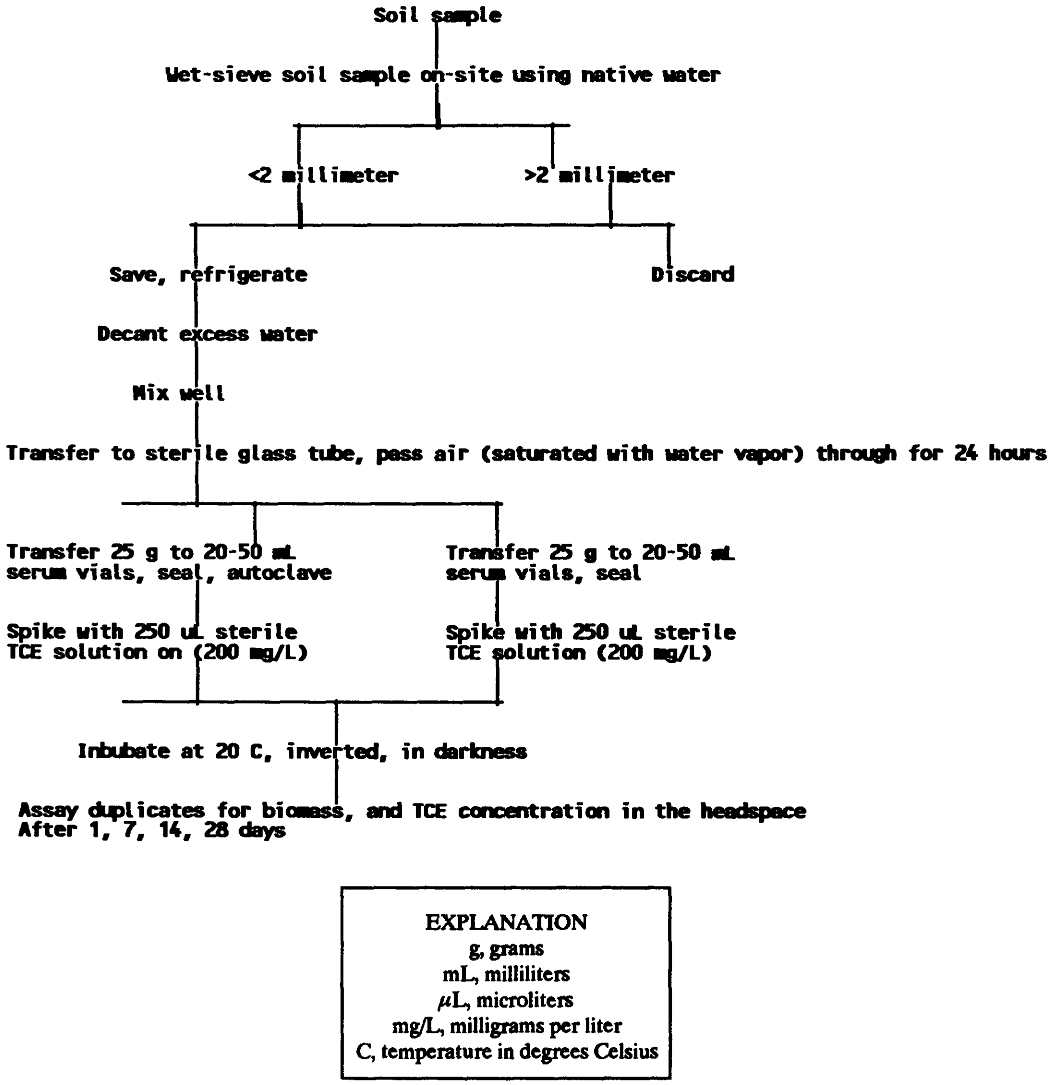

Figure F-15.—Procedure for evaluation of trichloroethylene (TCE) transformation.

Table F-4.—*Microbial population in soil in microcosms*

Incubation period, in days at 20 degrees Celsius	Number of bacteria per gram of soil Average of duplicate counts on spread plates of soil extract agar
1	4.9×10^7
7	5.1×10^7
14	3.4×10^7
28	3.5×10^7

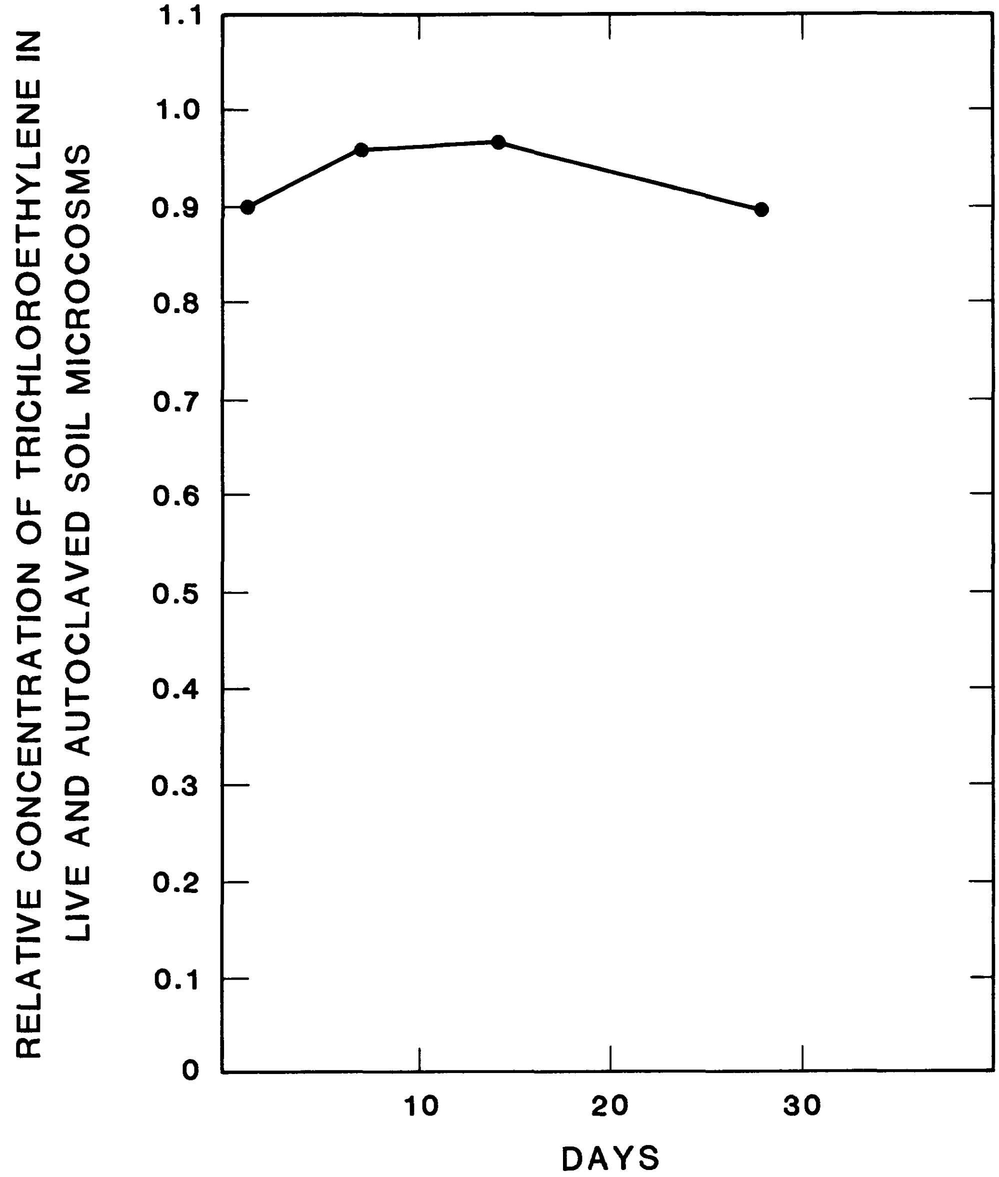

Figure F-16. – Change in trichloroethylene concentration in the headspace of soil microcosms from site E2 under aerobic conditions.

microcosms was initially approximately 700 ng/mL (nanograms per milliliter). This concentration is greater than the observed *in situ* TCE vapor concentration in the unsaturated zone. The TCE concentration in the soil gas at Picatinny Arsenal is estimated to range from less than 1 ng/mL to about 7 ng/mL near the source of contamination (J.A. Smith, U.S. Geological Survey, oral commun., 1988). The higher TCE concentration chosen for study (700 ng/mL) was intended to minimize analytical problems associated with TCE assay.

The TCE concentration in the headspace of the soil microcosms decreased 47 percent after incubation for 28 days, but there was no significant difference between autoclaved and live microcosms (fig. F-16), which indicates that biodegradation of TCE under aerobic conditions probably is negligible. The loss of TCE is attributed to adsorption to the soil matrix, to organic components, and losses through the Teflon-rubber seal.

Under aerobic conditions, TCE reportedly is very resistant to biodegradation in the absence of other degradable organic compounds. Recent research has shown that aerobic biodegradation of TCE occurs in the presence of natural gas (Wilson and Wilson, 1985), methane (Little and others, 1988), or phenol (Nelson and others, 1986). Aerobic biodegradation of TCE by methanotrophic bacteria results in the conversion of TCE to trichloroethyene epoxide and the rapid hydrolyzation to, as yet unidentified, nonchlorinated compounds (Fathepure and others, 1987). Because methane is present in ground water at the Picatinny Arsenal, the aerobic cometabolism of TCE is presently under investigation.

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PRELIMINARY RESULTS OF A STUDY TO SIMULATE TRICHLOROETHYLENE MOVEMENT IN GROUND WATER AT PICATINNY ARSENAL, NEW JERSEY

By Mary Martin[1]

ABSTRACT

Research activities at the Building 24 contaminant site at Picatinny Arsenal, New Jersey, include the development of a multilayer ground-water flow model, and an areal and a cross-sectional, two-dimensional, solute-transport model as a means to define the distribution and movement of chlorinated solvents in ground water. Although the models are not calibrated, the results of the preliminary simulations have been useful in improving the conceptual model and the modeling approach. Generally, the simulated head distribution is most sensitive to the areal and temporal distribution of ground-water recharge and is less sensitive to the definition of the hydrologic framework and hydraulic characteristics. In contrast, simulated ground-water velocities and flow rates are very sensitive to hydraulic characteristics.

The total trichloroethylene mass within the simulated contaminant plume is about 3,000 kilograms, or the equivalent of about 2,000 liters of pure trichloroethylene. About 70 percent of the solute mass is in areas with simulated concentrations between 1 and 10 milligrams per liter. About 15 percent of the solute mass is simulated in the near-source area, where trichloroethylene concentrations are greater than 10 milligrams per liter. Simulated rates of trichloroethylene loss from the unconfined ground-water flow system indicate that loss from volatilization may be on the order of hundreds of grams per day and may be one or two orders of magnitude more than the loss from the discharge of ground water to confined aquifers or to surface-water bodies.

INTRODUCTION

Research activities at the Building 24 contaminant site at Picatinny Arsenal, N.J., include simulation of the movement of selected solutes within the glacial-valley ground-water flow system as a means to define the distribution and movement of chlorinated solvents in ground water. Other major areas of research at the arsenal include: (1) movement of chlorinated solvents in the unsaturated zone, (2) geochemistry of the contaminated ground water, and (3) degradation of chlorinated solvents by microbes. The results and hypotheses of all the areas of research at the site are analyzed together in the solute-transport research activities to provide a complete and consistent understanding of the fate of chlorinated solvents in ground water.

The objectives of the solute-transport-modeling research activities at the Picatinny site are to: (1) quantify the factors that control the movement of chlorinated solvents in ground water, (2) determine the relative significance of these factors, and (3) test various hypotheses relating these factors to the fate of chlorinated solvents. These objectives will be accomplished through the calibration and sensitivity analysis of several solute-transport models that simulate the physical, chemical, and biological processes affecting the movement of chlorinated solvents in ground water.

Modeling activities include the development of a multilayer ground-water flow model of the southwestern third of Picatinny Arsenal, and two (areal and cross-sectional) two-dimensional solute-transport models of the contaminant site at Building 24 (fig. F-17). Preliminary solute-transport simulations generally reproduce the ground-water flow system and the measured concentrations of trichloroethylene (TCE) at the contaminant site. Water levels have been simulated to within 5 feet of measured water levels and the simulated TCE distribution generally is the same as that determined through field sampling (Fusillo, Ehlke, and Martin, 1987; Fusillo, Ehlke, Martin, and Sargent, 1987). Although the solute-transport models are not calibrated, the results of the preliminary simulations have been useful in improving the conceptual model and the modeling approach. The preliminary models also provide initial estimates of the ground-water flow budget and the TCE

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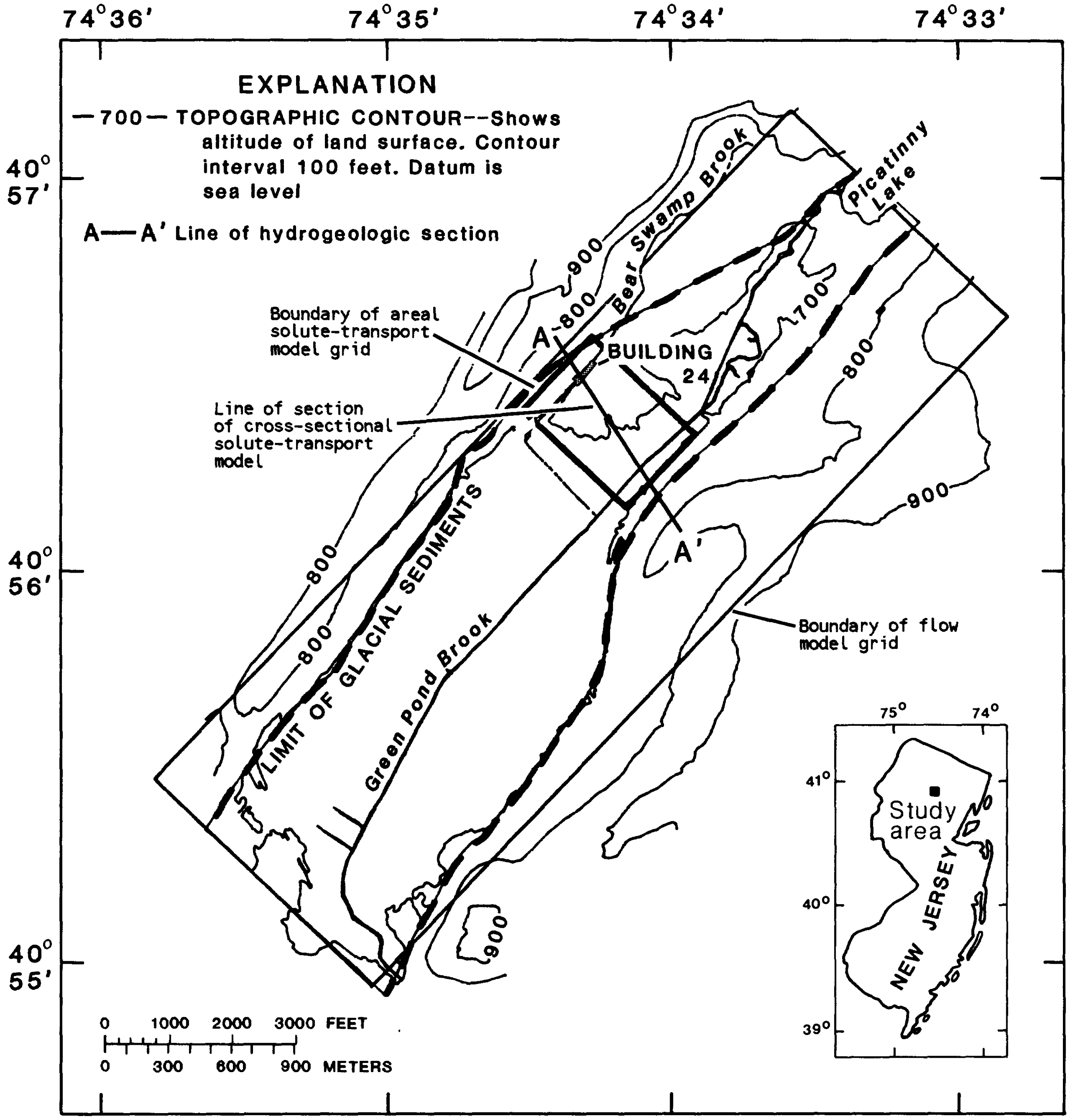
[1] U.S. Geological Survey, West Trenton, N.J.



Base from U.S. Geological Survey, 1:24,000 quadrangle, Dover, 1954.

Figure F-17. – Location of study area and model grids used to simulate ground-water flow and solute-transport at Picatinny Arsenal, New Jersey.

mass balance in the ground-water system. The purpose of this paper is to describe the ground-water flow system at the site, the modeling approaches, preliminary model designs, and preliminary results of the areal flow and solute-transport models.

GROUND-WATER FLOW SYSTEM

The glacial-valley flow system includes a long-term average areal ground-water recharge of about 23 inches per year to the water table. Near the bedrock slopes at the limit of the glacial sediments, rates of ground-water recharge are up to 10 times greater than the average areal rate because of surface runoff from the adjacent bedrock slopes that infiltrates quickly into the unconsolidated, flat-lying glacial sediments. This recharge generally moves downward through confining sediments to the confined aquifers and then upward near Green Pond Brook where it is discharged (fig. F-18). However, in some areas near the limits of the glacial sediments, there is upward flow from the bedrock to the confined or unconfined glacial sediments.

The general flow pattern from the limit of the glacial sediments to Green Pond Brook is evident in the map of the water table shown in figure F-19. The water-table contours also show a smaller, downvalley component of flow from the northeast to the southwest. Average linear ground-water velocities in the unconfined aquifer at the contaminant site range from 1 to 3 feet per day. The depth to water near the contaminant plume ranges from about 5 to 15 feet. Seasonal water-level fluctuations in the unconfined aquifer are 6 to 8 feet near Building 24 (the contaminant-source area) and are greatest (about 10 feet) near the limit of the glacial sediments at the bedrock valley walls.

The heads and hydraulic gradients of the underlying confined aquifers are similar to the water table. Horizontal gradients are toward the stream; however, seasonal water-level fluctuations are slightly less than those in the unconfined aquifers and there is a slightly larger downvalley component of flow. Vertical head differences between the confined and unconfined sediments range from about 0 to 2 feet. In most areas, small head gradients (less than 0.5 foot) and the relatively large contrast in hydraulic conductivity between the confined glacial sediments and the bedrock aquifer suggest that there are minor amounts of flow between the fractured bedrock and the confined sediments near the center of the valley. Large vertical head gradients (5 feet) near the limits of the glacial sediments in areas of upward flow from the bedrock may indicate larger amounts of flow between the bedrock and the sediments.

Withdrawals from each of two wells screened in the confined aquifers beneath the contaminant plume were about 250,000 gallons per day until mid-1983. These wells were used for potable water supply until 1981, when they were found to be contaminated with chlorinated solvents. Intermittent daily pumping produced water-level fluctuations of about 3 feet in the confined and bedrock aquifers. The withdrawals had little or no effect on water levels in the unconfined aquifer but increased downward leakage and contaminant movement from the unconfined aquifer to the confined aquifers.

The vertical distribution of TCE appears to be strongly controlled by the general ground-water flow pattern. The detailed distribution of TCE in the unconfined sediments shown by Fusillo, Ehlke, Martin, and Sargent (1987) is generalized in figure F-18. Movement of the contaminants generally is toward Green Pond Brook but downward near the source (Building 24) and upward near Green Pond Brook.

Factors other than the general ground-water flow patterns also affect the vertical distribution of contaminants. Concentrations of organic contaminants within the ground water may be greatly decreased by volatilization and microbial degradation near the water table. Although adsorption may be the most important chemical process that decreases the concentration of organic contaminants, it is highly dependent on the organic-carbon content of the glacial sediments. The lack of organic carbon in the glacial sediments (less than 0.1 percent by weight) suggests that this process may be less important than microbial degradation or volatilization. The land surface is paved near the source, and this may cause concentrations near the water table to remain above 0.1 mg/L (milligrams per liter) by limiting recharge and volatilization, and by inhibiting microbial degradation. Recharge to unpaved areas near Green Pond Brook cause concentrations near the water table to be less than 0.1 mg/L.

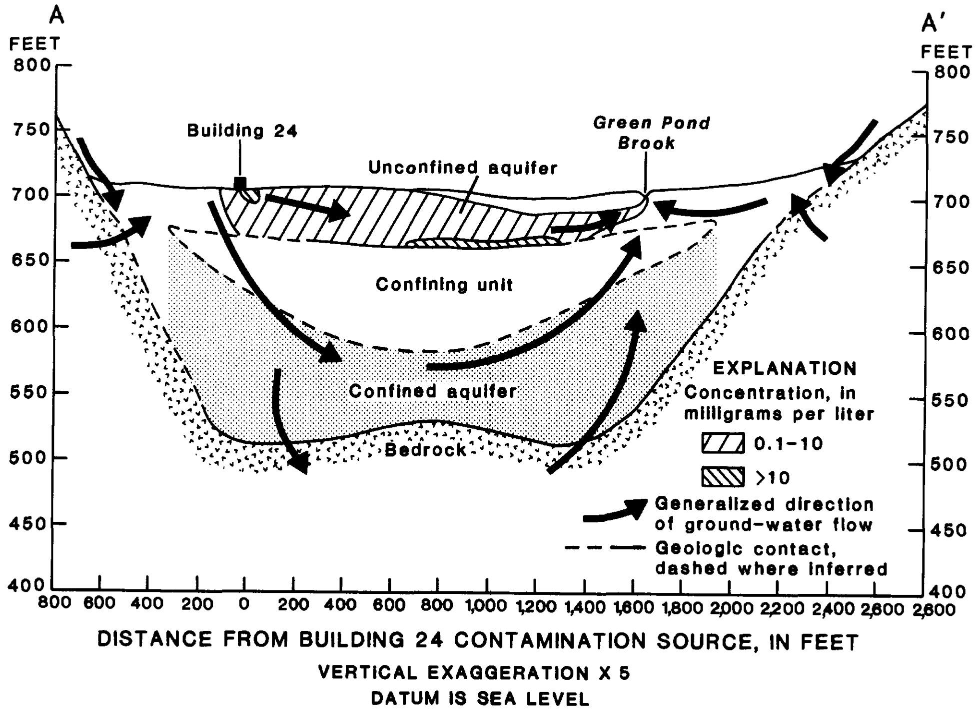


Figure F-18. – Generalized geohydrologic section showing trichloroethylene distribution in the unconfined aquifer and direction of ground-water flow along section A-A′. Location of section shown in figure F-17.

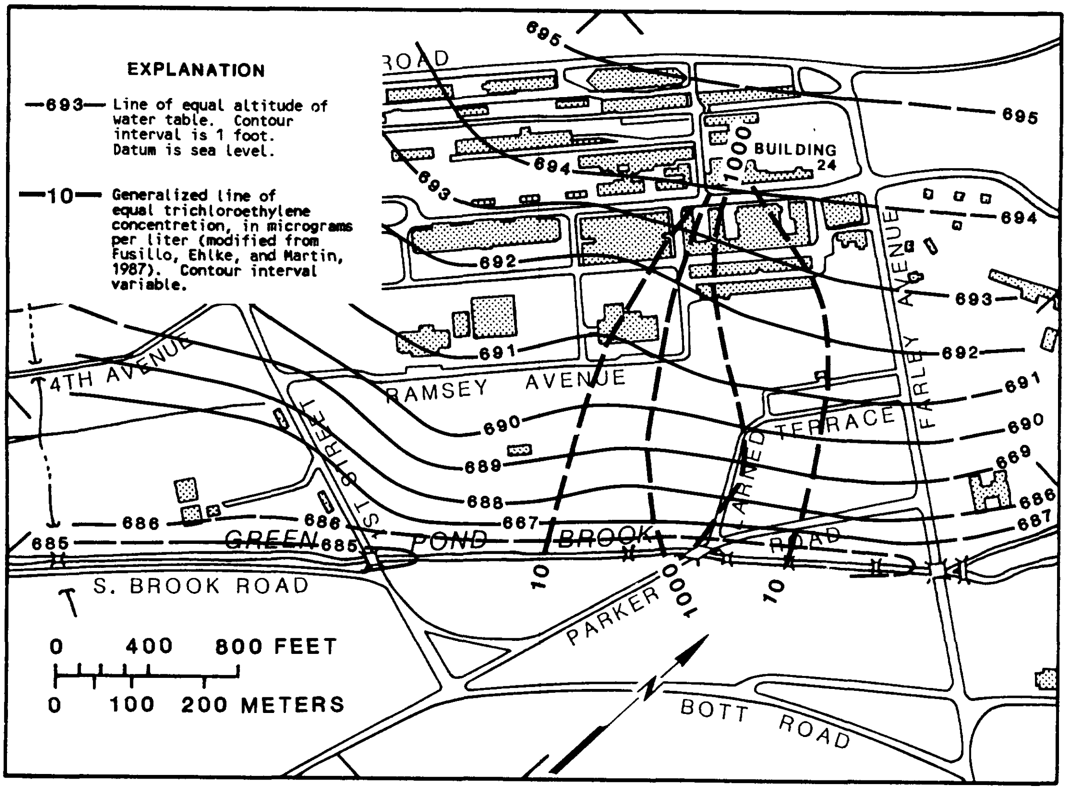


Figure F-19. – Altitude of the water table, June 1987, and general distribution of trichloroethylene in the unconfined glacial aquifer at the Building 24 site, August 1986.

Density and viscosity of the contaminants at the time of their introduction into the ground-water system may have also affected the vertical distribution of contaminants. TCE and other chlorinated solvents are significantly denser and less viscous than water. Although measured concentrations of the contaminants are too low to affect the density and viscosity of the ground water significantly, the movement of contaminants at the time of deposition may have been greatly affected by the density and viscosity of a high-concentration source fluid. Hypothesized deposition of pure TCE through an overflow pipe suggests that the contaminants may have entered the ground-water system in a separate, dense aqueous phase. Downward movement of a dense aqueous phase through the coarse unconfined-aquifer sediments may have been more rapid than the downward movement of the present contaminant plume. Although a separate TCE phase has not been found at the site, such an initial deposition could be the cause of measured TCE concentrations greater than 10 mg/L directly above the confining unit near Green Pond Brook (fig. F-18). This area of high TCE concentrations is apparently unassociated with the area of high TCE concentrations near the source, because TCE concentrations are less than 10 mg/L between these areas.

MODELING APPROACH AND MODEL DESIGN

Available hydrogeologic data were used to develop an areal ground-water flow model of three aquifers: the unconfined stratified-drift aquifer, the confined stratified-drift aquifer, and the bedrock aquifer. The model is quasi-three-dimensional with three layers. Horizontal grid spacing is 60 to 80 feet in the area of the contaminant plume. The boundary conditions controlling the movement of ground water at the site are best approximated at the physical limits of the aquifers. Therefore, the ground-water flow system within the glacial and bedrock aquifers is simulated for an area much larger than the contaminant site. The flow model has no-flow boundaries at the northwestern and southeastern limits of the glacial sediments and at the bottom of the bedrock aquifer underlying the glacial sediments. The northeastern and southwestern boundaries are specified-flux boundaries representing the downvalley flows into and out of the modeled area. Although these flux boundaries are not at the physical limits of the aquifers, which extend beyond the northeastern and southwestern model boundaries, they are in areas unaffected by ground-water withdrawals and are more than 5,000 feet from the contaminant site. The upper boundary is a specified-flux boundary representing the areal and temporal distribution of ground-water recharge and a specified-head boundary representing the stage of Green Pond Brook.

The two preliminary solute-transport models of the Building 24 contamination site include: an areal model of the unconfined aquifer and a cross-sectional model, along the central axis of the plume, of the unconfined and confined glacial aquifers and the bedrock aquifer. The cross-sectional model is based, in part, on the assumption that the differences in directions of ground-water flow in the confined and unconfined aquifers are not significant. Both solute-transport models are based on the same hydrogeologic framework as the ground-water flow model, and the flow system in the transport models is defined by specified-flux and specified-head boundary conditions calculated from the simulated flows and heads of the ground-water flow model.

The areal solute-transport model has a specified-head boundary within the unconfined aquifer beneath Green Pond Brook and specified-flux boundary elsewhere in the model representing the sum of horizontal and vertical flows into and out of the transport-model area. The grid spacing in the areal solute-transport model is 20 to 50 feet. The cross-sectional solute-transport model has no-flow boundaries representing the estimated base of the bedrock aquifer, a specified-flux boundary representing the ground-water recharge to the water-table, and a one-node, specified-head boundary representing the stage in Green Pond Brook where it intersects the axis of the contaminant plume. Vertical grid spacing in the cross-sectional solute-transport model is 5 to 8 feet in the unconfined sediments but increases with depth to 20 feet in the bedrock aquifer. The solute source is simulated as a specified concentration of TCE in both solute-transport models and a first-order decay process was used to simulate loss of TCE from the ground-water-flow system by volatilization.

The ground-water flow model will be calibrated by adjusting various hydraulic characteristics within acceptable ranges to minimize the difference between simulated and measured water levels and between simulated and measured stream discharges. Similarly, the solute-transport models will be calibrated by minimizing the difference between simulated and measured contaminant-concentration levels. During calibration, the hydraulic characteristics and boundary conditions in the solute-transport models are updated to ensure that they are equivalent to those in the ground-water flow model. Although water-level data of daily and seasonal fluctuations since 1983 are available for calibration, long-term water-level data are not available for the period of contamination, which is estimated to have begun in 1960. Although concentration data are available to show the areal, vertical, and temporal distribution of contaminant since 1981, concentration data near the time of initial contamination are not available.

Although 30-year transport simulations have been made, little information is available on the temporal variations in TCE concentration near the contaminant source. Preliminary results of the transient-flow simulation with a constant-concentration TCE source, show there is little change in the simulated TCE concentrations after 4 years. Also, measured TCE concentrations within the contaminant plume indicate that although concentrations have fluctuated, the range in fluctuations has been constant since 1981. Therefore, steady-state flow and transport simulations, with a constant-concentration source and a constant ground-water withdrawal rate from the confined sediments, were used to develop a preliminary conceptualization of the transport environment.

PRELIMINARY RESULTS AND PLANS FOR FUTURE RESEARCH

Initial calibration of the flow model has refined initial estimates of the hydraulic characteristics and the boundary conditions. Generally, the simulated head distribution is most sensitive to the areal and temporal distribution of ground-water recharge (definition of the upper boundary condition) and is much less sensitive to the definition of the hydrologic framework and hydraulic characteristics. However, simulated ground-water velocities and flow rates, including discharge to Green Pond Brook and leakage from the unconfined glacial aquifer to the confined aquifers, are very sensitive to hydraulic characteristics.

A three-dimensional flow model with increased detail is being developed that will have the same grid spacing as the preliminary flow model but will simulate flow in as many as 10 layers of interbedded sand, silt, and clay. This model will define flow rates vertically within the unconfined aquifer in increased detail and also will be used to simulate flow for shorter time periods. Initial transient-flow simulations were made with 3- to 5-year pumping periods; simulations using the detailed model will evaluate the effects on solute transport of seasonal changes in ground-water recharge and daily fluctuations in ground-water withdrawals.

Simulated longitudinal and transverse dispersivities were 50 and 10 feet, respectively. Simulated porosities for the aquifer and confining units were 30 and 40 percent, respectively. The total solute mass within the simulated contaminant plume (calculated from porosity, aquifer thickness, nodal spacing, and simulated concentrations) is about 3,000 kilograms (6,600 pounds) of TCE, or the equivalent of about 2,000 liters (540 gallons) of pure TCE. About 70 percent of the solute mass is in areas where simulated concentrations are 1 to 10 mg/L. Areas where simulated concentrations of TCE exceed 10 mg/L and areas where simulated TCE concentrations are 0.1 to 1 mg/L each contain about 15 percent of the total solute mass of TCE. Less than 1 percent of the solute mass is in areas with simulated concentrations of less than 0.1 mg/L. Although the distributions of solute mass are similar, the total simulated solute mass is about four times greater than that calculated from measured concentrations. The simulated solute mass may be greater than the calculated mass because of inaccuracies in either the calculated or simulated values. Simulated concentrations may be higher than measured concentrations because the preliminary model designs are too simplified or because the models are uncalibrated.

The simulated rate of TCE loss from the unconfined ground-water-flow system is about 100 grams (0.22 pounds) per day. About 90 percent of this loss represents loss from volatilization, about 7 percent represents downward movement of TCE through the confining sediments and less than 3 percent represents discharge of TCE to Green Pond Brook. These simulated loss rates are not accurate estimates of actual loss rates because the transport model is uncalibrated and because loss from microbial degradation and adsorption is not simulated. However, the simulated loss rates indicate that loss from volatilization may be on the order of hundreds of grams per day and may be one or two orders of magnitude more than the loss of TCE from the discharge of ground water to the confined aquifers or to Green Pond Brook.

Several additional aspects of the transport environment will be analyzed and included in the modeling research activities. The temporal, hydrologic, and chemical characteristics of the contaminants at the time of deposition are not well defined. Using the transport model to test various hypotheses on the source of contamination will be an important aspect of the modeling research activities and will aid in the understanding of the geochemical and biological factors affecting solute concentrations. It is particularly important to determine if the source of TCE contamination included a separate dense phase. Although the currently designed solute-transport models do not simulate two-phase flow, source terms in these models can be used to approximate the dense phase as a solute source if its location in time and space can be estimated.

Another aspect to be included in the modeling research activities is the analysis of variations in rates of biodegradation and volatilization in time and space. Although both processes can be approximated as a first-order decay processes, physical and geochemical factors make the rate of volatilization differ areally and the rate of biodegradation variable in time and space. Rates of volatilization are affected by paved areas and areal variations in the air-filled porosity of the unsaturated sediments. Areal and temporal variations in the amounts of oxygen and amendments, particularly methane, within the ground-water system affect the rates of microbial degradation. Modifications to the model design and model code to include areal and temporal changes in the decay terms in the solute mass-balance equation will improve the accuracy of simulated volatilization and biodegradation processes.

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(p. 385 follows)

DISTRIBUTION OF MAJOR AND TRACE ELEMENTS IN CORE SAMPLES FROM PICATINNY ARSENAL, NEW JERSEY

By Stephen A. Wilson[1] and Joseph E. Taggart, Jr.[1]

ABSTRACT

Core samples collected at various distances from a waste-disposal pit were analyzed for trace and major element concentrations using Inductively Coupled Argon Plasma Atomic Emission Spectroscopy and Wavelength Dispersive X-ray Fluorescence. It was determined that concentrations of chromium, copper, lead, nickel, and zinc were two to three times higher than background levels, and vanadium concentrations were one and a half to two times higher than background levels at sites downgradient from the disposal pit. Vertical variations in trace-metal concentrations also exist. Metal concentrations increased between 11 and 14 feet, then decreased to background concentrations below 14 feet at the sample site closest to the disposal pit. A similar variation in metal concentration was observed in cores from a site farther downgradient from the disposal pit, except that the maximum concentration occurred at the 29-foot depth.

INTRODUCTION

The U.S. Geological Survey is conducting investigations into the contamination of ground water at the Picatinny Arsenal caused by the disposal of metal-plating wastes at two disposal sites located at the arsenal. Ongoing investigations have revealed that the unconfined aquifer beneath the arsenal is contaminated with various organic solvents (Fusillo and others, 1987). Additional studies investigating the concentrations of heavy metals in the unconfined aquifer have revealed that the contamination caused by trace metals has diminished over the years (Harte and others, 1986; Sargent and others, 1986).

The focus of this investigation is to determine the distribution of heavy metals in the solid-phase aquifer material, with special interest directed toward developing a vertical and lateral model that explains the movement of these elements. In addition, work is also planned to investigate the phase associations that may have a role in the sorption of metals in the aquifer material. This work will focus on the use of sequential extractions to obtain important information on the relevant solid phase(s) and/or mechanisms at work in aquifer materials that were subjected to heavy-metal contamination.

RESULTS AND DISCUSSION

Initial studies have focused on the distribution of selected heavy metals in core samples downgradient (fig. F-20) from an electrochemical plating facility (site 1) located at the Picatinny Arsenal. The study was designed to trace the migration of these metals and determine the extent of basin contamination.

Analysis using Inductively Coupled Argon Plasma-Atomic Emission Spectrometry (ICAP-AES) (Crock and others, 1983) on samples collected downgradient (sites 2 and 3) from the disposal pit has shown elevated concentrations (relative to background) of chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), and vanadium (V). For this study, background levels were established by analyzing samples collected adjacent to Green Pond Brook (site 6), an area believed not to have been contaminated by heavy metals. A comparison of the data in table F-5 indicates that the concentrations of Cr, Cu, Pb, Ni, and Zn were two to three times higher than background levels at sites 2 and 3; concentrations of V were one and a half to two times higher.

The vertical distributions of heavy metals in the core also were studied. At sample site 2, the concentrations of heavy metals in the core material gradually increased in the 11- to 14-foot interval. Below a depth of 14 feet, the concentration of elements was similar to that of background levels. At sample site 3, farther downgradient, a similar vertical distribution was observed. Trace-metal concentrations increased with depth and reached a maximum level in the 19- to 29-foot core sections. Below this depth, heavy-metal concentration returned immediately

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

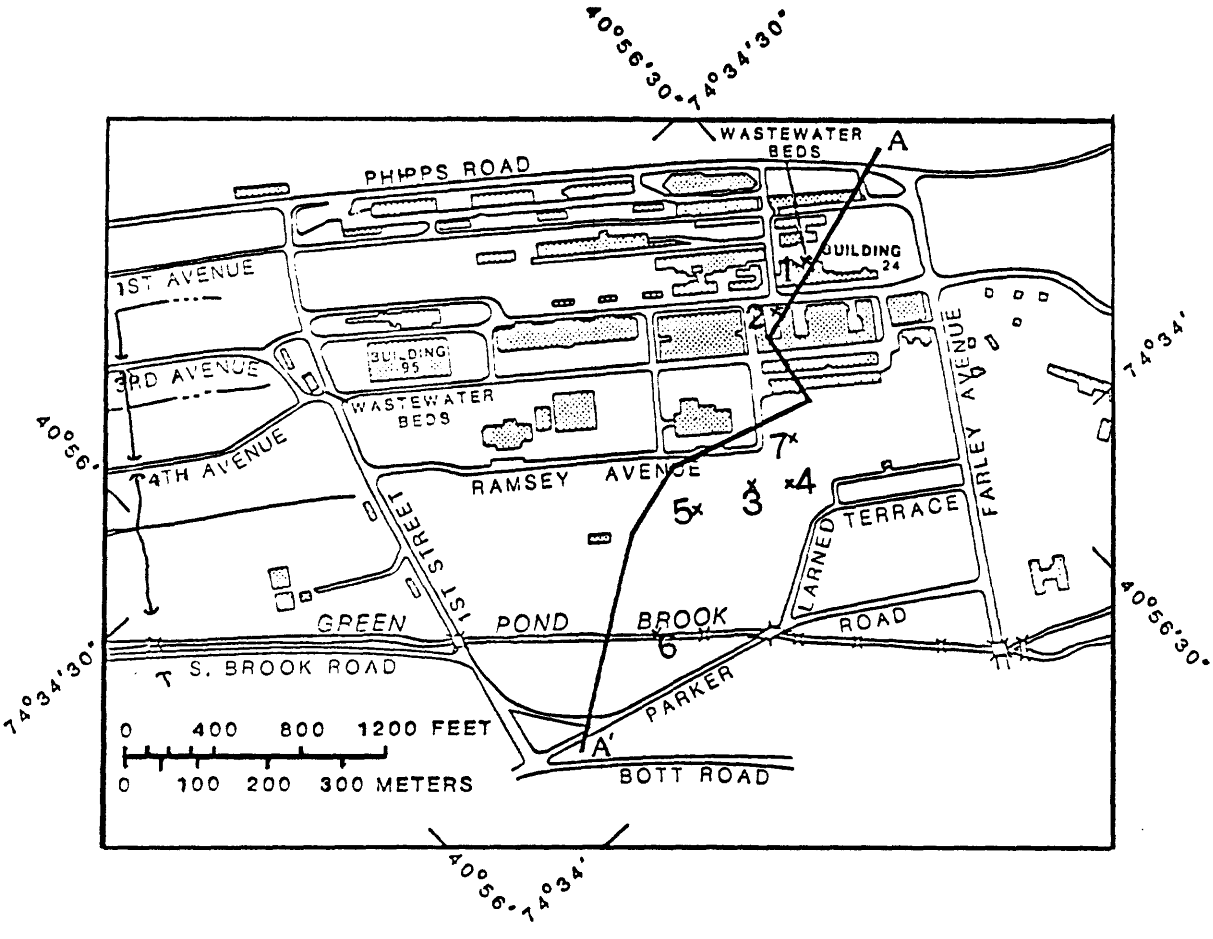

Figure F-20.—Location of sample sites at Picatinny Arsenal.

to background levels. The concentration of trace metals at the 29-foot level was two to three times the background levels for Cr, Cu, Pb, and Zn which is similar to what was observed at site 2. Elemental analysis at sites 4 and 5 (located east and west of site 3) showed no significant heavy-metal concentrations in any of the core segments examined.

In an attempt to test the homogeneity of the sampled part of the basin, a series of core samples from across the study area was examined to determine major-element concentrations using wavelength dispersive X-ray fluorescence spectroscopy. Results presented in table F-6 indicate that the samples studied are all similar with respect to their major element content. This would tend to support the hypothesis that the geochemistry of the basin area is uniform and that there are not significant differences in the major geologic components.

FUTURE INVESTIGATIONS

Plans for future investigations are to examine more closely the vertical and lateral distribution of metals in the area of sites 2 and 3, using samples collected from new sites to be drilled this summer. In addition, samples from this area will be subjected to a series of sequential extractions to elucidate the component that retains metals and possible causes of their remobilization.

Table F-5. — *Trace-metal concentrations in core samples from Picatinny Arsenal study area*

[Concentrations in solid material, in parts per million]

Site	Depth (feet)	Co	Cr	Cu	Ni	Pb	V	Zn
2	11	9	39	23	22	8	57	48
	13	9	48	29	21	13	49	59
	14	13	59	35	26	17	76	120
	16	9	25	19	16	9	42	39
	25	8	30	16	12	7	36	37
3	19	6	43	9	17	9	53	42
	21	8	45	20	19	9	52	45
	29	17	50	27	23	9	76	60
	31	9	28	14	12	6	33	31
	47	10	33	15	14	7	38	35
4	19	9	29	13	12	7	40	32
	21	8	32	19	14	9	46	38
	29	9	31	13	13	7	42	32
	31	9	32	14	13	8	42	31
	48	9	32	13	13	7	43	30
5	19	8	33	13	12	6	39	32
	21	7	25	12	11	6	36	30
	29	8	30	13	12	7	36	30
	31	8	31	12	12	7	39	31
	33	8	32	13	12	7	41	32
6	12	9	36	15	15	8	40	31
	17	8	30	15	13	5	35	28
	22	9	36	12	14	7	40	29
	29	9	35	14	14	8	39	32
	33	10	36	14	13	7	50	32

Table F–6.—*Major element concentration in core samples using wavelength dispersive x-ray fluorescence*

[Concentrations in sample, in percent]

Site	Depth (feet)	SIO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O
2	11	79.2	8.4	0.89	0.64	1.10	2.29
	13	78.9	8.4	0.87	0.74	1.39	2.25
	16	81.7	7.7	0.79	0.81	1.22	2.25
3	19	80.2	8.4	0.85	0.46	0.89	2.24
	21	80.4	8.2	0.84	0.54	1.05	2.26
	29	81.9	7.7	0.66	0.79	1.39	2.28
6	12	81.3	7.9	0.75	0.96	1.5	2.32
	22	79.5	7.5	1.22	1.91	1.38	2.21
	37	82.0	6.9	0.72	0.82	1.09	1.98
7	26	82.6	7.8	0.66	0.69	1.28	2.33

CONCLUSIONS

Analysis of trace-metal data indicates that some migration of heavy metals from the Picatinny Arsenal disposal site has occurred. At sites 2 and 3, the metals have moved approximately 1,200 feet from the disposal site. The absence of elevated heavy-metal concentrations at sites 4 and 5 indicates that heavy-metal plumes may be fairly small or that there has been a rapid change in plume direction. Improved definition of the metal plume will follow additional drilling. The vertical distribution of heavy metals at sites 2 and 3 indicates that the heavy metals sink lower in the basin with increasing distance from the disposal site.

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BIOTRANSFORMATION OF CHLORINATED HYDROCARBONS AND ALKYLBENZENES IN AQUIFER MATERIAL FROM THE PICATINNY ARSENAL, NEW JERSEY

By Barbara H. Wilson[1]

ABSTRACT

The most common ground-water contaminants are chlorinated solvents used as degreasers and the soluble constituents of petroleum products. Of these, trichloroethylene, 1,1,1-trichloroethane, tetrachloroethylene, benzene, toluene, and the xylenes are most commonly found. Trichloroethylene and 1,1,1-trichloroethane are not biologically degraded in oxygenated ground waters and persist in those environments. In anoxic subsurface materials, they may undergo a reductive dechlorination (chlorine is replaced with a hydrogen) to form new compounds that are more mobile than the parent compounds and, in the case of vinyl chloride, are more carcinogenic.

The ground water from Picatinny Arsenal in north-central New Jersey has been contaminated by two partially overlapping plumes from discharged wastewater from a metal-plating wastewater treatment system and from spilled diesel fuel. Trichloroethylene is the predominant contaminant from the wastewater-treatment system with tetrachloroethylene, 1,1,1-trichloroethane, cis-*1,2-dichloroethylene, and vinyl chloride also present. The presence of* cis-*dichloroethylene and vinyl chloride indicate that biological activity in the form of reductive dechlorination may be active in the plume. No information on the composition of the ground water from the diesel fuel spill has been provided, but the presence of significant concentrations of methane indicates methanogenic processes may be occurring.*

To confirm field evidence of biological transformation of the chlorinated solvents, the fate of trichloroethylene and 1,1,1-trichloroethane was monitored in aquifer material from the part of the plume exposed to trichloroethylene only and from the part of the plume exposed to both trichloroethylene and the diesel fuel. Their fate was observed both with and without the presence of benzene, toluene, chlorobenzene, and o-*xylene to determine their effect on reductive dechlorination. Initial results indicate the removal of a maximum of 65 percent trichloroethylene in material exposed to both trichloroethylene and the diesel fuel in microcosms not containing the alkylbenzenes. Substantial removals of the remaining compounds were also observed, with 2 percent of the original concentration of toluene remaining at the end of 4 weeks of incubation.*

INTRODUCTION

The organic contaminants found most frequently in ground waters used as drinking water supplies are the water-soluble constituents of petroleum products and the chlorinated solvents used as degreasers. The most common sources of these contaminants result from failures of storage tanks and associated plumbing or inappropriate disposal to evaporation pits and landfills. Among those contaminants commonly found are trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), benzene, and toluene (Westrick and others, 1984).

In oxygenated subsurface materials, TCE and TCA are not biodegradable and will persist under those conditions. TCE and TCA are biodegraded only in anoxic subsurface materials by undergoing a reductive dechlorination with the daughter products of TCE being the dichloroethylenes and vinyl chloride (VC) and those of TCA being 1,1-dichloroethane and chloroethane (Barrio-Lage and others, 1986; Barrio-Lage and others, 1987; Vogel and McCarty, 1987). TCA may also be nonbiologically transformed to 1,1-dichloroethylene (1,1-DCE) by elimination and to acetic acid by hydrolysis (Haag and others, 1986) with the potential of the biodegradation of 1,1-DCE to VC. These products of transformation of TCE and TCA are more mobile in ground waters than the parent compounds, and VC exhibits greater carcinogenicity.

Because they are soluble in water, benzene, toluene, ethylbenzene, and the xylenes are the

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[1] Environmental and Ground Water Institute, University of Oklahoma, Norman, Okla.

most common indicators of contamination from petroleum-derived products. These aromatic compounds are readily biodegraded in oxygenated environments but were previously believed to be biologically recalcitrant in the absence of molecular oxygen (Young, 1984). However, recent work indicates that aromatics can be biotransformed in the absence of molecular oxygen (Vogel and Grbiĉ-Galiĉ, 1986; Wilson and others, 1986; and Grbiĉ-Galiĉ and Vogel, 1987).

Ground water at the Picatinny Arsenal in north-central New Jersey has been contaminated by the disposal of metal-plating wastes and by a nearby spill of diesel fuel; these contaminants have formed two partially overlapping plumes. The plume that resulted from metal-plating wastes (discharged wastewater from a metal-plating wastewater-treatment system to an unlined infiltration pit) contains TCE as the major contaminant; tetrachloroethylene (PCE), TCA, *cis*-dichloroethylene (*cis*-DCE), and VC are also present. The composition of the diesel-fuel plume is not known, although measurable concentrations of methane have been observed.

This paper describes the results of laboratory studies conducted on aquifer materials containing the plumes to confirm field evidence of the biotransformation of TCE and TCA. Because of the potential for codisposal of the chlorinated solvents plus the soluble constituents of petroleum, the fate of TCE and TCA was observed both with and without the presence of benzene, toluene, chlorobenzene, and *o*-xylene to determine any potential effects of the additional compounds on reductive dechlorination.

SITE DESCRIPTION

The site of the contamination is the Picatinny Arsenal located in the Green Pond Brook Valley in New Jersey. The plumes are found in an unconfined glacial-stratified-drift aquifer approximately 11 meters thick underlain by a confining unit. A confined stratified-drift aquifer with a thickness of 6 to 25 meters underlies the confining unit. The depth to water ranges from about 1.5 to 5 meters below land surface. Aquifer material was provided by the U.S. Geological Survey with split-spoon sampling at four locations (fig. F-21) within the plumes, including the area of overlap. The aquifer solids were stored in sterile canning jars and then transported on ice to the R.S. Kerr Environmental Research Laboratory, Ada, Okla.

Material from three depths at site 31-2A (5.5, 8.1, and 9.1 meters) and one depth at 41-4 (3.6 meters) was used to construct living microcosms; material from 41-1 (3.6 meters) was used to construct the autoclaved controls. Each sample was split into two parts, one of which received an aqueous solution of TCE and TCA. In addition to TCE and TCA, the second part received benzene, toluene, chlorobenzene, and *o*-xylene.

The geochemistry of the aquifer material used for living samples is shown in table F-7. The material was highly reducing, with redox potentials ranging from -375 to -463. Measurable concentrations of methane ranged from 400 to 1,500 μg/L (micrograms per liter) in the plume exposed to diesel fuel; no methane was detected in the plume exposed only to TCE. TCE and its daughter products of reductive dechlorination, *cis*-DCE and VC, were observed in material from both plumes of contamination.

All manipulations for construction of the microcosms were completed in an anaerobic glove box to maintain the integrity of the reduced aquifer material. All equipment that came in contact with the aquifer material was sterilized before use. For construction of the microcosms, approximately 40 grams of aquifer material (wet weight) were added to fill 50-mL (milliliter) serum bottles. Each microcosm was dosed with the addition of 1.0 to 1.5 mL of the dosing solution so that no headspace remained, then immediately capped with a Teflon[2]-coated butyl-rubber septum and a crimp cap seal. The controls were autoclaved overnight at 121 °C (degrees Celsius), returned to the glove box, and dosed in the same manner as the living samples. The microcosms were incubated inverted in the dark at 15 °C under a nitrogen atmosphere.

ANALYSIS OF SAMPLES

Two to five replicate microcosms were collected for analysis at each time interval. The contents of the microcosms were transferred to a 100-mL serum bottle containing 35 mL of reverse osmosis water, then sealed with a Teflon-coated

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

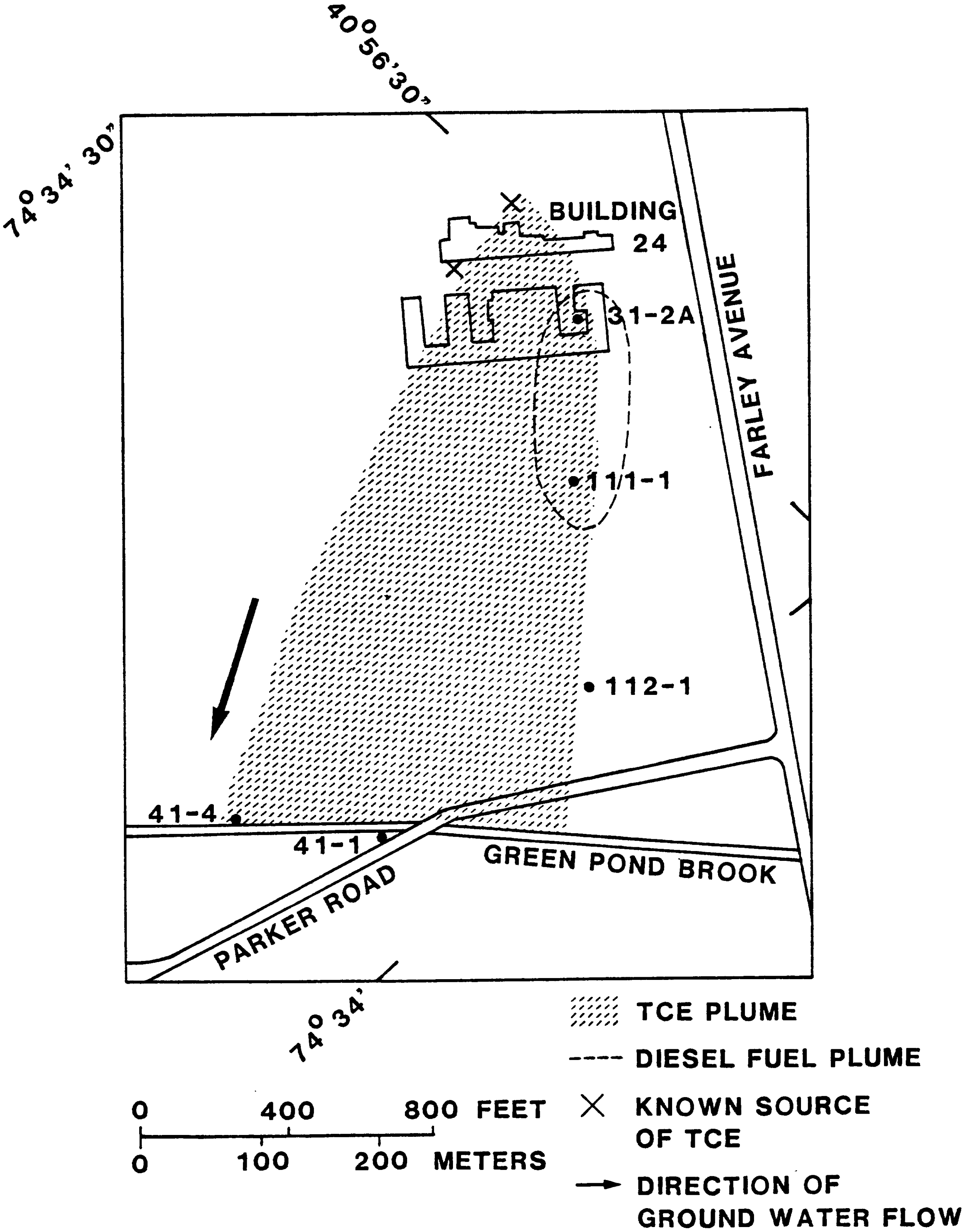

Figure F-21.—Location of wells in overlapping plumes at Picatinny Arsenal, N.J.

Table F–7. – *Geochemistry of samples from Picatinny Arsenal*

[m = meters, µg/L = micrograms per liter, < = less than, TCE = trichloroethylene, *cis*-DCE = *cis*-dichloroethylene. Numbers in parentheses are depths in meters below land surface]

Compound	Sample exposure			
	TCE plus diesel fuel			TCE only
	31-2A (5.5 m)	31-2A (8.1 m)	31-2A (9.1 m)	41-4 (3.6 m)
	Concentrations in ground water, in µg/L			
TCE[1]	2	9	5	60
cis-DCE[1]	4	7	6	4
Vinyl chloride[1]	8	2	20	<1
Methane[1]	400	1,500	1,500	<2
pH[2]	6.5	5.8	5.7	6.9
Redox potential[2,3] (millivolts)	-463	ND[4]	-375	-416

[1] Concentrations provided by the U.S. Geological Survey
[2] Measured prior to construction of the microcosms.
[3] Measured under a nitrogen atmosphere in a glove box
[4] Not determined.

silicone septum. The internal standard, 4-bromofluorobenzene, was added through the septum by syringe to the liquid part of each sample. The volatile compounds in the samples were purged onto a resin trap with nitrogen gas at a flow rate of 50 mL per minute for 15 minutes. The samples were desorbed in a thermal-tube desorber at 225 °C for 5 minutes onto the head of a 30 meter by 0.53 mm (millimeter) inside-diameter column. The column was held at 35 °C for 5 minutes then programmed at 8 °C per minute to 175 °C and held for 15 minutes. A gas chromatograph with flame ionization detection and N_2 carrier gas at 7 mL per minute flow rate was used.

RESULTS AND DISCUSSION

Each of the compounds studied had a biological fate in the aquifer material from Picatinny Arsenal. Initial concentrations and concentrations at specific incubation times are shown in table F-8.

Suite #1 Compounds

At the end of 4 weeks of incubation, the biological removal of TCE was seen in materials exposed to TCE and to diesel fuel as well as in the material exposed to TCE only. The largest removals were from sites 31-2A (5.5-meter depth) and 41-4 (3.6-meter depth) with removals of 65 percent and 60 percent, respectively. Removals at the other two sites (31-2A, 8.1-meter depth and 9.1-meter depth) were 41 percent and 34 percent, respectively. Biotransformation of TCA was not as consistent; for example, maximum removals of 37 percent were seen in 31-2A (5.5-meter depth). Interestingly, the other two depths from 31-2A (8.1 meters and 9.1 meters) showed little or no removal of TCA at the end of 4 weeks of incubation. Biodegradation of the initial concentration of TCA was observed in 41-4 (3.6-meter depth) where 77 percent remained after 4 weeks.

Suite #2 Compounds

Biotransformation of TCE and TCA was seen in all materials studied when added with the additional compounds. Biological removals ranged from 18 to 44 percent of the initial concentrations of the compounds. Biodegradation of benzene, toluene, *o*-xylene, and chlorobenzene also was observed, and dramatic reductions of toluene in the material previously exposed to diesel fuel were noted. After 4 weeks of incubation, removals of 98 percent, 97 percent, and 78 percent were seen in the respective depths of 5.5 meters, 8.1 meters, and 9.1 meters at site 31-2A.

Table F–8.—*Fate of TCA, TCE, benzene, toluene, o-xylene, and chlorobenzene in aquifer material from Picatinny Arsenal*

[mg/L = milligram per liter, TCA = 1,1,1- trichloroethane, TCE = trichloroethylene. Numbers in parentheses are depth of sample, in meters below land surface]

Compound	Initial concentrations, in microcosms (mg/L)	Elapsed time, in weeks	Autoclaved control	Sample exposure			
				TCE plus diesel fuel			TCE only
				31-2A (5.5 m)	31-2A (8.1 m)	31-2A (9.1 m)	41-4 (3.6 m)
			Percentage remaining[1]				
Suite #1							
TCA	1.6	2	106	56	95	101	82
		4	108	63	106	94	77
TCE	2.3	2	103	42	72	84	52
		4	99	35	59	66	40
Suite #2							
TCA	1.6	2	106	73	78	103	98
		4	108	63	66	81	82
TCE	2.3	2	103	64	88	85	102
		4	99	56	66	68	79
Benzene	3.1	2	106	75	97	79	106
		4	110	68	76	79	85
Toluene	2.4	2	103	27	93	95	97
		4	102	2	3	22	76
o-xylene	2.2	2	98	72	102	105	92
		4	98	62	65	77	72
Clorobenzene	3.1	2	97	62	89	90	92
		4	98	54	67	69	71

[1] Percentage remaining is based on two to five replicates of each suite of compounds at each sampling interval compared to their time-zero values.

Biological removal of toluene also was seen at site 41-4, where 76 percent of toluene remained after 4 weeks of incubation. Although biological activity was seen for benzene, *o*-xylene, and chlorobenzene, two-thirds to three-fourths of the original concentrations remained after 4 weeks. For the Suite #2 compounds, the biological activity of only toluene was observed to be significantly greater in the aquifer material exposed to both TCE and the diesel fuel compared to aquifer material exposed to TCE only.

Previous work studying the fate of TCE and TCA in conjunction with four alkylbenzenes in methanogenic aquifer material found no biotransformation of either chlorinated solvent at the end of 8 weeks of incubation (Wilson and others, 1987). However, in this same study, removals of an order of magnitude were observed for benzene, toluene, *m*-xylene, and *o*-xylene. Other work (Barrio-Lage and others, 1987; Suflita and others, 1988) has shown biological activity against chlorinated organics in anoxic aquifer materials.

CONCLUSIONS

The fate of six compounds commonly found as contaminants in ground water was studied in aquifer material from the Picatinny Arsenal, N.J. The biological fates of TCE and TCA were studied both with and without the presence of benzene, toluene, *o*-xylene, and chlorobenzene to determine the effect of codisposal of contaminants to the subsurface in aquifer material exposed to both TCE and diesel fuel or exposed to only TCE. Biotransformation of all compounds was observed in materials from both sites that received all the compounds studied. Biological removals of one-third to one-half were noted for all compounds with the exception of toluene, which had dramatic removals of up to 98 percent. The amounts of biotransformations observed did not vary greatly for TCE with or without the presence of benzene, toluene, *o*-xylene, or chlorobenzene Removals of TCA were greater with the additional compounds for the 8.1-meter depths; no biodegradation of TCA was seen at site 31-2A at depths of 8.1 meters and 9.1 meters when only TCE and TCA were added to the aquifer material. However, these depths may need additional time to acclimate before adaptation occurs.

Field evidence indicates that biotransformation of TCE has occurred in the ground water at Picatinny Arsenal with the formation of *cis*-DCE and VC as daughter products. This study confirms the biotransformation of TCE in the anoxic aquifer material from Picatinny Arsenal. However, definitive confirmation of daughter-product formation for TCE and the remaining compounds awaits GC/MS analysis. The aquifer material studied has been shown to be biologically active against the compounds found as contaminants in that same aquifer. With the exception of toluene, the biological removals observed after 4 weeks of incubation do not appear substantial; however, they may be environmentally significant when coupled to the long residence times that typically prevail in aquifers.

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CHAPTER G – RESEARCH ON NONPOINT SOURCES OF CONTAMINATION

(p. 397 follows)

REGIONAL APPRAISAL OF GROUND-WATER QUALITY IN FIVE DIFFERENT LAND-USE AREAS, LONG ISLAND, NEW YORK

By David A. V. Eckhardt[1], Steven F. Siwiec[1], and Stephen J. Cauller[1]

ABSTRACT

Water-quality data from 90 shallow wells screened in the upper glacial (water-table) aquifer beneath five different land-use areas in Nassau and Suffolk Counties, Long Island, were compared to assess the effects of human activities and land-use practices on ground-water quality. The areas, which range from 22 to 44 square miles, represent suburban land sewered more than 22 years (long-term sewered), suburban land sewered less than 8 years (recently sewered), unsewered suburban land, agricultural land, and undeveloped (forested) land. All five areas overlie the regional water-table divide, where downward-moving water recharges the deeper aquifer system.

The most frequently detected volatile organic compounds were 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene; these were found primarily in samples from the recently sewered and unsewered suburban areas. None were detected in samples from the agricultural or undeveloped areas. Semivolatile organic compounds were detected most frequently and at highest concentrations in samples from the long-term sewered suburban area. Carbamate insecticide residues, mainly aldicarb metabolites and carbofuran, were found almost exclusively in samples from the agricultural area. Organochlorine insecticide residues, mainly dieldrin and chlordane, were detected at low concentrations in all five areas.

Maximum-likelihood logistic regression analysis of three predictor variables--population density, percentage of industrial and commercial land, and precentage of residential land within a 1/2 mile radius of the 90 wells--was used to predict the probability of volatile organic compound detection in shallow ground water. Recent water-quality data from more than 300 wells across the two-county area were used to verify model results.

INTRODUCTION

Water-quality data from 90 shallow wells screened in the upper glacial (water-table) aquifer beneath five different land-use areas in Nassau and Suffolk Counties, Long Island, were compared to assess the effects of human activities and land-use practices on ground-water quality. The areas, which range from 22 to 44 mi^2 (square miles), represent suburban land sewered more than 22 years (long-term sewered), suburban land sewered less than 8 years (recently sewered), unsewered suburban land, agricultural land, and undeveloped (forested) land. All five areas are on the regional ground-water divide (fig. G-1), where downward-moving water recharges deeper parts of the Long Island aquifer system.

The approach used in this study was based on the premise that water quality in shallow aquifer systems may be related to land use because the type and amount of chemicals introduced at land surface frequently are related to the type of land use. Once contaminants have entered the ground-water system, hydrogeologic, physical, chemical, and microbiological factors control their movement and fate. As in all natural systems, however, local variability in the type and number of contaminant sources and numerous other factors that control the fate of contaminants introduce uncertainty into the evaluation of water-quality differences as a function of land use. These uncertainties can be appraised statistically. Therefore, evaluation of ground-water quality requires (1) representative sampling and accurate

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[1] U.S. Geological Survey, Syosset, N.Y.

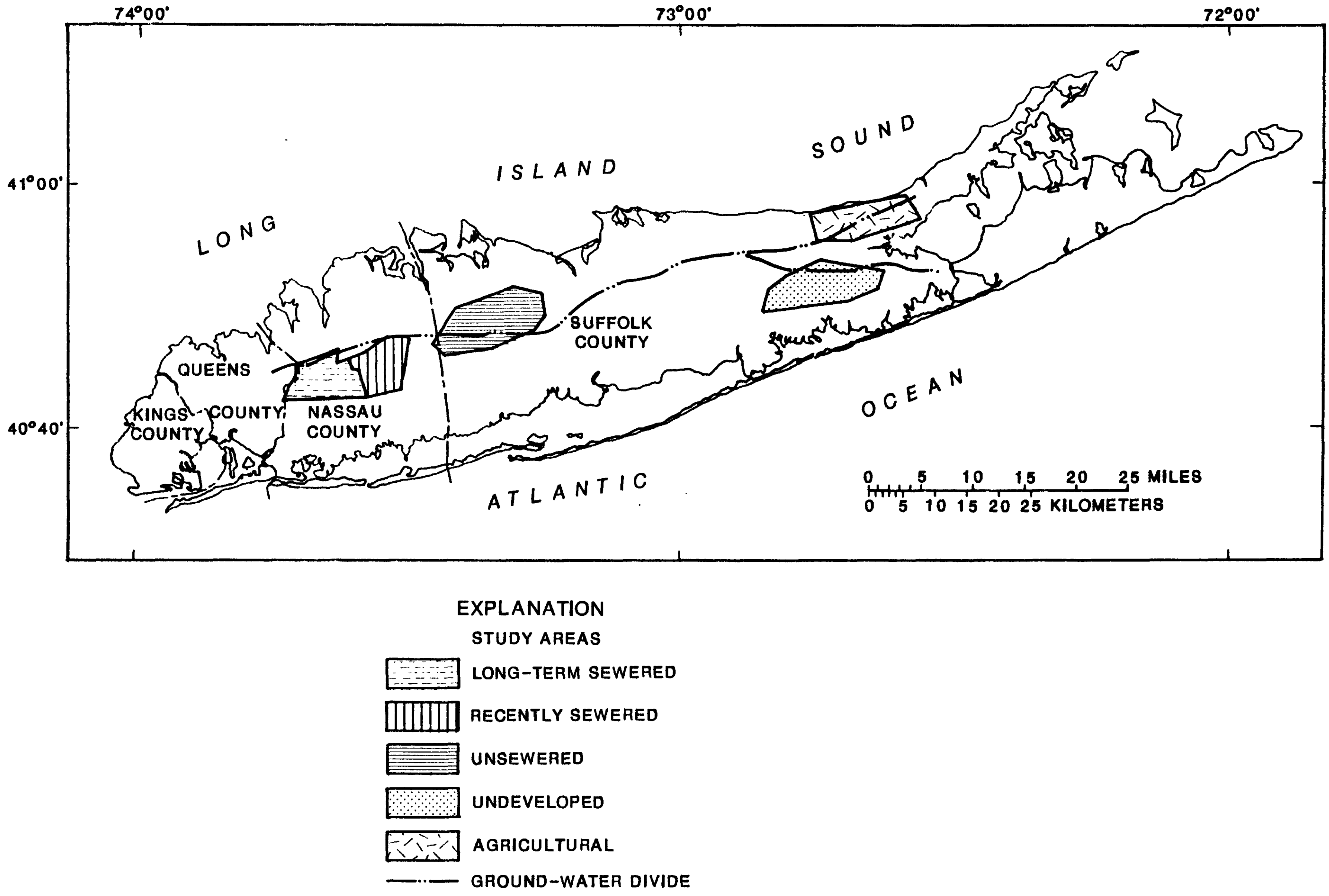

Figure G-1.–Location of the five land-use areas in Nassau and Suffolk Counties, Long Island, New York.

water-quality analyses, (2) accurate characterization of land use and hydrogeologic conditions, and (3) valid statistical analyses.

Statistical analyses for this appraisal required procedures designed for skewed distributions and censored (less-than) values typical of water-quality data. Four types of statistical procedures were used to evaluate the data: (1) exploratory data analysis, primarily boxplots and scatterplots; (2) nonparametric procedures that compared ranks of concentrations within and among land-use groups; (3) contingency-table analysis that compared detection frequencies among land-use groups for data with censored observations; and (4) logistic-regression analysis that developed predictive equations of the probability of occurrence of selected contaminants in shallow ground water.

DATA COLLECTION

Data on water quality in the shallow ground-water system (less than 45 feet below the water table) were collected at 90 wells in five land-use areas from June through October 1987. At all wells, at least three casing volumes of water were evacuated, and drawdown, specific conductance, pH, and temperature stabilized before sample collection. Dissolved oxygen was measured in the field by the Winkler-titration method. Water-quality analyses were provided by the U.S. Geological Survey (Arvada, Colo.) and by cooperating county Department of Health laboratories for (1) major inorganic ions, (2) trace elements, (3) volatile organic compounds (VOCs), (4) semivolatile (liquid-extraction) organic compounds, and (5) three types of insecticides (carbamate, organochlorine, and organophosphorus) and two types of herbicides (triazine and chlorophenoxy-acid).

SUMMARY OF WATER-QUALITY EVALUATION IN THE FIVE AREAS

Comparison of water-quality data from 90 shallow wells in the five land-use areas indicated that samples from the undeveloped area had the lowest and least variable concentrations of most human-derived constituents. Concentrations of inorganic constituents in samples from the three suburban areas generally were intermediate to high, but those in samples from the agricultural area generally were the highest and most variable. The lowest median concentration of nitrate (0.24 mg/L (milligram per liter) as nitrogen) was in the undeveloped area (fig. G-2); the highest median concentration (8.9 mg/L) was in the agricultural area, which receives extensive applications of nitrogen-rich fertilizers. Concentrations of nitrate in the agricultural area were not statistically different from those in the three suburban areas, where nitrogen sources include septic effluent and lawn fertilizers. Ammonium ion was detected most frequently in samples from the agricultural area (47 percent of wells) and least frequently in samples from the undeveloped area (7 percent). The highest median concentration of dissolved boron (fig. G-2) was in the agricultural area (80 μg/L (micrograms per liter)), where boron is applied in row-crop fertilizers, and in the recently sewered (80 μg/L) and long-term-sewered (60 μg/L) suburban areas, where it is a constituent of laundry soaps. The median concentration of boron in the unsewered residential area was 20 μg/L, and that in the undeveloped area was 10 μg/L. Other inorganic trace elements were detected infrequently in all areas.

Significant differences in the detection frequency of VOCs were indicated among the five land-use areas by contingency tables. The most frequently detected VOCs were1,1,1-trichloroethane and trichloroethylene (figs. G-3A, G-3B). These compounds were detected in samples from the three suburban areas but not in samples from the agricultural or undeveloped areas. Detection frequencies of VOCs were related to population density, which ranges from 0 to 20 people per acre in the two-county area. The highest detection frequency of 1,1,1-trichloroethane was in areas with a population density of 6 to 8 people per acre, whereas the lowest detection frequency was in areas of fewer than 6 people per acre. Semivolatile organic compounds were detected most frequently and at highest concentrations in samples from the long-term sewered suburban area. The carbamate and organochlorine insecticides were the most frequently detected pesticides.

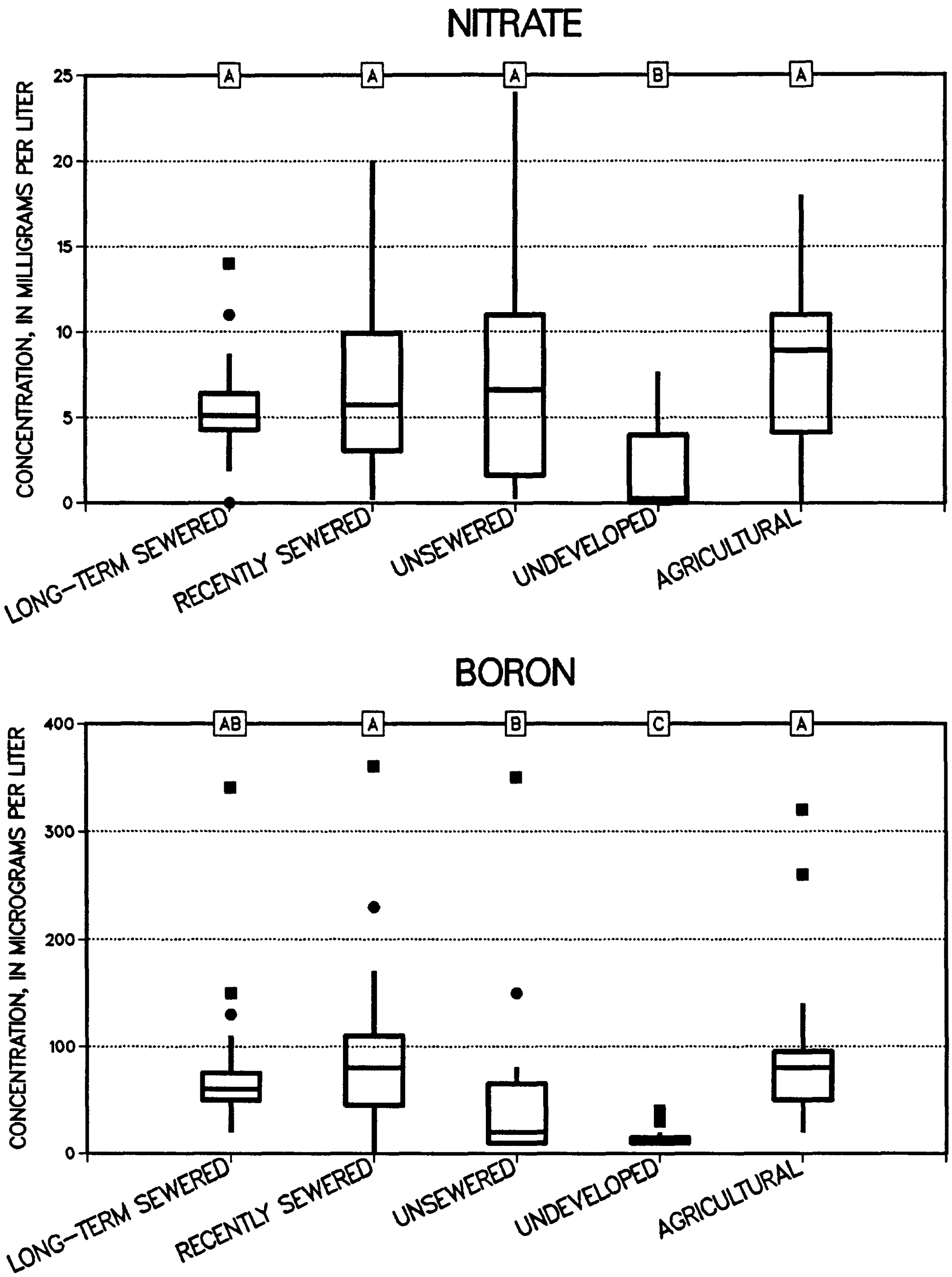

Figure G-2.—Nitrate and boron concentrations in five land-use areas. Boxes represent interquartile range (IQR) of data, between the 25th and 75th percentiles; horizontal bar indicates median. Whiskers (vertical lines) denote range of data within 1.5 times the IQR. Outliers are indicated by circles (1.5 to 3.0 times the IQR) or squares (beyond 3.0 times the IQR). Letters above box plots indicate results of multiple comparison tests (Tukey's studentized range test; groups of data with common letters do not differ statistically).

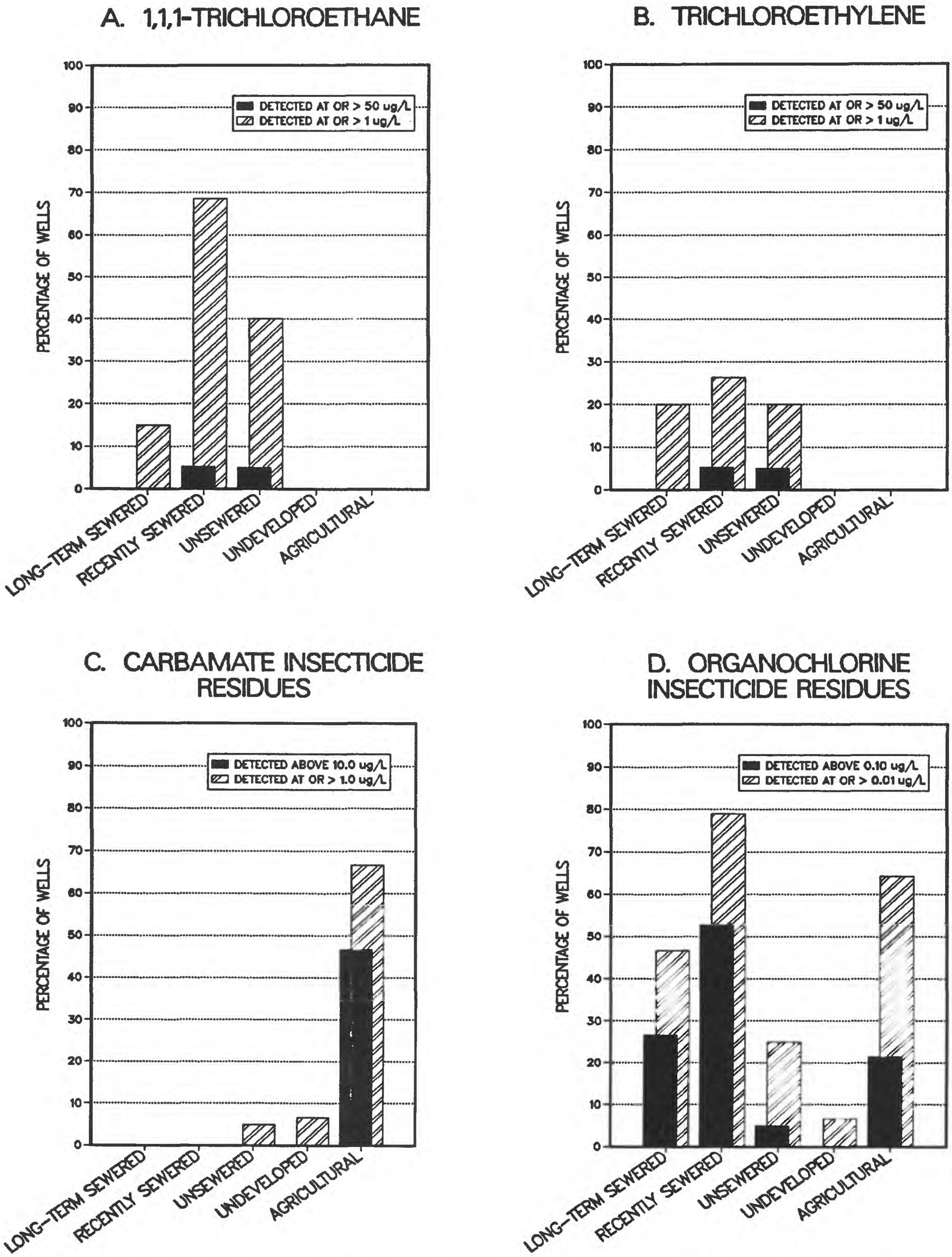

Figure G-3.—Percentage of wells in which selected constituents were detected: (A) 1,1,1-trichloroethane. (B) Trichloroethylene. (C) Carbamate insecticide residues. (D) Organochlorine insecticide residues. (Reported levels are in micrograms per liter (μg/l).)

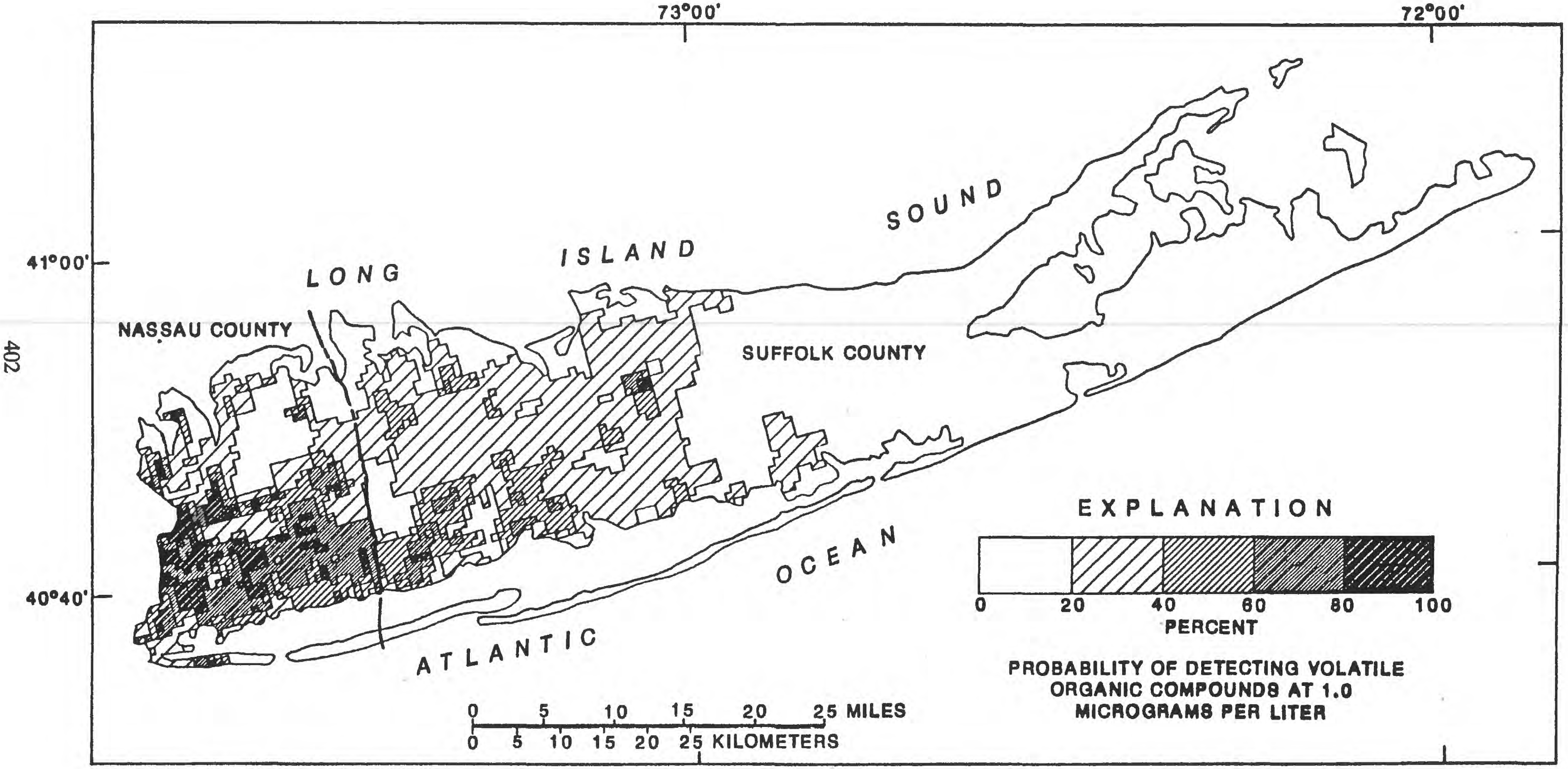

Figure G-4.–Probability of detecting volatile organic compounds at the 1 microgram-per-liter level in shallow ground water, according to a population-density logistic-regression model.

Carbamate insecticide residues (fig. G-3C), mainly aldicarb metabolites and carbofuran, were found almost exclusively in samples from the agricultural area. Organochlorine insecticide residues (fig. G-3D), mainly dieldrin and chlordane, were detected in samples from all five areas but most frequently in the agricultural and sewered suburban areas.

LOGISTIC-REGRESSION ANALYSIS

Maximum-likelihood logistic-regression equations that characterize the probability of VOC detection in shallow ground water were developed from explanatory variables such as (1) population density and (2) percentage of industrial/commercial land and percentage of residential land that describe the degree of human development in the five study areas. Explanatory variables were determined for the 1/2-mile radial area around each of the 90 wells through geographic information system software. These continuous explanatory variables were then related to the binary response variable--the detection or nondetection of any VOC at each well--through logistic regression.

Logistic-regression equations with statistically significant slope and intercept coefficients were used to predict probabilities of VOC detection in shallow ground water in the entire two-county area by determining the values for appropriate explanatory variables for each cell within a 1/4-mile^2 grid overlay of the counties. The associated probabilities of VOC detection at 1 μg/L for a univariate population-density equation are displayed in figure G-4. A second, independent logistic-regression equation also was developed that uses two explanatory variables--percentage of industrial/commercial land, and residential land. In both equations, predicted probabilities of VOC detection were directly related to explanatory variables. To verify predictions, an independent data set of VOC concentrations at more than 300 shallow wells across the two-county area were compared with the predictions at mutual cell locations.

(p.405 follows)

METHODS OF EVALUATING THE RELATION OF GROUND-WATER QUALITY TO LAND USE IN A NEW JERSEY COASTAL PLAIN AQUIFER SYSTEM

By Eric F. Vowinkel[1] and William A. Battaglin[1]

ABSTRACT

Three methods were developed and tested to evaluate statistical relations of shallow ground-water quality to land use in a New Jersey Coastal Plain aquifer system. Each method indicates significant relations of nitrate nitrogen (nitrate) and purgeable organic compounds to land use. The effect of buffer radius on test results for each method is evaluated by using land-use percentages within circular buffers with radii of 1, 100, 250, 400, 600, 800, and 1,000 meters about each well. The most significant relations between constituent concentrations and land use typically are at radii of 600 or 800 meters. The study area is divided into two subareas (Area I and Area II) to determine if statistical results are similar in each area. The results for all wells are not always the same as the results for Area I and Area II. In most cases, the test results indicate that relations for Area I are more statistically significant than those for Area II.

INTRODUCTION

An objective of the U.S. Geological Survey's Toxic Substances--Ground-Water Contamination Program is to develop and test methods to determine if statistically significant relations exist between the quality of shallow ground water and land use (Helsel and Ragone, 1984, p. 2-3). The purpose of this paper is to summarize three methods of relating ground-water quality to land use. The effect of the land-use-buffer radius around wells on the statistical relation of a nonpoint-source contaminant (nitrate) and a point-source contaminant (purgeable organic compounds) (POC) to land use is evaluated. The study area is divided into two subareas (Area I and Area II) to compare the results of the statistical tests; this comparison provides a test of the transfer value of the land-use methods used in one study area to other areas of similar land use, hydrogeologic, and climatic settings (Helsel and Ragone, 1984, p. 30).

The Coastal Plain of New Jersey (fig. G-5) is underlain by a wedge of unconsolidated

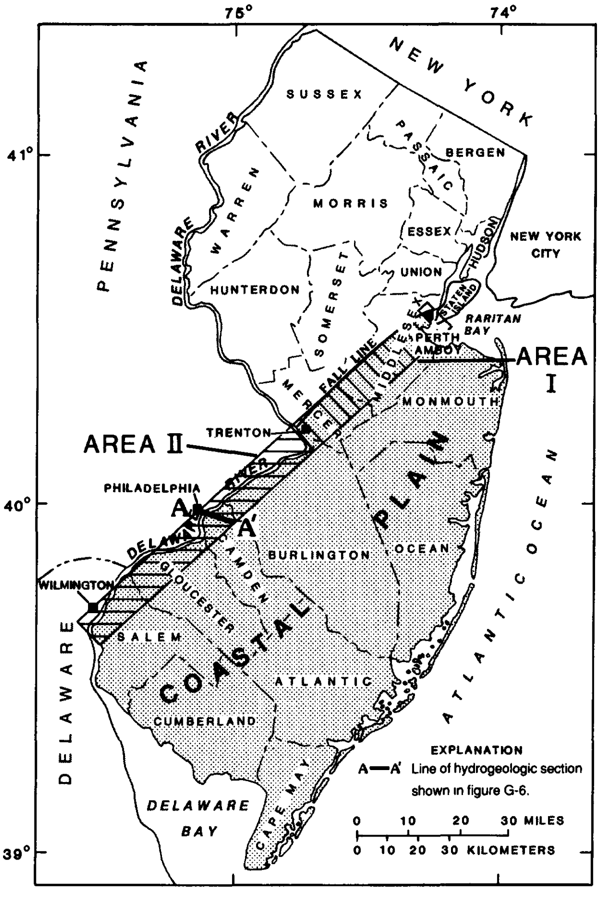

Figure G-5.–Location of the study area and line of hydrogeologic section.

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

sediments consisting of alternating layers of sand, silt, and clay. The Potomac-Raritan-Magothy aquifer system underlies the entire Coastal Plain of New Jersey and is comprised of the Potomac Group and Raritan and Magothy Formations of Cretaceous age (Zapecza, 1984 p. 12-18). The aquifer system consists of three aquifers (upper, middle, and lower) separated by two confining units (fig. G-6). In New Jersey, the aquifer system crops out in a 3- to 6-mile-wide strip of land that extends from Raritan Bay to Delaware Bay. Most of the 314-mi^2 (square mile) outcrop area lies within the industrial corridor between New York and Philadelphia. In 1974, the outcrop area consisted of 32 percent undeveloped land, 23 percent agricultural land, and 45 percent urban land. About 25 percent of the land use is residential, and 5 percent is industrial.

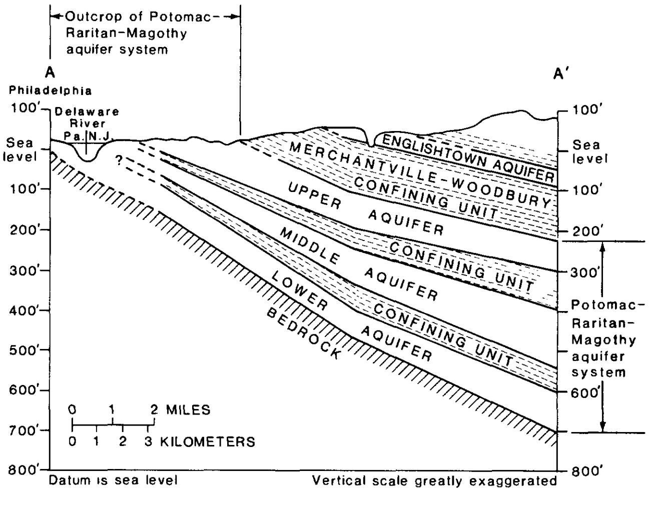

Figure G-6.—Hydrogeologic section A-A'. Line of section shown on figure G-5. Modified from Fusillo and others, 1984, figure 2.

The study area is divided into two regions (fig. G-5) for this analysis. The northern region (Area I) lies within Middlesex and Mercer Counties, and the southern region (Area II) lies along the Delaware River. The ground-water- flow system in Area II is more complex than that in Area I. Ground-water withdrawals in Area II have induced water to flow from the Delaware River into parts of the aquifer system (Leahy and others, 1987).

DATA-BASE DEVELOPMENT

Water samples from 253 wells, located in or near the aquifer system outcrop, were analyzed for field characteristics, major ions, nutrients, metals, and POC (Fusillo and others, 1984; Barton and others, 1987). A stratified subsample of water-quality data from 98 wells was selected for statistical analysis. The criteria used to select these 98 wells were designed to reduce biases related to hydrogeology, well construction (E.F. Vowinkel, and others, U.S. Geological Survey, written commun., 1988), and statistical problems, such as autocorrelation and double accounting (T.H. Barringer, and others, U.S. Geological Survey, written commun., 1988). Factors evaluated in the well-selection criteria included distance between wells, aquifer confinement, and well depth. The subsample consisted of 41 wells in Area I and 57 wells in Area II.

Digital land-use and land-cover data (Fegeas and others, 1983) were used to create polygon coverages in a geographic information system (GIS). Land use is classified into two levels of detail, Level I and Level II, by means of the classification system developed by the U.S. Geological Survey (Anderson and others, 1976). Land-use percentages within circular buffers centered about each well were determined at radii of 1, 100, 250, 400, 600, 800, and 1,000 meters in an attempt to determine the radius that provides the strongest relation between a water-quality constituent and a particlular land-use group.

STATISTICAL METHODS

Nonparametric procedures were used to test for significant differences in constituent concentrations in ground water or land-use percentages because these factors are not normally distributed. The Kruskal-Wallis (KW) test was used to test the null hypothesis (Ho) that all subgroups have similar distributions of concentrations or land-use percentages against the alternative hypothesis (H_1) that some subgroups have different distributions (Helsel and Ragone, 1984 p. 27). If the KW-test statistic (adjusted for ties) meets or exceeds a 0.05 significance level, then the distribution of one or more of the subgroups is considered significantly different from the others. Variations in the KW-test statistic for different radii (figs. G-7-G-9) are evaluated for nitrate and POC. In a previous investigation of data in Area I, a partial correlation statistical method was developed to test the relation of ground-water quality to land use. This method indicated variations in the test result with buffer radius (L.E. Hay, and W.A. Battaglin, U.S. Geological Survey, written commun., 1988). Prior to evaluating the relation of nitrate and POC to land use, the data were evaluated for possible differences in hydrogeologic and well-construction factors among land-use groups. Statistical tests indicate no significant differences in depth to water, well depth, well discharge rate, and use of well among land-use groups.

Method I -- The Predominant Land-Use Method

Each well is classified by predominant land-use class (undeveloped, agricultural, or urban) on the basis of percentage of each class within a buffer. This method assumes that the land use comprising the largest areal extent within a buffer has the greatest effect on the water quality at a well. The H_0 is that nitrate and POC concentrations are similar for the three land-use classes. The H_1 is that one or more classes have different concentrations. This method is useful to evaluate gross differences in ground-water quality among aggregated land-use groups.

The H_0 is accepted for nitrate concentrations at most buffer radii (fig. G-7A). There usually is no significant difference in nitrate concentration in water from wells, regardless of predominant land use. The only exception is in Area I at the 800-meter-buffer radius where nitrate concentrations at wells that are surrounded by predominantly urban or agricultural land are significantly higher than concentrations at wells surrounded by predominantly undeveloped land. At this radius, median nitrate in water from wells surrounded by predominantly agricultural land is 5.5 mg/L (milligrams per liter) compared to 2.5 mg/L and 0.1 mg/L at wells that are surrounded by predominantly urban or undeveloped land, respectively.

The H_0 is accepted for POC concentrations at most buffer radii (fig. G-7B). In general, there is no significant difference in POC concentration among wells in undeveloped, agricultural, or urban land. The lack of significant differences may be a result of the low detection frequency of POC. In Area I, only 4 of 41 (9.8 percent) of the wells had detectable POC compared to 9 of 57 (15.8 percent) of the wells in Area II. Because the

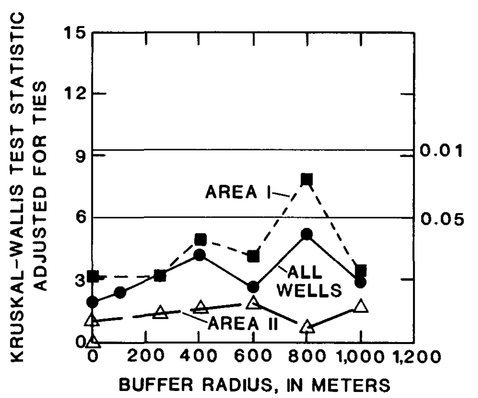

Figure G-7A.—Results of Kruskal-Wallis tests using Method I: nitrate nitrogen as a function of predominant land use.

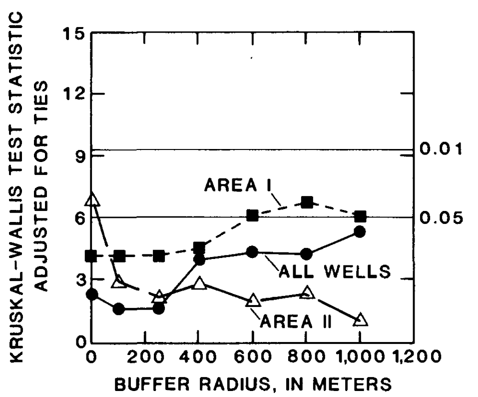

Figure G-7B.—Results of Kruskal-Wallis tests using Method I: purgeable organic compounds as a function of predominant land use.

sample size in Area I is small, comparisons between Areas I and II could be spurious. However, the KW-test results indicate that there is a difference in POC concentrations among the predominant land-use classes at buffer radii of 600, 800, and 1,000 meters in Area I. At these buffer radii, POC concentrations are significantly lower in water from wells that are predominantly surrounded by agricultural land than in wells surrounded by predominantly urban or undeveloped land.

Method II--Present/Absent Land-Use Method

Each well is classified by the presence or absence of a land-use class within a buffer. This method assumes that the presence of a land use within a buffer, regardless of the areal extent, may affect the water quality from that well. This method is useful for evaluating the effects of land uses that do not cover large areas and are rarely the predominant land use.

The H_0 is that nitrate concentrations at wells where undeveloped land is present are similar to nitrate at wells where undeveloped land is absent. The H_1 is that nitrate concentrations are higher where undeveloped land is absent. The H_0 is rejected at most buffer radii (fig. G-8A). At all wells, nitrate concentration is significantly higher in water from wells where undeveloped land is absent compared to those wells where undeveloped land is present. This relation is most significant at a buffer radius of 600 meters. The median nitrate concentration at wells where undeveloped land is absent within a 600 meter buffer is 4.5 mg/L compared to 0.1 mg/L where undeveloped land is present. Areas I and II indicate higher nitrate concentrations where undeveloped land is absent. No significant differences are determined at 1 or 1,000 meter radii.

The H_0 is that POC concentrations at wells where industrial land is present are similar to concentrations at wells where industrial land is absent. The H_0 is that POC concentrations are higher at wells where industrial land is present. The H_0 is rejected at all buffer radii, except 1 meter, for all wells and for Area I (fig. G-8B). POC concentrations are significantly higher in water where industrial land is present than in water where industrial land is absent. In Area II, the H_0 is accepted at all buffer radii.

Method III--Land-Use Percentage Method

The percentage of each land use within every buffer radius was determined for each well. The well can be classified by the occurrence of a constituent below or above a minimum detection limit, water-quality standard, or a specified concentration. This method assumes that the occurrence of a constituent is related to the percentage of a land use within the buffer. This method is useful for evaluating the relation of a

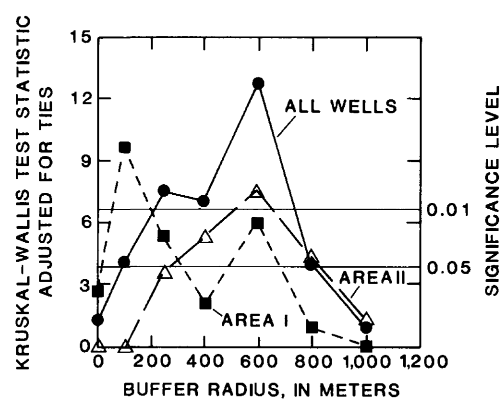

Figure G-8A.—Results of Kruskal-Wallis tests using Method II: nitrate nitrogen as a function of presence/absence of undeveloped land.

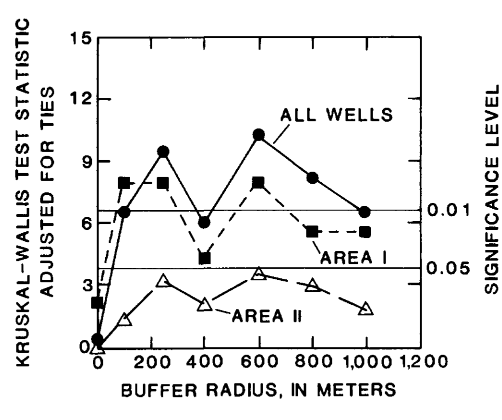

Figure G-8B.—Results of Kruskal-Wallis tests using Method II: purgeable organic compounds as a function of presence/absence industrial land.

land-use class prior to development of logit-regression models that determine the probability of the occurrence of a contaminant based on land use percentages.

The H_0 for nitrate is that the percentage of undeveloped land near wells where the nitrate concentration equals or exceeds 3 mg/L is similar to the percentage of undeveloped land near wells where nitrate is less than 3 mg/L. The H_1 is that the percentage of undeveloped land near wells is lower where nitrate equals or exceeds 3 mg/L. The H_0 is rejected at most buffer radii (fig. G-9A). In most cases, the percentage of undeveloped land near wells where the nitrate concentration equals or exceeds 3 mg/L is lower than the percentage of undeveloped land near wells where nitrate is less than 3 mg/L. No difference in the percentage of undeveloped land occurs at the 1-meter radius for either Area I or Area II. The relation between the occurrence of nitrate concentration equal to exceeding 3 mg/L and the percentage of undeveloped land is most significant at the 600-meter buffer radius for all wells and for Area II. This relation is most significant at the 100-meter buffer radius for Area I.

The H_0 for POC is that the percentage of industrial land near wells where POCs are detected, at concentrations equal to or exceeding 3 ug/L (micrograms per liter), is similar to the percentage of industrial land near wells where POCs are undetected. The H_1 is that the percentage of industrial land is greater where POCs are detected. The H_0 is rejected for all wells and for Area I at all buffer radii except 1 meter (fig. G-9B). The percentage of industrial land use near wells where POC are detected is significantly higher than at wells where the POC are not detected. The relation between the detection of POC and the percentage of industrial land is most significant for all 98 wells and for Area I at the 600-meter buffer radius. The H_0 is accepted for all buffer radii in Area II.

SUMMARY

Three methods were developed and tested to evaluate statistical relations of nitrate and POC to land use on a regional scale by use of water-quality and land-use data from the outcrop of a New Jersey Coastal Plain aquifer system. The statistical tests indicate that the size of the buffer radius around a well used to characterize land use had an effect on whether a hypothesis was accepted or rejected. Significant relations rarely occurred at the 1-meter buffer radius. In most cases, relations of nitrate or POC to land use were most significant at the 600- or 800-meter buffer radii.

The predominant land-use method generally did not indicate significant relations of nitrate or

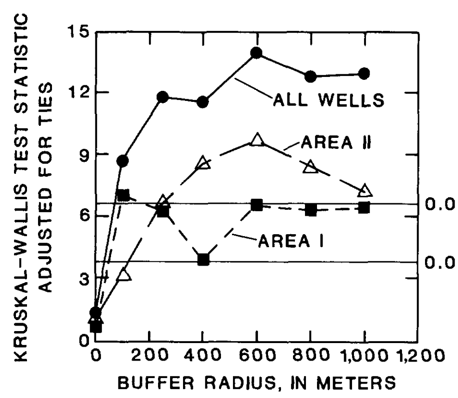

Figure G-9A.—Results of Kruskal-Wallis tests using Method III: nitrate nitrogen equal to or greater than 3 micrograms per liter as a function of percentage of undeveloped land.

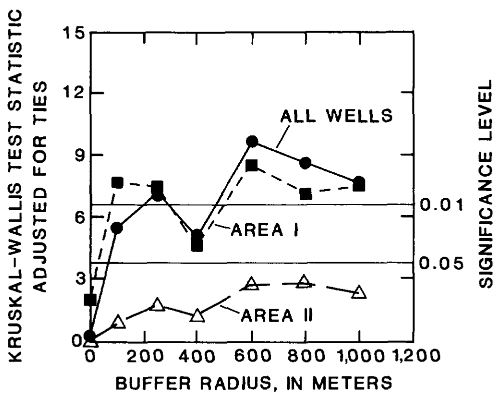

Figure G-9B.—Results of Kruskal-Wallis tests using Method III: purgeable organic compounds equal to or greater than 3 micrograms per liter as a function of percentage of industrial land.

POC to land use. The predominant land use within a buffer may not always be the most influential land use affecting water quality at a well. The present-absent land-use method indicates significant relations of nitrate and POC to land use at several buffer radii. This method is useful in evaluating the effect of a land use that is rarely predominant, such as industrial land use. The land-use percentage method indicates differences in the percentage of a land use near wells where nitrate or POC were detected compared to wells where nitrate or POC were not detected. This method is useful for making predictions of the probability of occurrence of a constituent in the ground water based on local and regional land use.

These statistical analyses indicate that the scale or size of the area used to evaluate relations of ground-water quality to land use can affect whether the hypothesis is accepted or rejected. The results for all wells were not always the same as the results for Area I and Area II. In most cases, the test results indicate that the relation of nitrate or POC to land use are more significant for Area I than for Area II. These differences may be related to the more complex hydrogeology of Area II compared to Area I and the influence of the Delaware River on the aquifer system in Area II.

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OVERVIEW OF THE RELATIONS OF NONPOINT-SOURCE AGRICULTURAL CHEMICAL CONTAMINATION TO LOCAL HYDROGEOLOGIC, SOIL, LAND-USE, AND HYDROCHEMICAL CHARACTERISTICS OF THE HIGH PLAINS AQUIFER OF NEBRASKA

By A. Douglas Druliner[1]

ABSTRACT

Concentrations of nitrate higher than the U.S. Environmental Protection Agency's 10 milligrams per liter standard for drinking water and detectable concentrations of atrazine herbicide have been found in ground water in many areas of the High Plains aquifer of Nebraska. The concentrations of these contaminants depend on local hydrogeologic, soil, land use, and prevailing hydrochemical characteristics. Scatter plots and statistical analyses of many of these explanatory variables as functions of nitrate and atrazine concentrations in ground water have revealed relations that may be useful in predicting areas susceptible to ground-water contamination by agricultural chemicals.

Multiple linear-regression techniques were used to determine the relative significance of 22 and 24 explanatory variables to concentrations of nitrate and atrazine in ground water, respectively. Specific conductance, average hydraulic conductivity of the unsaturated zone, and the clay content of the soil, together accounted for the largest variations in the nitrate concentrations in ground water. Average hydraulic conductivity of the unsaturated zone, specific conductance, irrigation-well density, herbicide-application date, average screened well depth, and depth to water, together accounted for the largest variations in atrazine concentration in ground water.

INTRODUCTION

This study discusses contamination of ground water by nitrogen fertilizers and by pesticides in the High Plains aquifer of Nebraska in terms of hydrogeology, climate, soils, land-use, and hydrochemical characteristics. It was one of 14 nonpoint-source areas in the U.S. Geological Survey's Toxic Waste--Ground-Water Contamination Program (Helsel and Ragone, 1984).

The objectives of the study are (1) to determine the extent of ground-water contamination by selected agricultural chemicals in Nebraska and (2) to produce mathematical models that represent the physical and chemical relations of identified explanatory variables to the distribution of ground-water contamination from agricultural chemicals within the High Plains aquifer of Nebraska. These models then could be used to predict areas of potential ground-water contamination from selected agricultural chemicals on a local basis.

The purposes of this paper are (1) to describe apparent relations between concentrations of nitrate fertilizer and pesticides in ground water with selected explanatory variables, and (2) to present preliminary multiple-regression equations that relate concentrations of nitrate and atrazine to the explanatory variables.

APPROACH

Twenty-one variables relating to the hydrology, climate, soil, and land-use characteristics of the study area were selected (Chen and Druliner, 1986). As the study progressed, variables were added and existing ones were modified. Table G-1 lists the explanatory variables that have been and are being investigated.

Six areas encompassing 12 counties in Nebraska were selected for study (fig. G-10) to provide a wide range of values for the explanatory variables and to take advantage of those areas for which some data were available concerning contamination of ground water by agricultural chemicals. Because few data were available for pesticides in ground water for most areas of the State, ground-water samples were collected from private irrigation, domestic, and stock wells, and from public wells during the summers of 1984,

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[1] U.S. Geological Survey, Lincoln, Nebr.

Table G-1.-*Explanatory variables suspected of affecting concentrations of nitrate and atrazine in ground water*

Hydrogeologic

- Hydraulic gradient [1]
- Specific discharge [1]
- Specific yield [1]
- Rate of flow
- Average hydraulic conductivity:
  - Unsaturated zone [2,3]
  - Saturated zone [2,3]
  - Total [1,2,3]
- Clay thickness
  - Unsaturated zone [2,3]
  - Saturated zone [2,3]
- Well depth [1,2,3]
- Average screened well depth [2,3]
- Depth to water [1,2,3]
- Precipitation recharge [4]

Land Use

- Irrigation well density [1,2,3]
- Nitrogen application rate [2]
- Acres of irrigated land in
  - 1 square mile area [2,3]
  - 4 square mile area [2,3]
- Herbicide application rate [3]
- Date of pesticide application [3]
- Date of nitrogen application [2]
- Date of irrigation commencement [2,3]
- Time lapsed between
  - Pesticide application & irrigation [3]
  - Pesticide application & sampling [3]
  - Irrigation commencement & sampling [2,3]
  - Nitrogen application & sampling [4]
  - Nitrogen application & irrigation commencement [4]

Climatic

- Annual precipitation [1]
- Evapotranspiration [4]
- Mean annual temperature [1]
- Seasonal precipitation [4]

Geomorphic

- Drainage area [1]
- Drainage density [1]

Soil

- Average water capacity [4]
- Organic matter [4]
- Permeability [1,2,3]
- Percent clay [2,3]
- Percent surface slope [1,2,3]
- pH [2,3]
- Water content [4]

Hydrochemical

- Dissolved oxygen [4]
- pH [2,3]
- Specific conductance [2,3]
- Temperature [2,3]
- Total organic carbon [4]

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[1] Indicates variables that were investigated during the initial phase of the study.

[2] Indicates variables that were investigated in the second phase of the study and were used to produce the regression models with nitrogen as the dependent variable.

[3] Indicates variables that were investigated in the second phase of the study and were used to produce regression models with atrazine as the dependent variable.

[4] Indicates variables that are presently being investigated.

1985, and 1987. These samples were analyzed for nitrite plus nitrate, hereafter referred to as nitrate and reported as total nitrogen, and a variety of pesticides. Data quantifying each of the explanatory variables were collected for each of the sample sites.

Nitrate, an oxidized derivative of anhydrous ammonia and urea-ammonium nitrate fertilizers and atrazine, a triazine herbicide used for control of broadleaf weeds in corn and sorghum, were the most commonly detected contaminants in the ground-water samples; accordingly, they were selected as the dependent variables. Scatter plots and correlations of the dependent variables with each explanatory variable were produced. A variety of multiple-linear-regression techniques, which included Step-wise and R-square (SAS Institute, Inc., 1982), were used to determine the combined influences of significant explanatory variables.

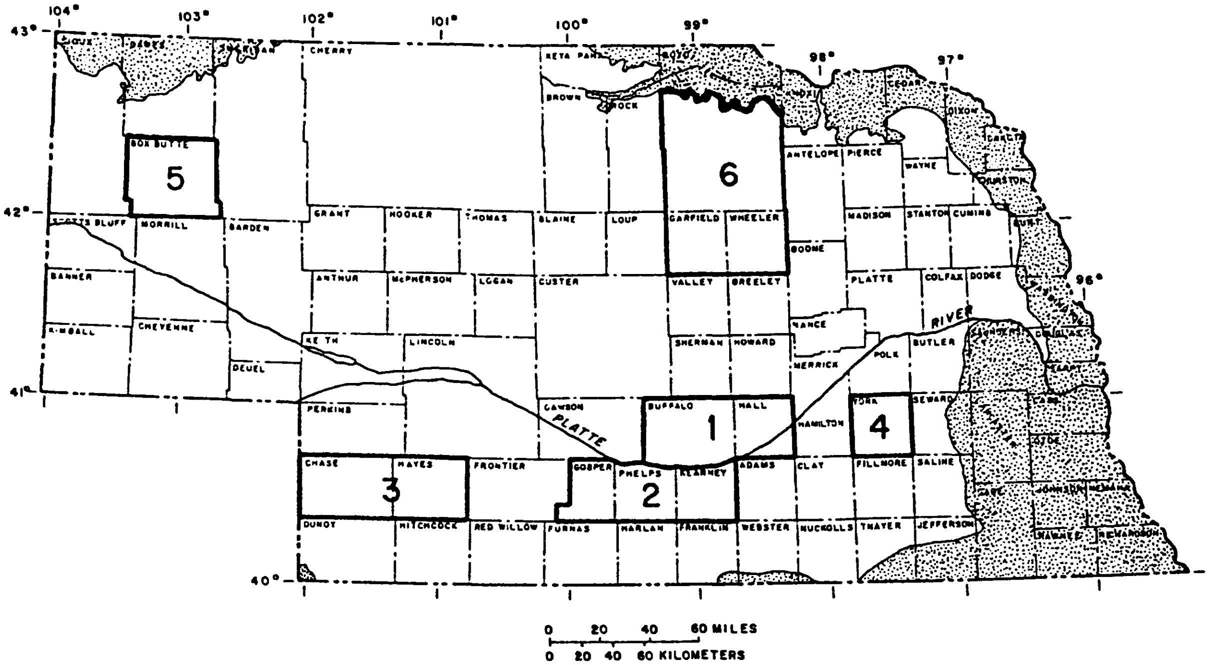
Hydrogeology

The six study areas are located in the Nebraska part of the High Plains aquifer (fig. G-10). The High Plains aquifer is a water-table aquifer system composed of hydraulically connected Tertiary and Quaternary silts, sands, and gravels that underlie 65,000 mi^2 (square miles) of the State. The potentiometric surface of the aquifer slopes gently to the east, and the estimated average rate of ground-water flow in the study areas is about 0.4 ft/d (foot per day). The saturated thickness in the study areas ranges from 100 to greater than 600 feet, and the depth to water in sampled wells ranges from less than 20 feet to 250 feet. The average hydraulic conductivity of the aquifer system based on ground-water sampling sites used in this study ranges from 5 to greater than 700 ft/d with a median of 37 ft/d.

Recharge to the aquifer system in the six study areas occurs primarily through the percolation of precipitation, mostly in the upland areas. This is supplemented by irrigation return flows, seasonal river and stream recharge, and canal leakage. Discharge occurs principally through irrigation-well pumpage, and evapotranspiration.

Soils

Water samples were collected from wells at sites characterized by a variety of soil types. These soils range from clayey to sandy in texture and have permeabilities of 0.67 to 12.0 in/h (inches per hour). The clay content of the soils usually is 18 to 25 percent, and the soil slope of the sampled sites commonly is less than 3 percent. The organic-carbon content of the topsoil at sampling



EXPLANATION

☐ HIGH PLAINS AQUIFER

▨ HIGH PLAINS AQUIFER NOT PRESENT

1	BUFFALO AND HALL COUNTIES
2	GOSPER, PHELPS, AND KEARNEY COUNTIES
3	CHASE AND HAYES COUNTIES
4	YORK COUNTY
5	BOX BUTTE COUNTY
6	GARFIELD AND WHEELER COUNTIES AND PART OF HOLT COUNTY

Figure G-10.—Extent of High Plains aquifer and location of the six study areas.

sites ranged from 0.22 to 3.38 percent, with a median of 1.34 percent. The median soil pH was 6.70.

Land Use

An average of 94 percent of the surface area of the six study areas is classified as agricultural, and corn is the dominant crop in all areas except area 5. More chemicals are used on corn fields than any other major crop grown in the State. Nitrogen fertilizer and atrazine herbicide are the two most heavily used chemicals in the study areas. Most farmers interviewed apply about 200 lb (pounds) of total nitrogen and 2 to 3 lb of atrazine per acre per year of corn production. Most of the nitrogen is applied as anhydrous ammonia prior to planting in the spring, and the herbicides are frequently applied during planting.

SELECTED PRELIMINARY RESULTS

Of the various compounds analyzed, only nitrate and atrazine were detected in enough samples to permit the use of correlation and regression to establish possible relations among these compounds with the explanatory variables (table G-2). Results of these analyses indicate that some explanatory variables are closely related to nitrate and atrazine concentrations in ground water in the study areas.

Correlation Analysis

Nitrate and atrazine concentrations were plotted as functions of each of the explanatory variables, and Lowess, a locally weighted scatterplot-smoothing technique (Cleveland, 1979), was used to highlight patterns in the data. Spearman's rho, which is a ranked correlation technique, was used to compare the strengths of relations among the dependent variables and the explanatory variables, because most of the variable pairs (dependent and explanatory variables) displayed monotonic rather than linear relations and because outliers were present in most variable pairs.

Total average hydraulic conductivity, which is a measure of local aquifer permeability from the land surface to the maximum screened depth of the sampled well, had a positive correlation with nitrate concentrations and with atrazine concentrations in the ground water (fig. G-11). Concentrations of nitrate appeared to increase uniformly as the total average hydraulic conductivities increase. Also, the frequency of detection for atrazine tended to be higher in water samples from wells where total average hydraulic conductivities exceeded 80 ft/d than in water samples from wells where average hydraulic conductivities were lower.

Concentrations of nitrate and atrazine in ground water generally decreased with increased depth as indicated by Spearman's ρ of -0.46 and -0.62 for nitrate and atrazine, respectively (fig. G-12). Eighty-three percent of the concentrations of nitrate in ground water that exceeded the U.S. Environmental Protection Agency's (USEPA) primary drinking water regulation of 10 mg/L (milligrams per liter) (U.S. Environmental Protection Agency, 1986) were in samples from wells less than 150 feet deep. Furthermore, nitrate was detected in water from wells greater than 400 feet deep. Water samples from these deeper wells usually contained less than 5 mg/L of nitrate and may represent background conditions in some areas or possible mixing of shallow and deep water from wells with multilevel screens. By comparison, most of the detectable concentrations of atrazine in ground water were from wells less than 80 feet deep. Only two water samples from wells greater than 200 feet deep contained detectable atrazine.

Depth to water of a sampled well is the distance from the land surface to the water table. Although depth to water is related to well depth (Spearman's $\rho = 0.69$), depth to water is a potentially important explanatory variable because it indicates the distance that contaminants must travel to reach the saturated zone. The relation between depth to water and nitrate and atrazine concentrations had Spearman's ρ of -0.39 and -0.60, respectively (fig. G- 13). Eighty-eight percent of the water samples that contained concentrations of nitrate greater than 10 mg/L were from sites where depths to water were less than 50 feet, although concentrations of nitrate in excess of 10 mg/L were detected in some water samples from wells where depths to water were 50 to 110 feet. Similarly, 76 percent of the water samples

Table G-2.—*Statistical summary of atrazine concentration, nitrate concentration, and selected explanatory variables associated with water samples from the High Plains aquifer of Nebraska*

Variable	Number	Detection limit	Number detected	Mean	Minimum	25th percentile	50th percentile	75th percentile	Maximum
Nitrate[1]	240	0.01	238	8.38	0.10	2.00	4.25	9.98	57.00
Atrazine[2, 3]	159	.02	94	.03	.0002	.0025	.03	.40	6.26
Total average hydraulic conductivity[4]	157	--.[12]	--	56.6	5	22	34	73	709
Well depth[5]	238	--	--	182	20	93	170	251	550
Average depth to water[6]	232	--	--	67	1.5	23	47	96	270
Percent clay	78	--	--	20.3	4.17	18.97	21.08	24.50	31.0
Irrigation well density[7]	158	--	--	4	0	2	3	5	12
Number of irrigated acres per 4-square miles[8]	78	--	--	1,670	40	1,176	1,715	2,223	2,560
Herbicide application date[9]	77	--	--	123	105	115	124	130	170
Dissolved oxygen[10]	36	--	--	6.42	0.27	4.73	6.69	9.38	10.55
pH	240	--	--	7.08	6.20	6.90	7.10	7.30	8.30
Specific conductance[11]	238	--	--	710	78	384	606	937	2,380

[1] In milligrams per liter
[2] Estimated atrazine concentrations using Helsel and Gilliom, 1985
[3] In micrograms per liter
[4] In feet per day
[5] In feet
[6] In feet
[7] In active irrigation wells per square mile
[8] In acres
[9] In Julian days
[10] In milligrams per liter
[11] In microseimens per centimeter at 25 degrees Celsius
[12] Not applicable

with detectable concentrations of atrazine were from sites where depths to water were less than 40 feet.

Concentrations of nitrate and of atrazine in ground water also appear to be related to irrigation-well density, which is the number of active irrigation wells in 1 mi^2 of the sampled well (fig. G-14). When median concentrations of nitrate and atrazine were calculated for each irrigation-well-density value and correlated with those values, Spearman's ρ of 0.87 and 0.82, respectively, were obtained.

A more direct measure of agricultural land use is the number of estimated irrigated acres in each block of 4 mi^2 containing a sampled water well. This estimation is based on a compilation of acreages intended for irrigation at the time each irrigation well was drilled.

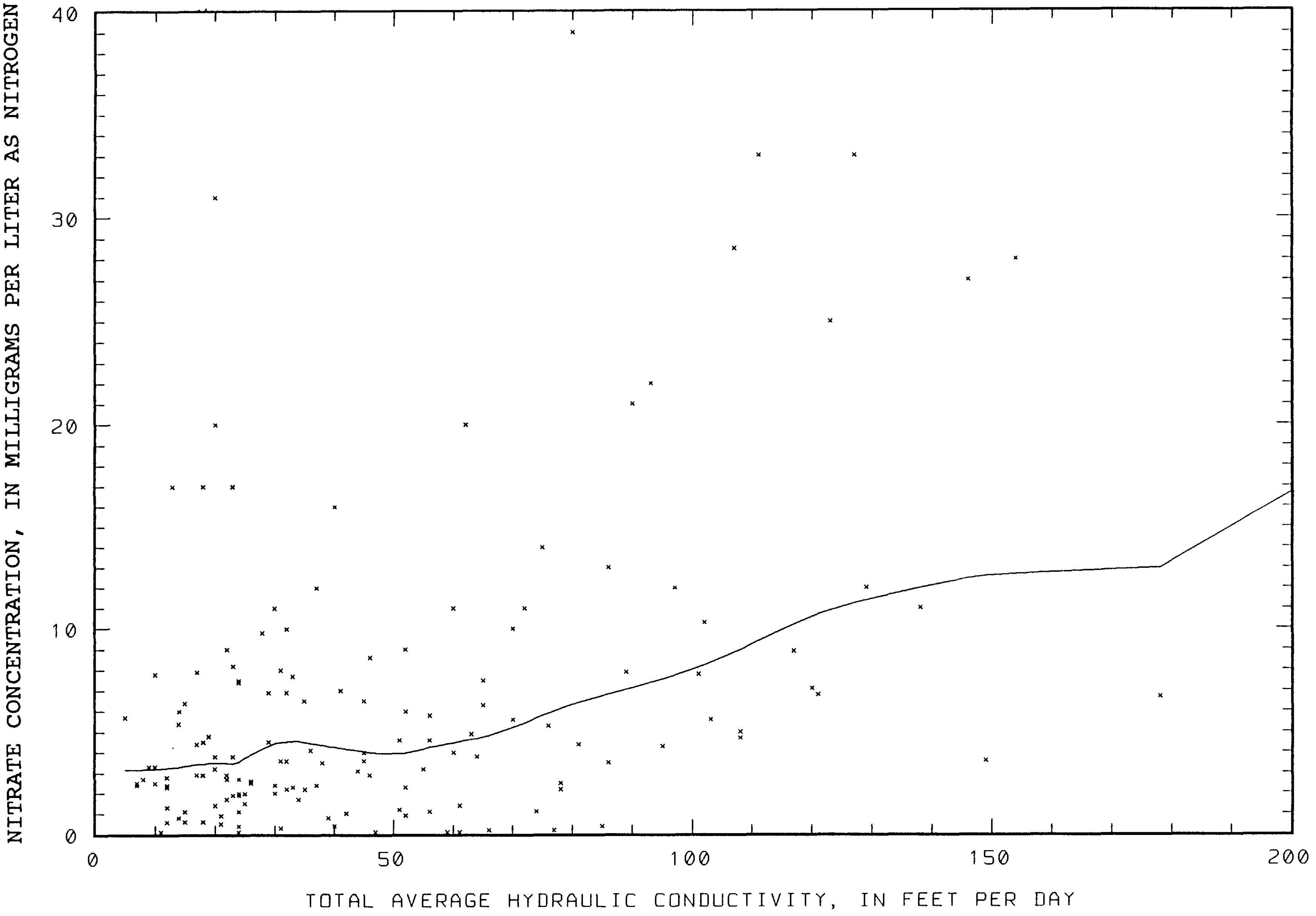


Figure G-11A.–Relation between nitrate concentration and average hydraulic conductivity in water from the High Plains aquifer of Nebraska.

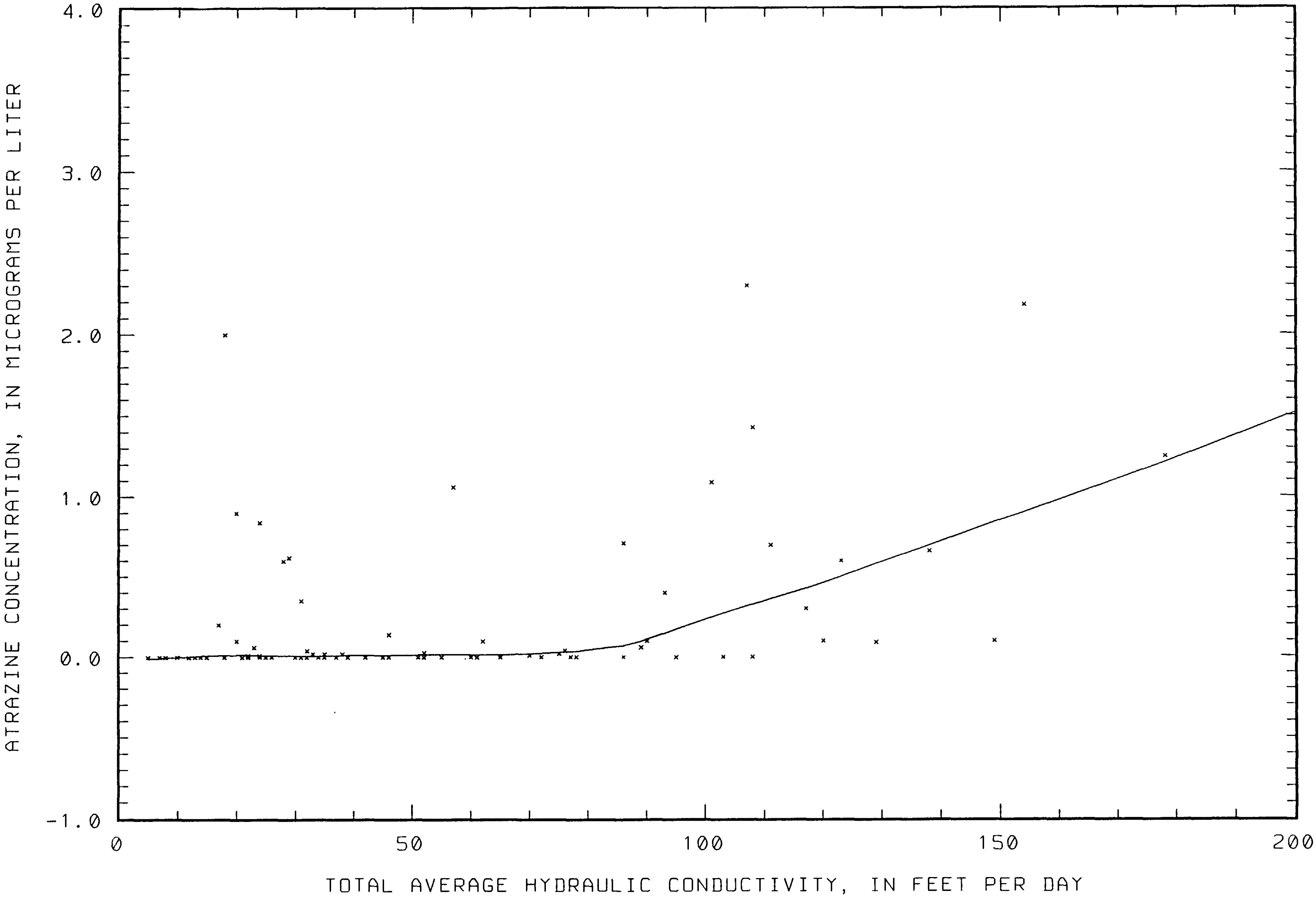


Figure G-11B.–Relation between atrazine concentration and average hydraulic conductivity in water from the High Plains aquifer of Nebraska.

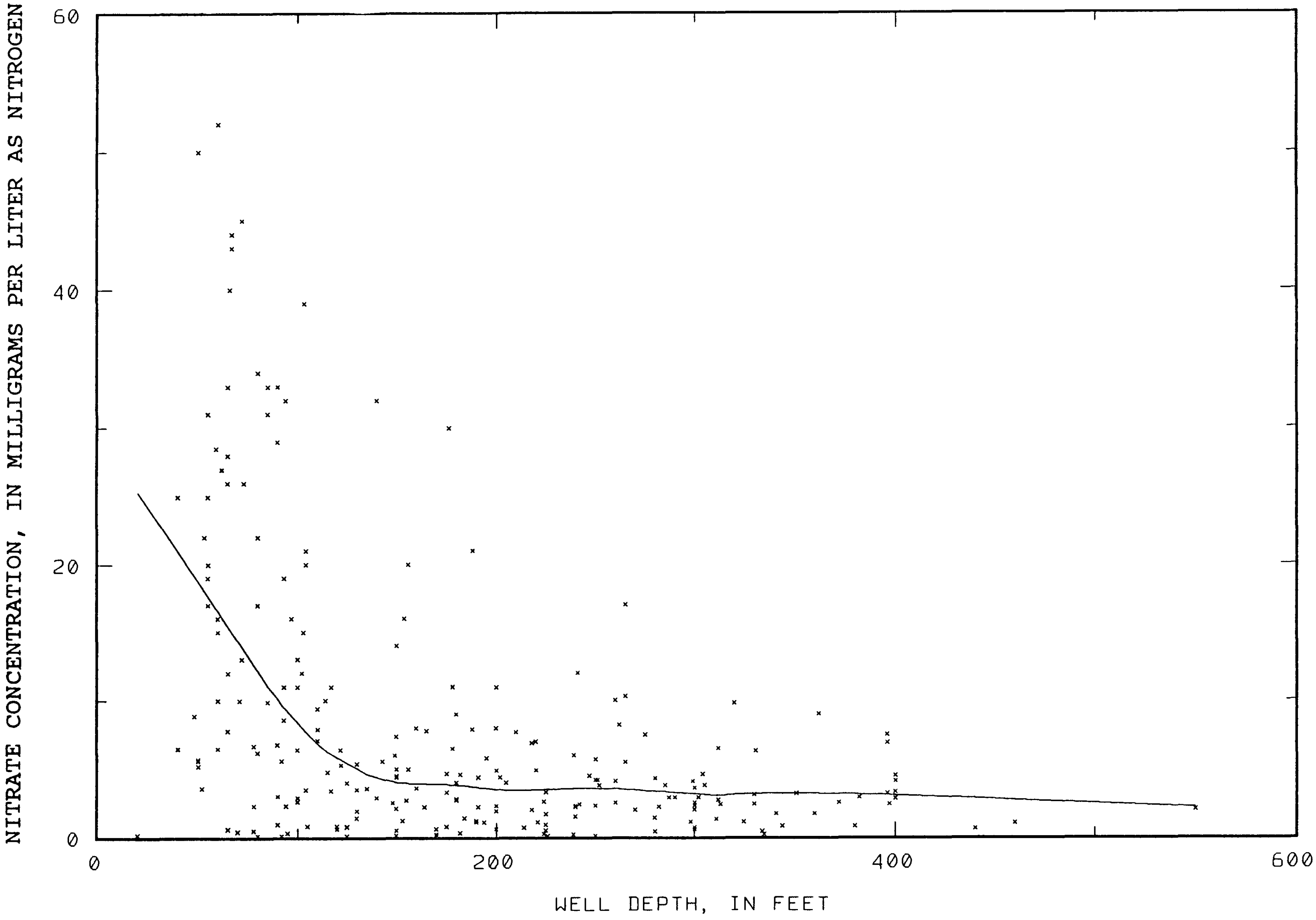


Figure G-12A.—Relation between nitrate concentration and well depth of water samples from the High Plains aquifer of Nebraska.

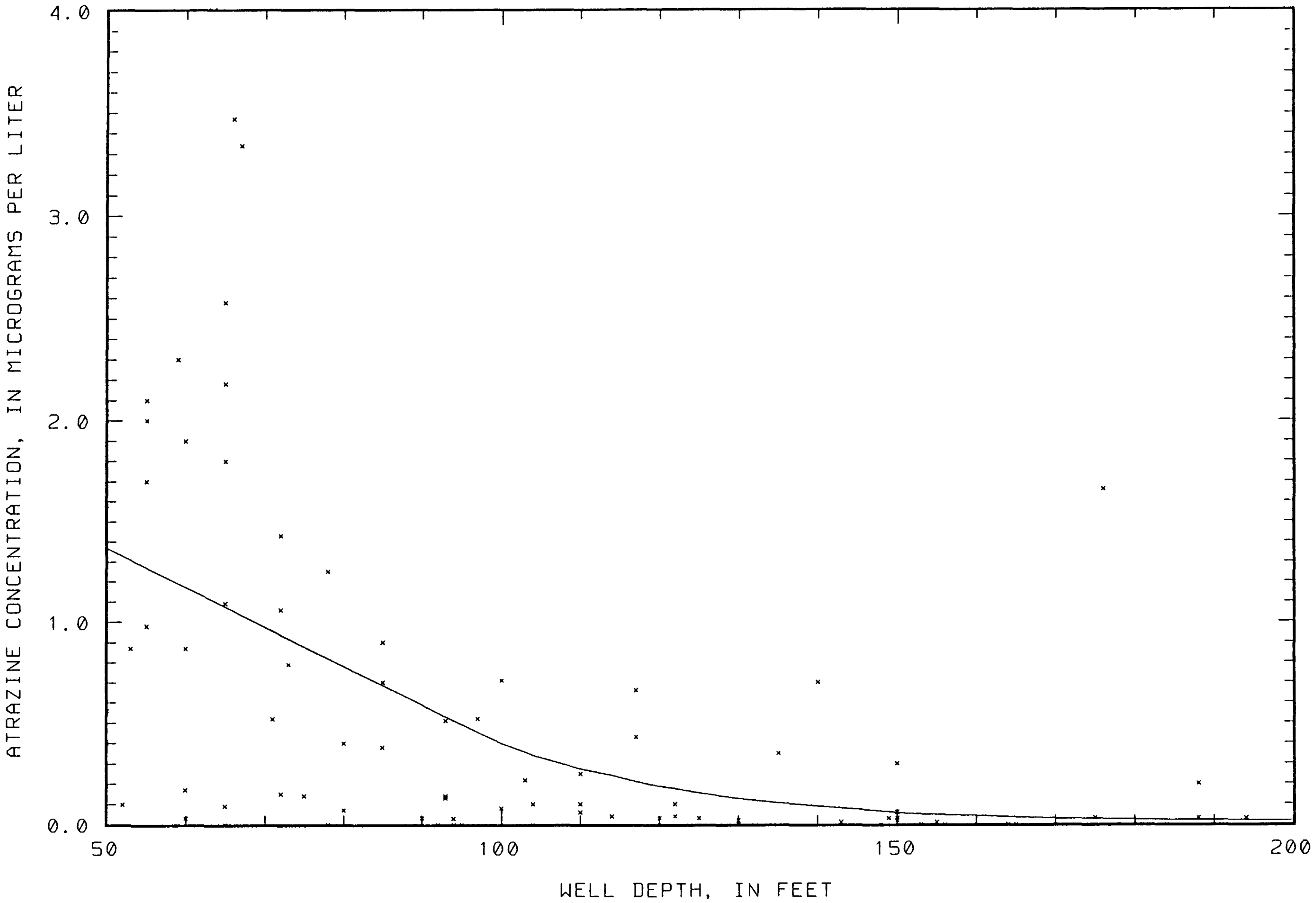


Figure G-12B. –Relation between atrazine concentration and well depth of water samples from the High Plains aquifer of Nebraska.

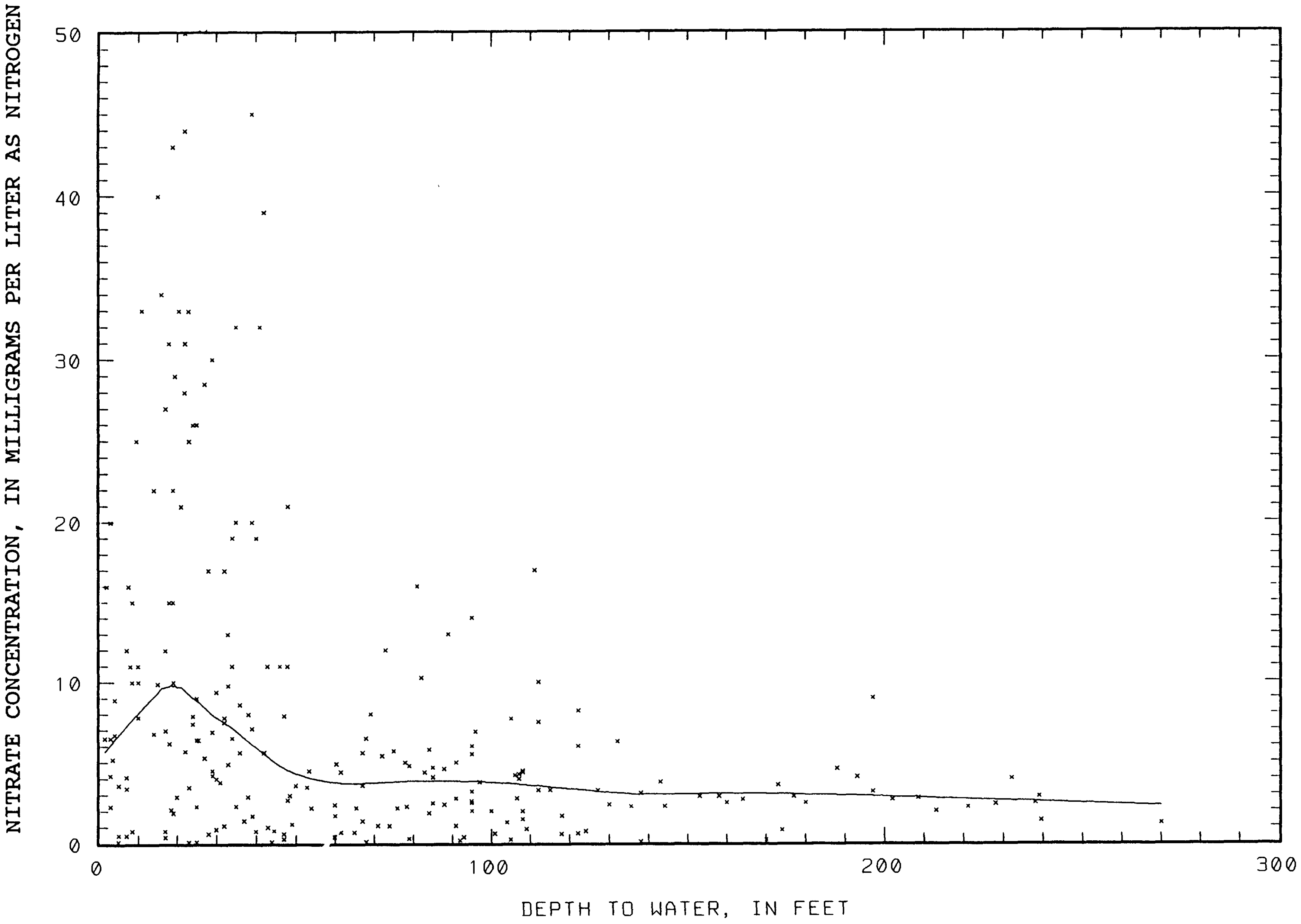


Figure G-13A. –Relation between nitrate concentration and depth to water for water samples from the High Plains aquifer of Nebraska.

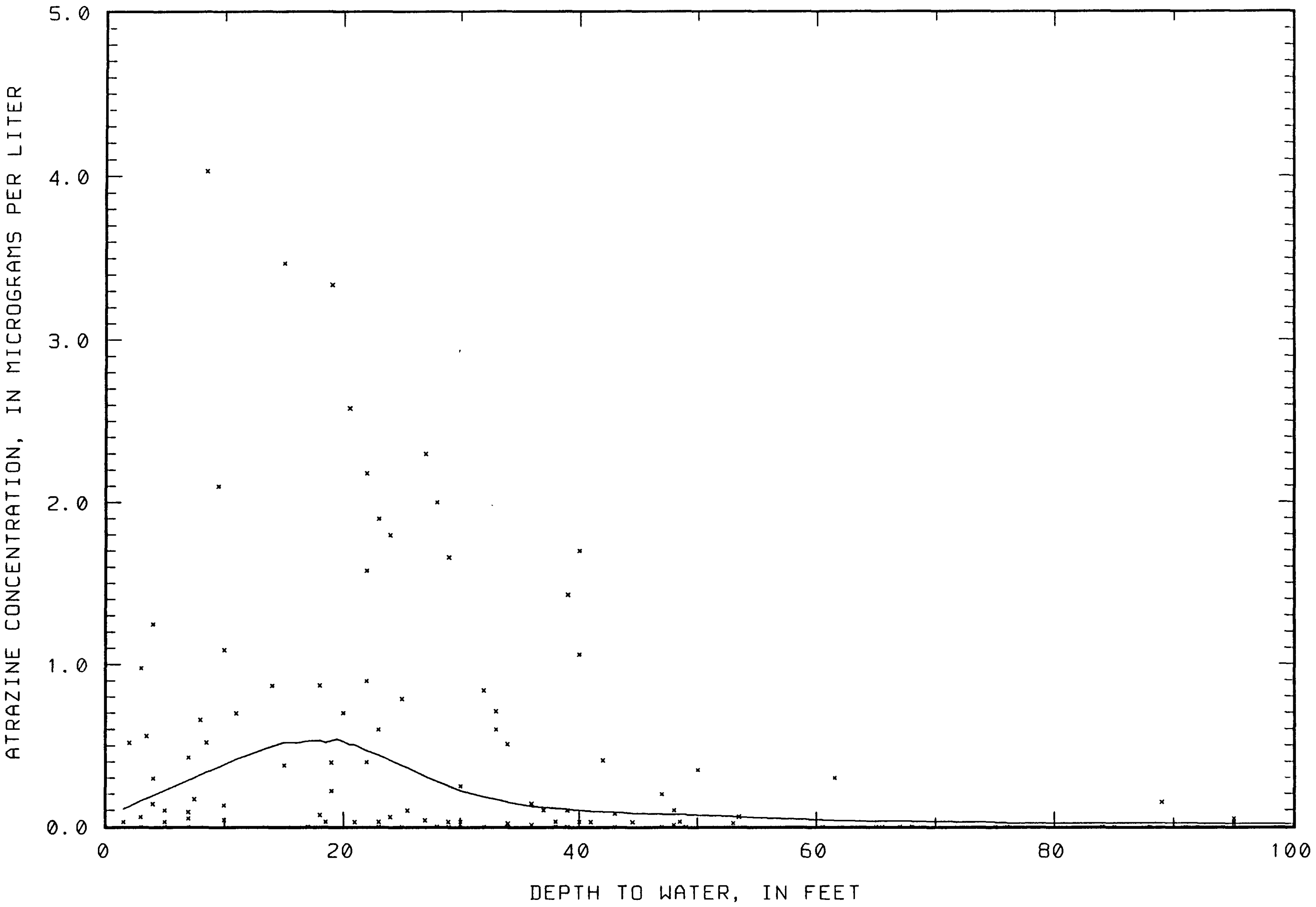


Figure G-13B. –Relation between atrazine concentration and depth to water for water samples from the High Plains aquifer of Nebraska.

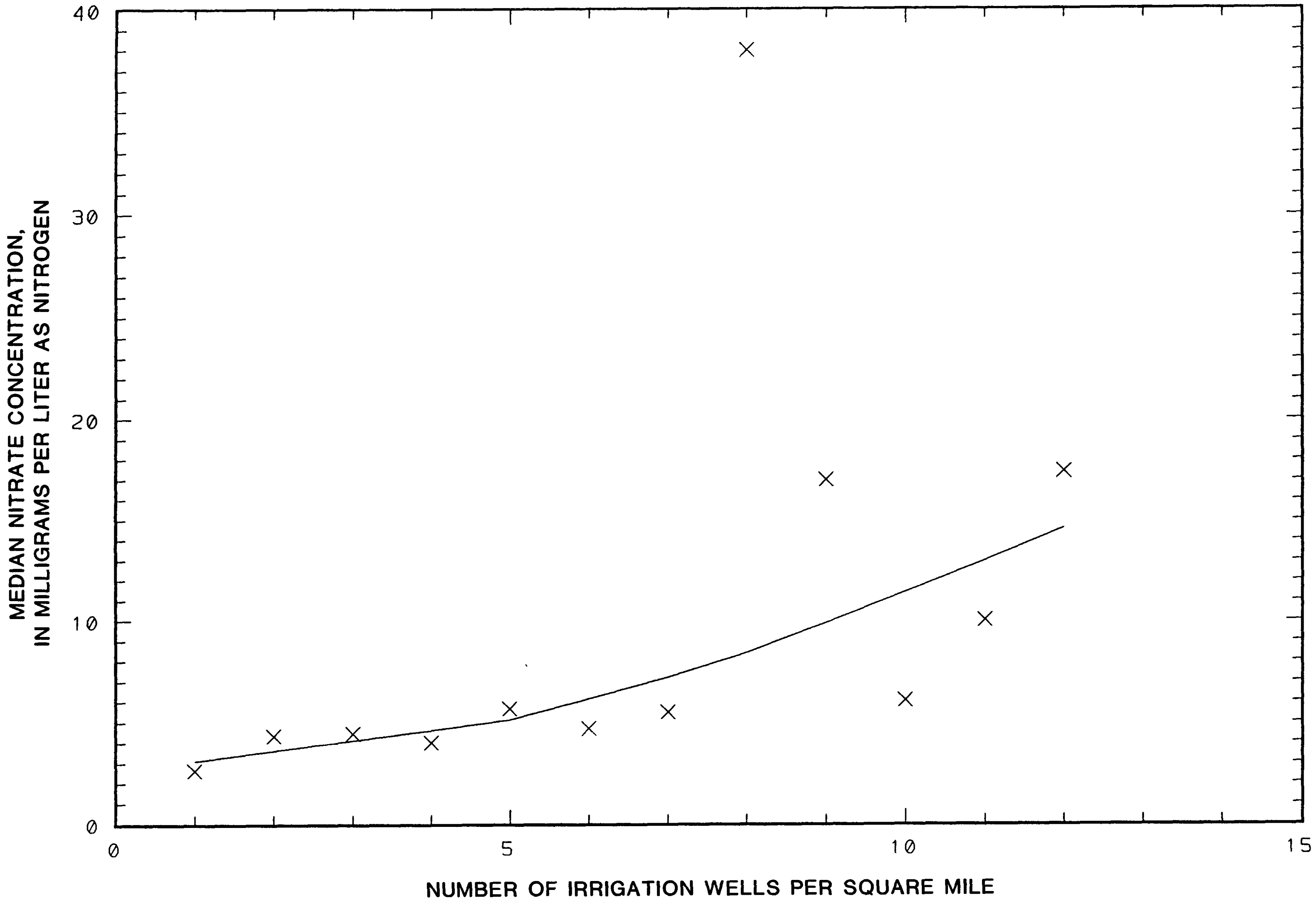


Figure G-14A. –Relation between median nitrate concentration and irrigation well density for water samples from the High Plains aquifer of Nebraska.

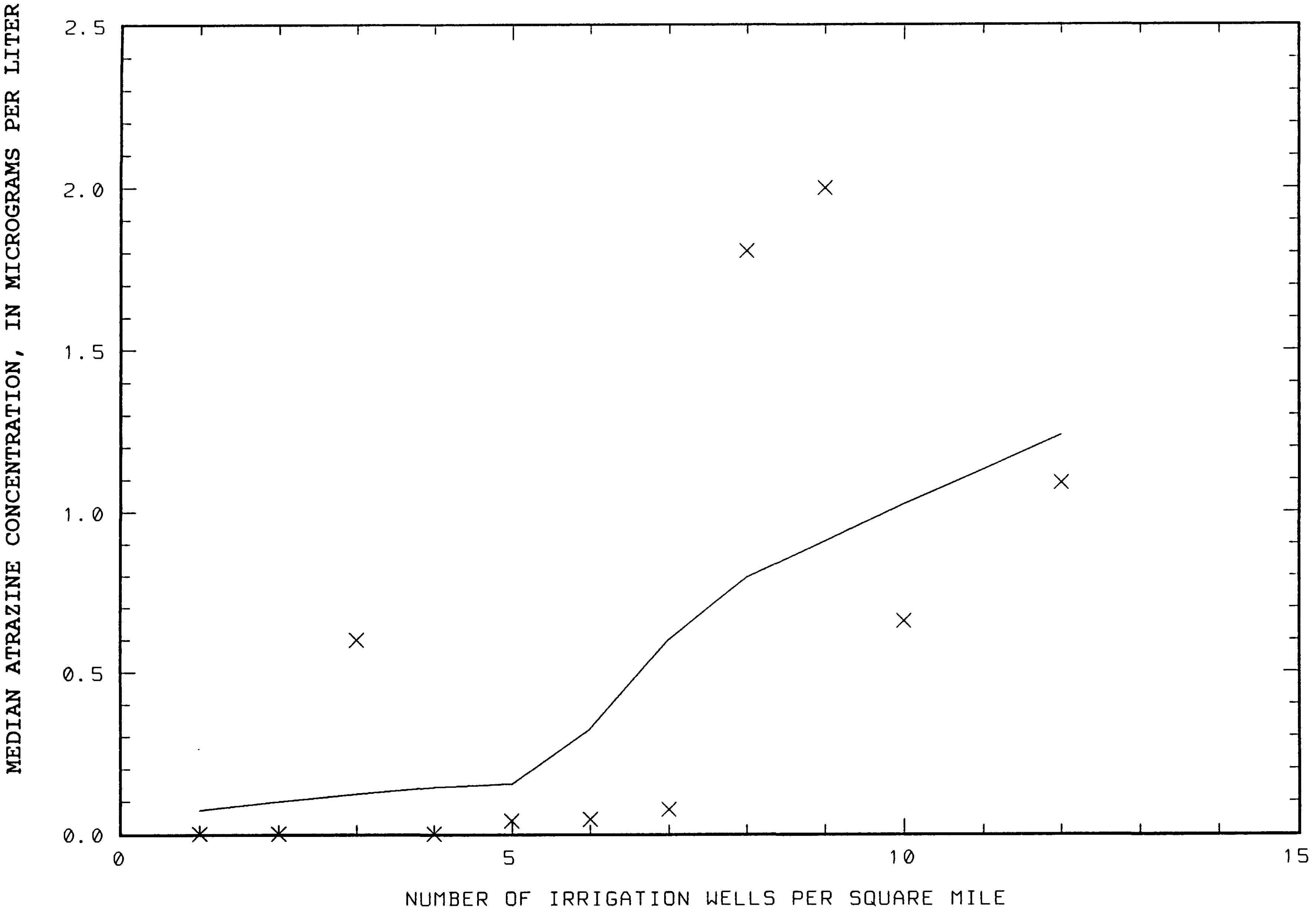


Figure G-14B.—Relation between median atrazine concentration and irrigation well density for water samples from the High Plains aquifer of Nebraska.

The results indicate that nitrate and atrazine concentrations increased with increasing estimated irrigated acreages per 4-square-mile block (fig. G-15).

Nitrate and atrazine concentrations were plotted and correlated with one another (fig. G-16). This analysis yielded a Spearman's rho of 0.70, which suggests that nitrate concentrations in ground water may be an appropriate surrogate for atrazine concentrations. This relation may be valuable for predicting potential contamination of ground water with atrazine for relatively large areas where nitrate analyses are available.

Dissolved-oxygen (DO) concentration was determined in samples collected from selected observation wells in area 1 during 1987. DO concentrations had a Spearman's rho of 0.70 with nitrate concentrations and -0.80 with atrazine concentrations (fig. G-17). The direct (positive) correlation between concentrations of nitrate and dissolved oxygen probably is related to the oxidation-reduction potential of the water. As ground-water conditions become more reducing, free oxygen is consumed and nitrate is reduced to other nitrogen forms. The inverse (negative) correlation between concentrations of dissolved oxygen and atrazine indicates that the presence of free oxygen facilitates the degradation of atrazine. In areas in which oxygen is limited, such as at depth below the water table, the rate of atrazine degradation may be reduced.

Specific conductance correlated positively with both nitrate and atrazine concentrations (fig. G-18). Nitrate concentration and specific conductance yielded a Spearman's rho of 0.45 and atrazine concentration and specific conductance yielded a Spearman's rho of 0.49. Assuming that specific conductance is a measure of nitrate concentration superimposed on the naturally occurring dissolved solids, specific conductance could be a useful indicator of nitrate contamination in aquifer systems with reasonably uniform specific conductance. Because of the wide variation in specific-conductance values found in ground-water samples in the study areas, specific conductance probably is not a reliable predictor of nitrate contamination.

Regression Analysis

Data in table G-1 representing 21 to 22 and 22 to 24 of the explanatory variables were related to nitrate and atrazine concentrations, respectively, in ground water collected at sites visited in the second phase of the study through the use of multiple-linear-regression techniques. The R-square program (SAS Institute, Inc., 1982) was used to select the best possible 1 to 12 variable models from all possible variable combinations. Minitab[2] (Ryan and others, 1985) was used to test the significance of explanatory variable combinations for each of the models. Explanatory variables were excluded from the models when the T-ratio (the fitted slope coefficient divided by its standard error) for that variable was less than 2.00, which indicated that the regression coefficient was not significantly different from zero at the 95-percent-confidence level.

Two models with nitrate concentration as the dependent variable (table G-3, models A-B) and three regression models with atrazine concentration as the dependent variable (table G-3, models A-C) were generated. The models were produced by intentionally excluding from one to three explanatory variables prior to running the regression programs. Explanatory variables were excluded to examine the influences of less highly correlated explanatory variables that were not significant when the more highly correlated variables were used. Additionally, well depth was excluded from the models because it was highly correlated with average screened well depth and violated the assumption of explanatory variable independence. Those explanatory variables intentionally excluded from the regressions are listed for each model in table G-3.

A total of 3 to 6 explanatory variables possessed T-ratios larger than 2.00 and are included in the 5 models presented, although from 21 to 24 explanatory variables were used to generate the models. The explanatory variables that were used frequently and explained the most variation in the dependent variables (that is, exhibited the largest R-squared value) were average hydraulic conductivity of the unsaturated zone, specific conductance, irrigation-well density, depth to water, and average screened well depth.

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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.

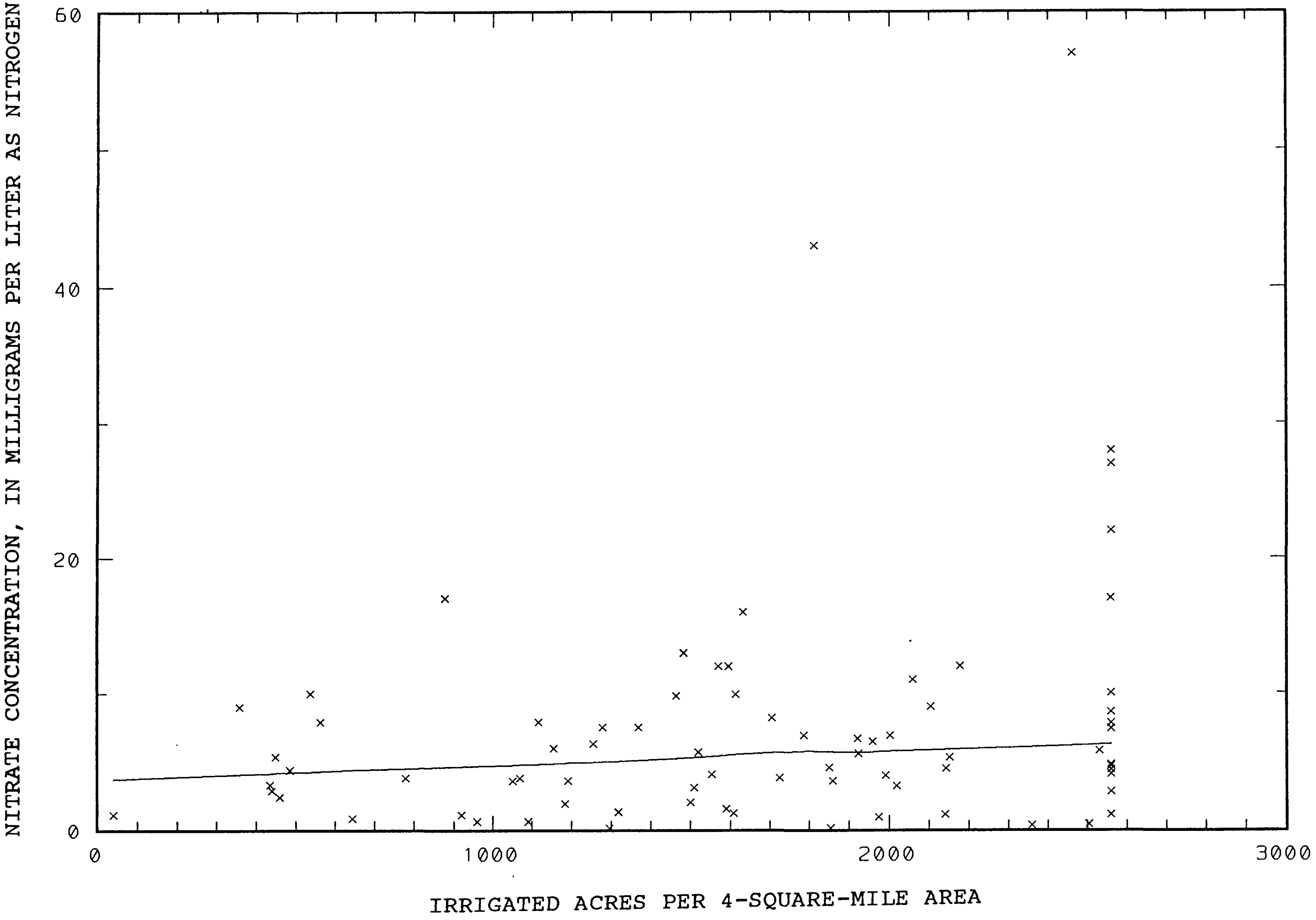

Figure G-15A. –Relation between nitrate concentration and the number of irrigated acres per 4-square-mile area in the High Plains aquifer of Nebraska.

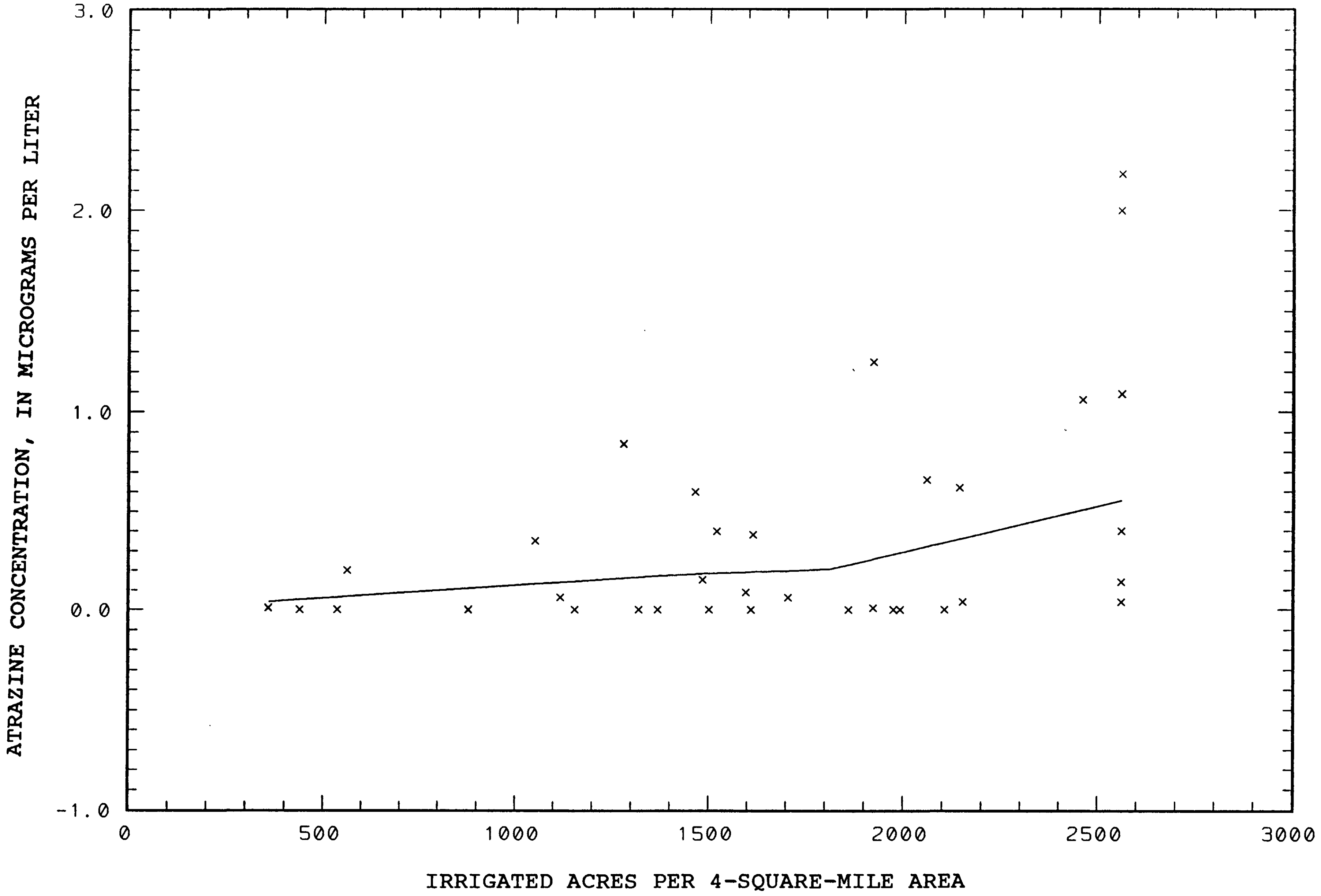

Figure G-15B.-Relation between atrazine concentration and the number of irrigated acres per 4-square-mile area in the High Plains aquifer of Nebraska.

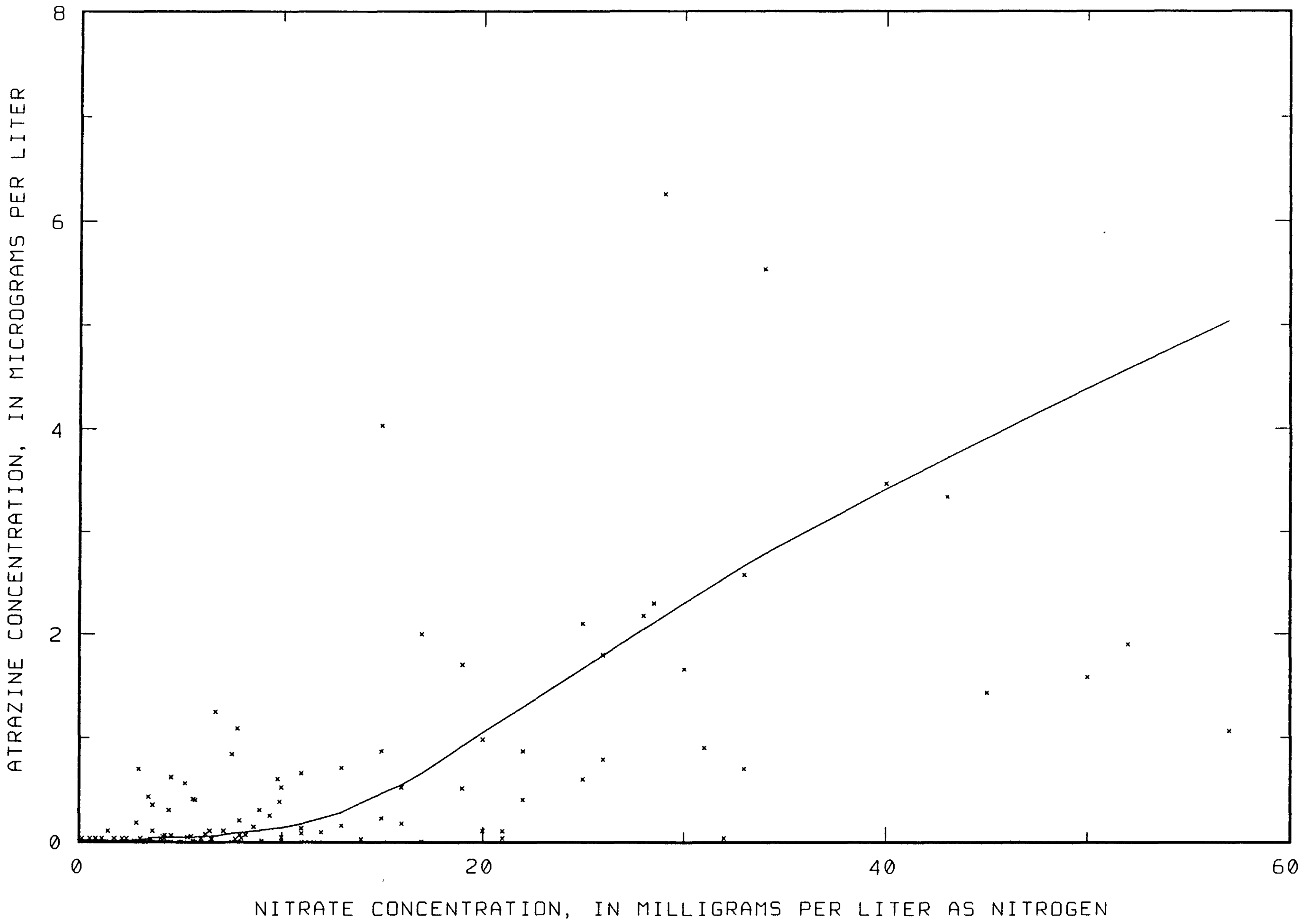

Figure G-16. –Relation between concentrations of nitrate and atrazine in water from the High Plains aquifer of Nebraska.

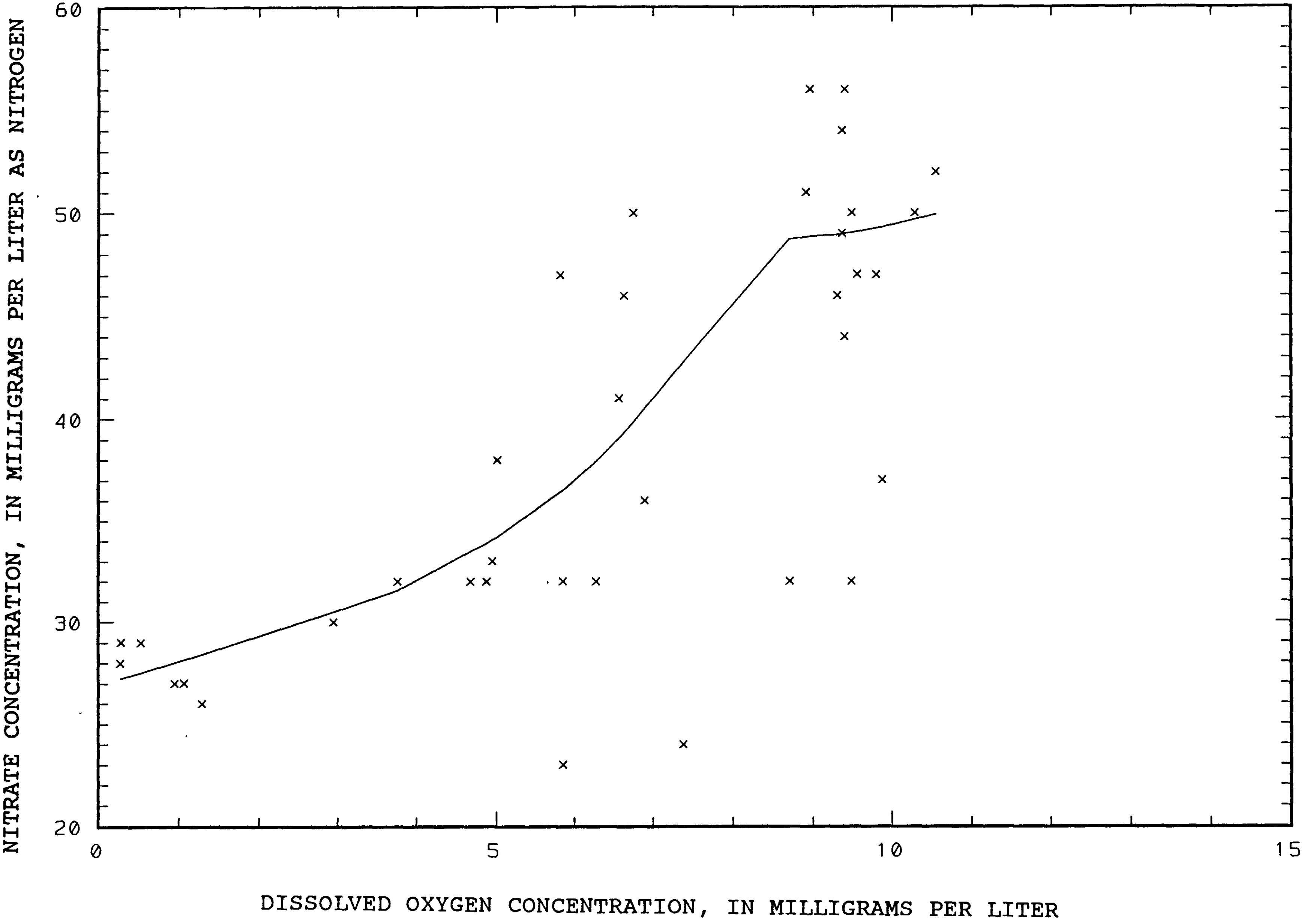

Figure G-17A.--Relation between concentrations of nitrate and dissolved oxygen in water from the High Plains aquifer of Nebraska.

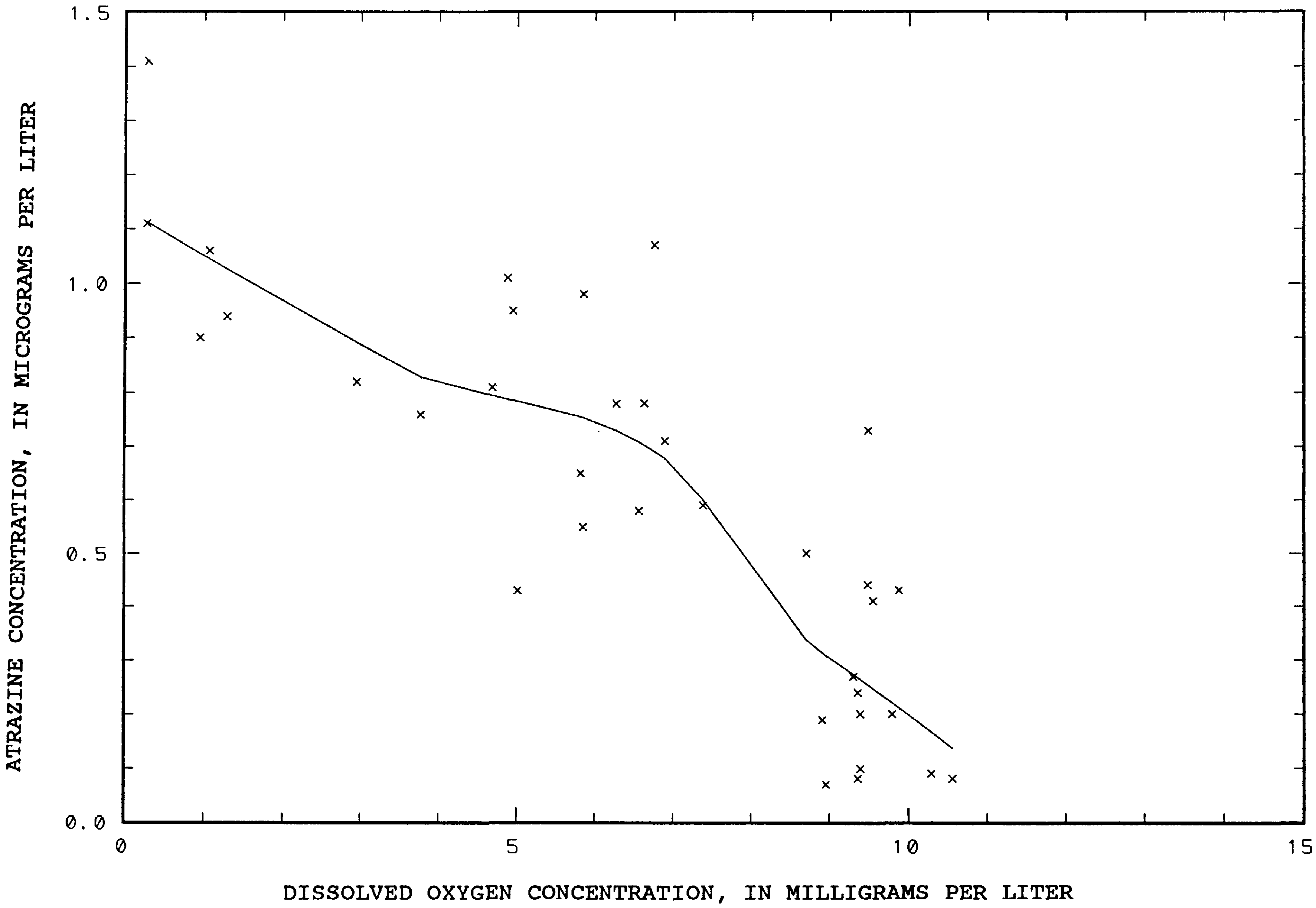

Figure G-17B.—Relation between concentrations of atrazine and dissolved oxygen in water from the High Plains aquifer of Nebraska.

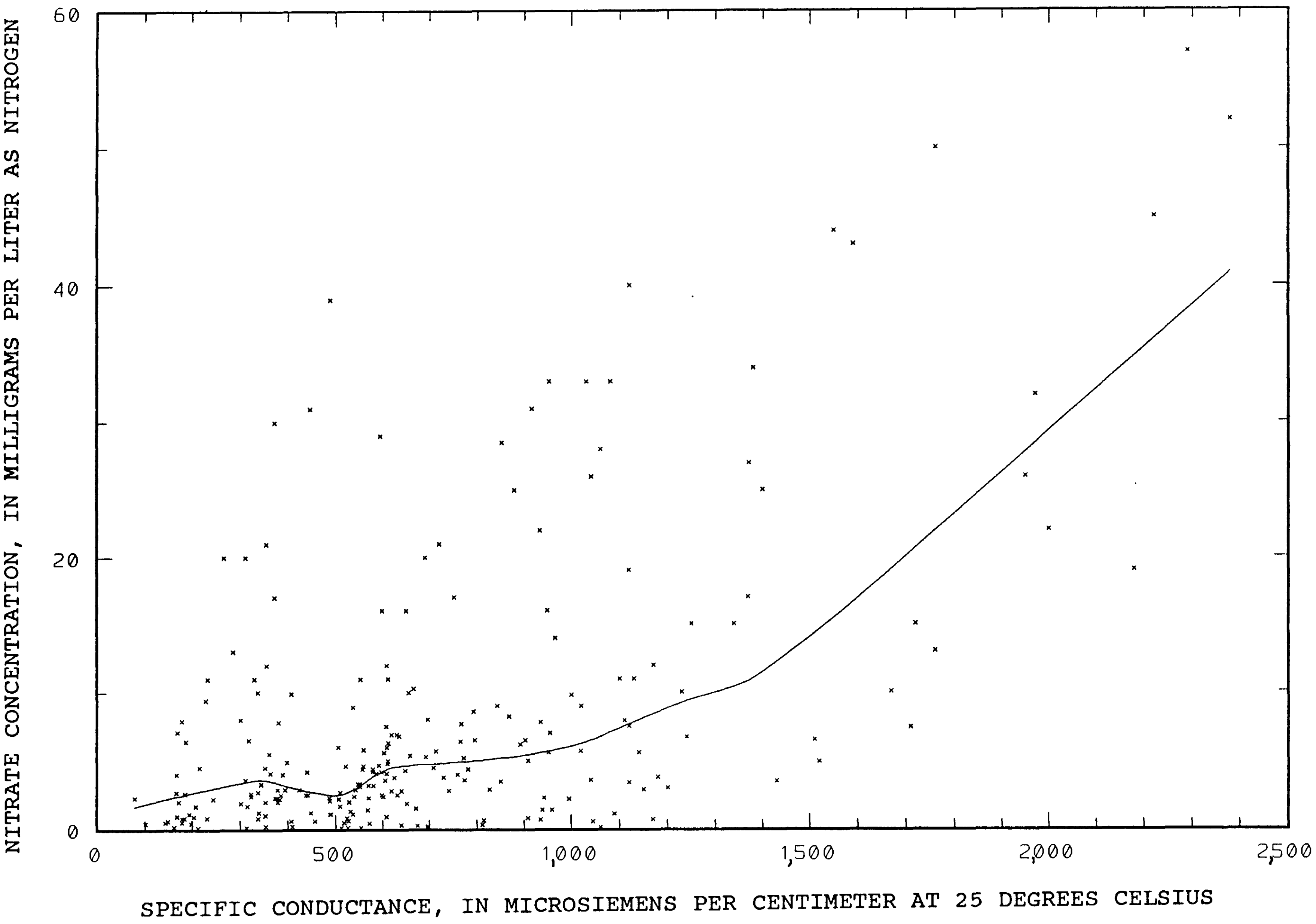

Figure G-18A. –Relation between nitrate concentration and specific conductance in water from the High Plains aquifer of Nebraska.

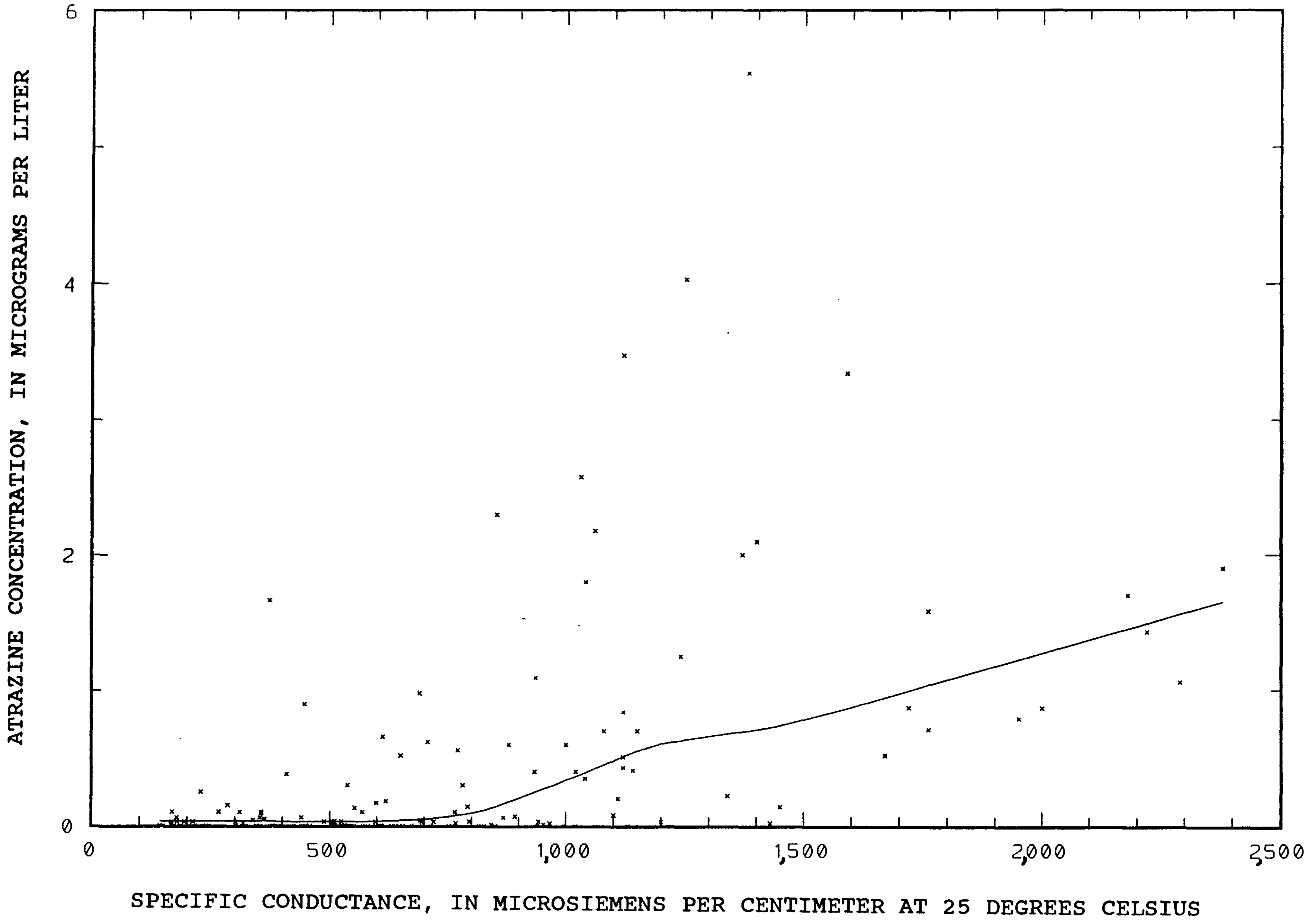

Figure G-18B.–Relation between atrazine concentration and specific conductance in water from the High Plains aquifer of Nebraska.

Table G-3.-*Multiple-linear regression models with nitrate (models A-B) and atrazine (models C-E) concentrations as the dependent variables.*

Model A

Dependent variable: Nitrate concentration

Variables omitted [1]: Atrazine concentration, well depth

Explanatory variable [2]	Multiple R-squared	Change in R-squared	T-ratio	Regression coefficient
Specific conductance	0.409	0.409	7.84	0.01528
Average unsaturated hydraulic conductivity	.647	.238	6.49	.08049
Percent clay in soil	.668	.028	-2.13	-.23030

Model B

Dependent variable: Nitrate concentration

Variables omitted [1]: Atrazine concentration, well depth, specific conductance

Explanatory variable [2]	Multiple R-squared	Change in R-squared	T-ratio	Regression coefficient
Average unsaturated hydraulic conductivity	0.385	0.385	29.787	0.08848
Average screened well depth	.449	.064	3.372	-.01764
Irrigation-well density	.465	.016	2.155	.51992

Model C

Dependent variable: Atrazine concentration

Variables omitted [1]: Well depth

Explanatory variable 2	Multiple R-squared	Change in R-squared	T-ratio	Regression coefficient
Average unsaturated hydraulic conductivity	0.431	0.431	6.45	0.00569
Specific conductance	.671	.240	3.44	.00055
Irrigation well density	.752	.081	3.64	.10210
Herbicide application date	.781	.029	-2.04	-.00541
Average screened well depth	.805	.024	3.09	.00229
Depth to water	.838	.033	-2.40	-.00411

Model D

Dependent variable: Atrazine concentration

Variables omitted [1]: Well depth, specific conductance

Explanatory variable [2]	Multiple R-squared	Change in R-squared	T-ratio	Regression coefficient
Average unsaturated hydraulic conductivity	0.431	0.431	6.83	0.00645
Irrigation well density	.610	.179	4.52	.13158
Herbicide application date	.674	.064	-2.28	-.00618
Average screened well depth	.722	.048	3.93	.00405
Depth to water	.771	.049	-3.11	-.00540
pH	.808	.037	-2.32	-.42873

Model E

Dependent variable: Atrazine concentration

Variables omitted [1]: Specific conductance, well depth, average unsaturated hydraulic conductivity

Explanatory variable [2]	Multiple R-squared	Change in R-squared	T-ratio	Regression coefficient
Nitrate concentration	0.422	0.422	3.97	0.00307
Irrigation well density	.546	.124	2.13	.08150
Average saturated hydraulic conductivity	.574	.028	2.94	.00427
Average screened swell depth	.648	.074	2.52	.00479
Depth to water	.702	.054	-2.29	-.00501

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[1] Variables omitted refers to those explanatory variables that were intentionally deleted from the data set prior to running the regression programs. All explanatory variables not included in this list were used by the regression programs to generate the model.

[2] This list includes only those explanatory variables that explained significant amounts of variation in dependent variable (T-ratio greater than 2.00).

Other explanatory variables that were used in the models were herbicide application date, soil clay content, and ground-water pH.

Model A, which intentionally excluded only well depth as an explanatory variable, explained the most variation in nitrate concentration (R-squared = 0.668). Of the 22 explanatory variables used, only 3 had sufficiently large T-ratios to be used in this model. Atrazine concentration was intentionally omitted from the explanatory variables used prior to generating model A in addition to well depth, because nitrate concentration was considered to be a possible surrogate for atrazine concentration. Specific conductance explained the most variation in nitrate concentration (40.9 percent and, as was mentioned, may be an indirect measure of nitrate concentration. Average hydraulic conductivity of the unsaturated zone explained 23.8 percent of the variation in nitrate concentration, underscoring the importance of hydrogeologic influences on ground-water contamination. The percentage of clay in the soil accounted for 2.8 percent of the variation in nitrate concentration and indicated that locations with clayey soils are not as susceptible to non-point-source ground-water contamination by nitrate than are locations with sandy soils. The absence of land-use variables from this model may be attributed to the relative uniform rates and times of nitrogen application.

Specific conductance, in addition to well depth and atrazine concentration, was intentionally omitted prior to producing model B, because of the large variation in specific conductance observed in the study areas and the inferred difficulty in using specific conductance as a major indicator of nitrate contamination. Model B explained 46.5 percent of the variation in nitrate concentration and showed that only 3 of 21 input explanatory variables were significant. Average hydraulic conductivity of the unsaturated zone explained 38.5 percent of the variation in nitrate concentration, followed by average screened well depth, which explained 6.4 percent of the variation, and irrigation-well density, which explained 1.6 percent of the variation.

The models with atrazine as the dependent variable yielded considerably larger R-squared values than did the nitrate models. Model C, which intentionally excluded only well depth as an explanatory variable, explained the most variation in atrazine concentration (R-squared = 0.838). Of the 24 explanatory variables used, only 6 had sufficiently large T-ratios to be used in this model. The average hydraulic conductivity of the unsaturated zone and specific conductance explained 67.1 percent of the variation in atrazine concentration. Irrigation-well density accounted for 8.1 percent of the variation in atrazine concentration, indicating the importance of land use on water-table aquifers. Herbicide-application date explained 2.9 percent of the variation in atrazine concentration, suggesting that the concentration of atrazine in ground water is time dependent. Average screened well depth and depth to water explained an additional 5.9 percent of the variation in atrazine concentration.

Specific conductance was removed from the explanatory variables, in addition to well depth, prior to generating model D, because specific conductance was believed to be closely related to nitrate concentration and might be causing the exclusion of other more appropriate explanatory variables from the model. Model D used 6 of 23 explanatory variables to explain 80.8 percent of the variation in atrazine concentration. The first five explanatory variables in model D were the same and in the same order as the last five variables in model C, although the amount of explained variation in atrazine concentration increased for each variable. The variation in atrazine concentration was explained largely by the average hydraulic conductivity of the unsaturated zone and by irrigation-well density, accounting for 43.1 and 17.9 percent of the variation, respectively.

The only new explanatory variable added in model D was pH, and it explained 3.7 percent of the variation in atrazine concentration. Although the relation between atrazine concentration and pH would be expected to be positive (Hiltbold and Buchanan, 1977), the negative regression coefficient for pH in this model represents the difficulty in interpreting individual variable relations given the multiple-dimensional nature of the equations.

Average hydraulic conductivity of the unsaturated zone was intentionally omitted from the input explanatory variables in addition to well depth and specific conductance prior to generating model E to examine the possible influences of other explanatory variables on the variation in atrazine concentration. Model E showed that 5 of 22 explanatory variables used to generate the model were significant and that the 5 variables explained 70.2 percent of the variation in atrazine concentration. Nitrate concentration explained most of the variation in atrazine concentration (42.2 percent). As in the previous two models, irrigation-well density, average screened well depth, and depth to water were included in model E, and average hydraulic conductivity of the saturated zone was added. Average hydraulic conductivity explained an additional 2.8 percent of the variation in atrazine concentration.

SUMMARY

Concentrations of nitrate greater than the USEPA 10-mg/L primary drinking-water regulation and detectable concentrations of atrazine can be found in many areas of the High Plains aquifer in Nebraska. Hydrogeologic, soil, land-use, and hydrochemical variables apparently can influence concentrations of these contaminants in ground water within the study areas.

Plots of concentrations of nitrate and atrazine in ground water as functions of selected explanatory variables have yielded insights into these relations. Ground water in areas with a large average total hydraulic conductivity were commonly contaminated by nitrate and atrazine. Concentrations of nitrate and atrazine generally were lower in water from deep wells and from wells where depths to water were great. The extent of irrigated agriculture in the form of irrigation-well density and the number of irrigated acres per 4-mi^2 area shows some relation to ground-water contamination by agricultural chemicals. One of the most notable relations is the relatively strong correlation of nitrate and atrazine concentrations. Concentrations of atrazine and DO were negatively correlated, indicating that atrazine may be less stable in oxygen-rich water than in oxygen-poor water. Nitrate and atrazine concentrations were positively correlated to specific conductance.

Multiple-linear-regression techniques were used to determine the relative significance of 22 and 24 explanatory variables to nitrate and atrazine concentrations in ground water, respectively. The largest variation in concentrations of nitrate in ground water was explained, in descending order of importance, by specific conductance, average hydraulic conductivity of the unsaturated zone and the percentage of clay in the soil. The largest variation in atrazine concentration was explained, in descending order of importance, by average hydraulic conductivity of the unsaturated zone, specific conductance, irrigation-well density, herbicide-application date, average screened well depth, and depth to water.

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RELATIONS BETWEEN LAND USE AND WATER QUALITY IN THE HIGH PLAINS AQUIFER OF SOUTH-CENTRAL KANSAS

By J.O. Helgesen[1] and A.T. Rutledge[2]

ABSTRACT

Results of sampling from the High Plains aquifer in south-central Kansas indicate differences in ground-water quality between rangeland areas and irrigated cropland areas of several square miles. Concentrations of several dissolved inorganic constituents are higher beneath cropland areas than beneath rangeland as a result of the application of irrigation water and agricultural chemicals. The rarity of atrazine herbicide in samples of ground water may reflect degradation and (or) retardation of atrazine in the vadose zone. Clay layers in the vadose zone probably restrict downward movement of water and chemicals in most of the study area. Within irrigated cropland areas, water quality as characterized by samples from irrigation wells is not significantly different than water quality as characterized by samples from small-yield wells away from irrigated fields, reflecting lateral solute transport within the discrete areas.

INTRODUCTION

Ground-water quality in an agricultural area of south-central Kansas has been evaluated as part of an increasing need to improve an understanding of regional nonpoint-source contamination. This evaluation will assist the U.S. Geological Survey's Toxic Waste--Ground-Water Contamination Program in assessing ground-water quality and its relation to human activities (Helsel and Ragone, 1984). Use of land for agricultural purposes is particularly extensive in the Midwestern United States; attendant practices of irrigation and application of pesticides and fertilizers pose a potential threat to ground-water quality in unconfined aquifers, such as the High Plains aquifer.

A part of the High Plains aquifer in south-central Kansas (fig. G-19) may be particularly susceptible to contamination from activities at the land surface because of the relative shallowness of the water table (generally less than 40 feet below land surface) and the typically high permeability of its sandy soils. A preliminary reconnaissance of ground-water quality in late August-early September 1984 in the western part of this area (Stullken and others, 1987) indicated the presence of significantly higher concentrations of sodium and alkalinity beneath irrigated cropland than beneath nonirrigated rangeland. Triazine herbicides (primarily atrazine) were detected only beneath cropland areas but not at the frequency or in the concentrations that might be expected in view of the widespread use of those chemicals. Triazine herbicides were detected in 3 of 13 samples from irrigated-cropland areas and at concentrations of 0.2 μg/L (micrograms per liter) or less.

Results of the reconnaissance raised questions concerning the factors that may influence the occurrence and distribution of contaminants in the ground-water system. One possible factor is the presence of fine-textured materials within the vadose zone, which can inhibit downward movement of water and chemicals. Clay deposits reportedly are common at shallow depths within the study area (Stullken and Fader, 1976; Sophocleus and Perry, 1987). Another factor may be the source of the water sample; samples collected from irrigation wells, which generally are located within the fields, might be expected to contain higher concentrations of a contaminant than samples from small-yield wells located away from the fields, because irrigation wells collect water from directly beneath the area of chemical application. Only one irrigation well was sampled in the preliminary reconnaissance.

An expanded reconnaissance was conducted in July 1987 to examine relations between land use and ground-water quality, particularly in light of the factors discussed above. This paper describes

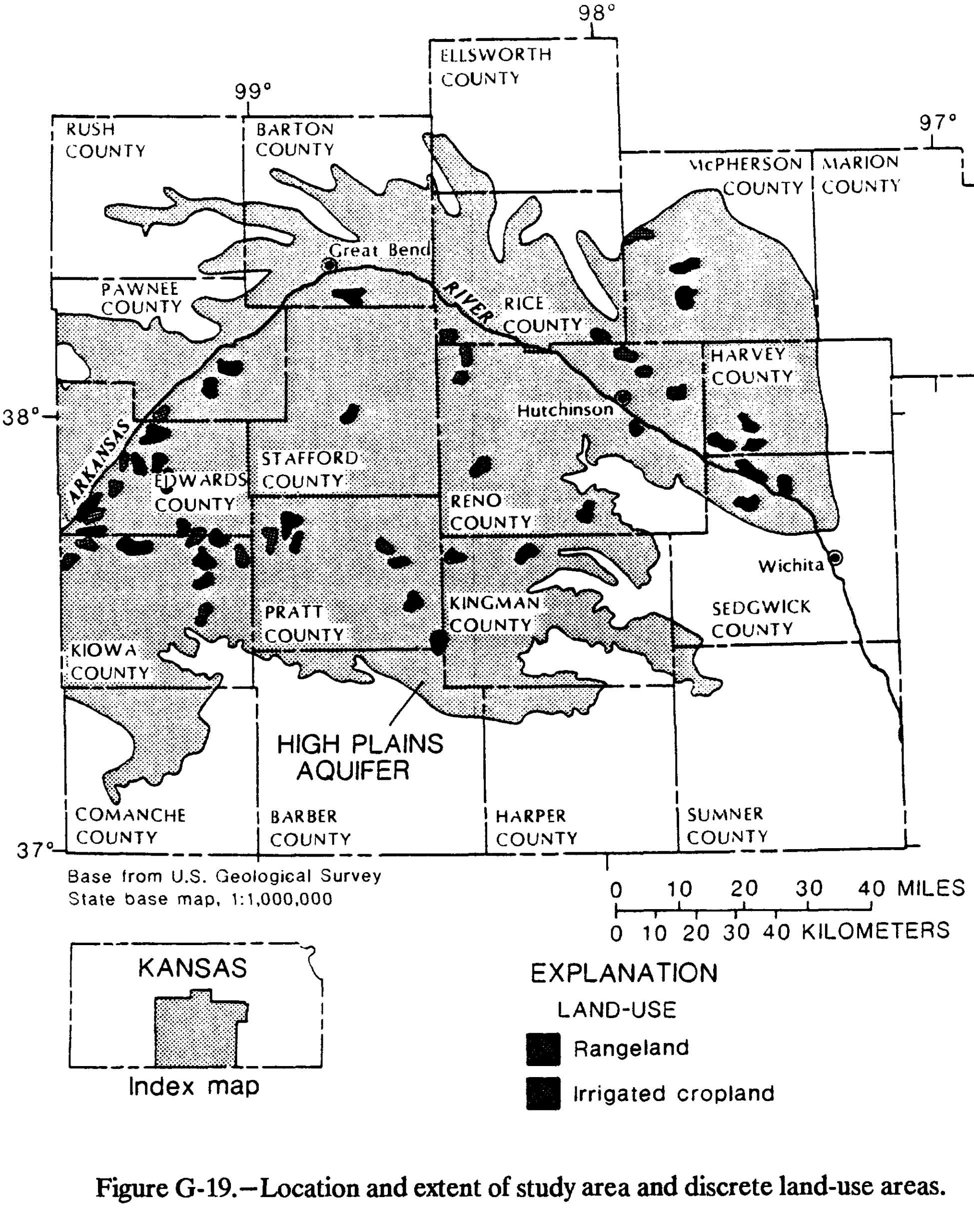
[1] U.S. Geological Survey, Lawrence, Kans.

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

some results of the expanded reconnaissance. Specifically, this paper presents comparisons of water quality with respect to prevailing land use, vadose- zone lithology, and type of well sampled.

SAMPLING DESIGN

Because the primary focus of this evaluation is on relations between land use and ground-water quality, an appropriate sampling design depends on the premise that some features of water quality reflect the overlying land use. Discrete areas of 3 to 10 mi^2 (square miles) were identified for two land uses of interest--irrigated cropland and non-irrigated rangeland (fig. G-19). Such a size is appropriate considering the slow natural movement of ground water; lateral velocity is less than 1 ft/d (foot per day) in the area, according to Stullken and others (1987). Therefore, in the last few decades, during which most agricultural chemicals have been applied, ground water probably is not displaced significantly from beneath such areas and may somehow be characterized by the overlying land use.



Base from U.S. Geological Survey State base map, 1:1,000,000

Figure G-19.--Location and extent of study area and discrete land-use areas.

The discrete land-use areas were delineated primarily by using Landsat-satellite imagery for midsummer 1984. Identification of 30 irrigated cropland areas and 22 rangeland areas provided the framework for comparisons in terms of land use. Within each area, a small-yield well (generally a domestic or stock well) was randomly selected for sampling from well-record files of the Kansas Department of Health and Environment (Topeka). Although water-quality characteristics could vary depending on depth of wells sampled, depths of wells in an area tend to be similar, and results are assumed to be representative.

Comparisons based on lithology of the vadose zone also were attempted. On the basis of generalized mapping of the upper 20 feet of the subsurface throughout the study area, each land-use area was designated as either a "clayey" or "sandy" area. Actual lithologies are complex, but about 80 gamma-ray logs and about 350 descriptive logs were used to develop the best possible regional interpretation. An area was arbitrarily designated as clayey if clay beds comprise at least 25 percent of the upper 20 feet.

Within each irrigated cropland area, a randomly selected irrigation well also was selected for sampling. This allowed additional analysis of differences in water quality between irrigation wells and nearby small- yield wells.

The sampling design enabled several factors to be evaluated (fig. G-20). Ground-water samples were collected within a few weeks of the start of the 1987 irrigation season. Specific conductance, pH, water temperature, and alkalinity were determined onsite. Concentrations of major ions, several other inorganic constituents, and the triazine and chlorophenoxy acid herbicides were determined by the U.S. Geological Survey Laboratory in Denver, Colo.

DATA ANALYSIS AND RESULTS

Sample distributions for concentrations of individual constituents were typically nonnormal and positively skewed. Thus, statistical comparisons of interest were made by using the nonparametric two-tailed Wilcoxon-Mann-Whitney rank-sum test (Iman and Conover, 1983). In all comparisons, the null hypothesis was that the median concentrations of the two groups of data were equal. The rank-sum test was not applicable for the pesticides that were analyzed, except for atrazine; all pesticide concentrations were less than detection limits except for eight occurrences of atrazine and one occurrence of 2,4-D.

Comparisons between samples from small-yield wells in the two land-use groups indicate significant differences (null hypothesis is rejected) between median concentrations for several inorganic constituents (fig. G-21). Median concentrations of most major cations, alkalinity, and hardness are significantly higher at the 95-percent confidence level beneath irrigated cropland areas than those beneath rangeland areas. Also, dissolved-solids concentrations are higher beneath irrigated cropland areas, but at the 93-percent confidence level. Unlike the results of the initial (1984) reconnaissance, median sodium concentrations were not found to be significantly different between land-use groups. Overall, these results probably reflect increased dissolution of minerals by applied irrigation water and its subsequent percolation through the soil and vadose zone.

Significantly higher median concentrations of nitrite plus nitrate, at the 95-percent confidence level, beneath irrigated cropland compared to rangeland, probably are derived from fertilizers. However, the same relation is not apparent for orthophosphate, perhaps because the presence of animal wastes near the rangeland wells may be a contributing factor. Significantly higher median concentrations of fluoride, at the 95-percent confidence level, in the irrigated cropland areas may result partly from its association with a common phosphate-mineral component of fertilizer. Significantly higher median concentrations of dissolved iron, at the 95-percent confidence level, were found in rangeland-area samples compared to irrigated cropland samples; a clear explanation for this difference is not evident.

Concentrations of atrazine ranged from less than 0.1 μg/L to 3.8 μg/L. Atrazine was detected in eight samples, seven of which were from irrigated cropland areas. However, comparisons based on these data do not indicate statistically significant differences associated with land use. In view of the commonly elevated concentrations of several, basically conservative, inorganic

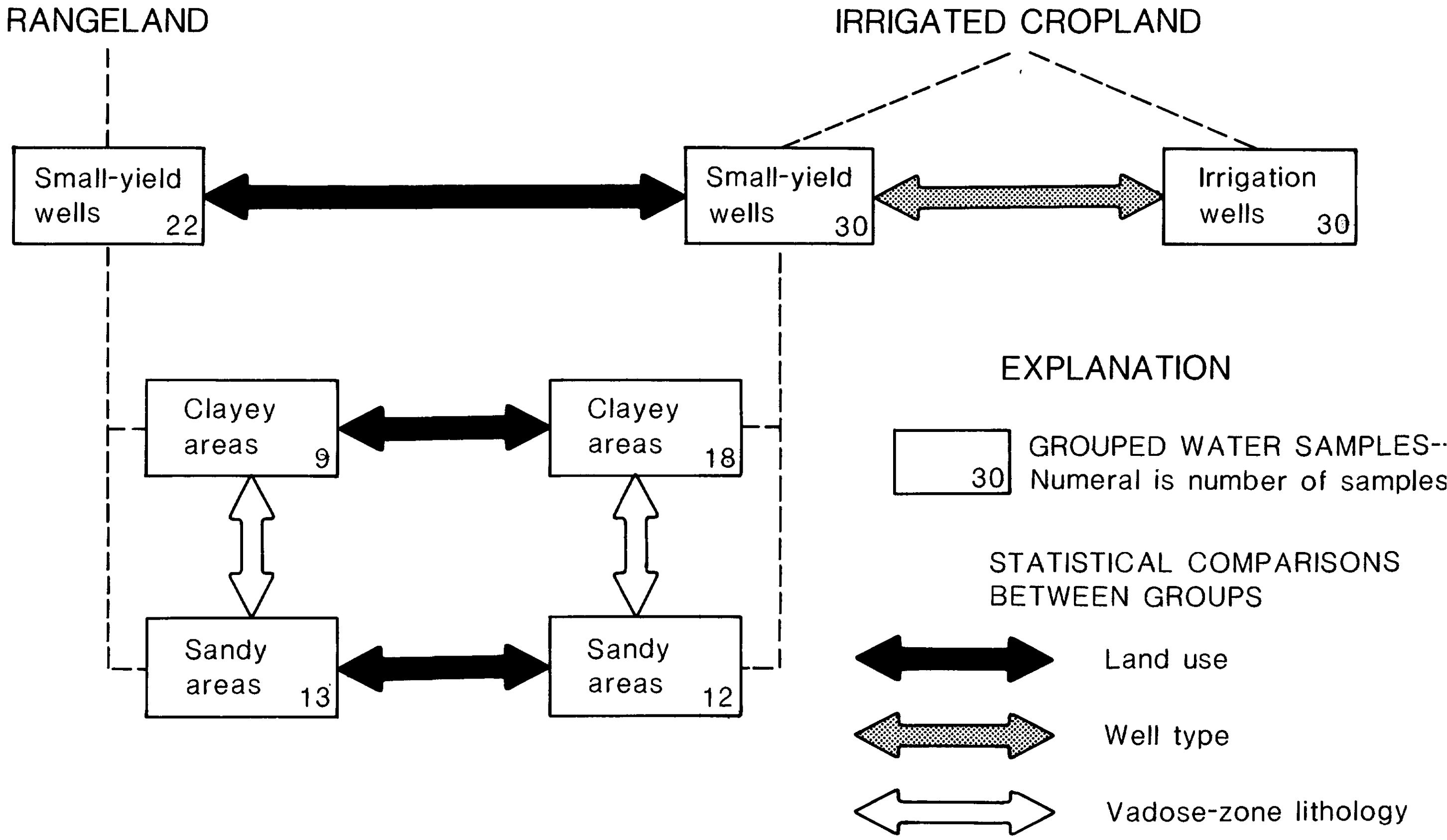


Figure G-20.—Grouping of water samples and statistical comparisons between groups.

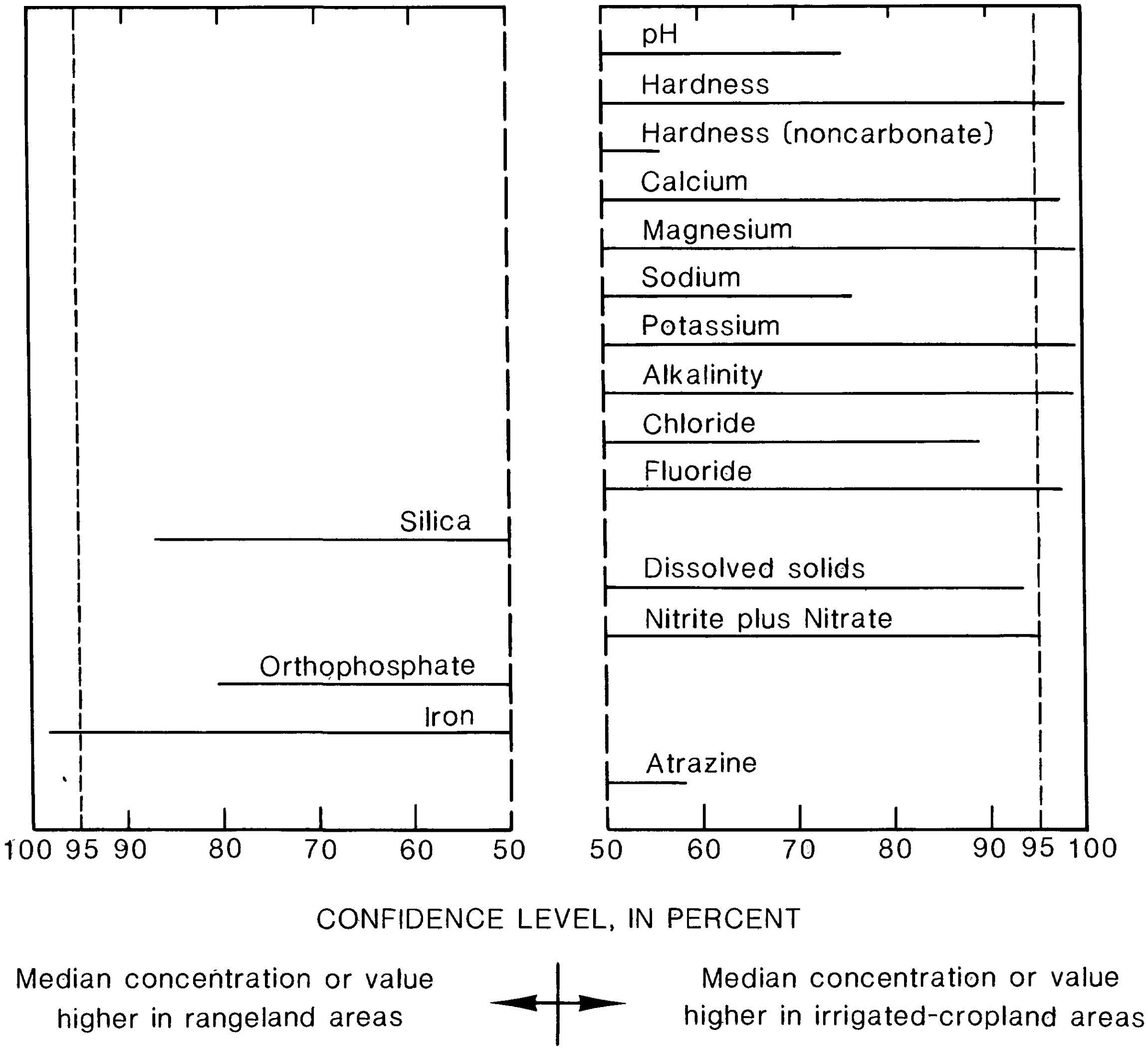


Figure G-21.—Confidence levels of differences between median concentrations or pH in samples from rangeland and irrigated cropland areas, according to two-tailed Wilcoxon-Mann-Whitney rank-sum tests.

constituents beneath irrigated cropland, the infrequency of atrazine detections may be caused, at least in part, by degradation and (or) retardation of the herbicide in the vadose zone.

Comparisons in terms of vadose-zone lithology (clayey compared to sandy areas) also were done using data only from the small-yield wells. Significant differences were indicated only for two minor constituents; orthophosphate and silica concentrations were larger in clayey areas than in sandy areas at the 95-percent confidence level.

Comparisons between samples from small-yield wells and from irrigation wells within the irrigated cropland areas indicated two differences significant at the 95-percent confidence level. Median concentrations of orthophosphate and median water temperature were both larger in samples from the small-yield wells than in samples from the irrigation wells. The orthophosphate concentrations may be attributable to animal wastes associated with the farmsteads. Elevated water temperatures may be related to the collection point; samples commonly were collected from taps within domestic pipe systems where some warming occurred.

Results of the expanded reconnaissance generally reinforce and build on the previous (1984) reconnaissance results. Water quality in the High Plains aquifer of south-central Kansas is characterized, to some degree, by prevailing land use (rangeland or irrigated cropland) of the surrounding area. Differences in concentrations of several inorganic constituents relate to the irrigation water and chemicals applied to the cropland areas. The infrequency of atrazine detections in the saturated zone probably reflects the nonconservative properties of that compound and the effectiveness of degradation and (or) retardation of that herbicide in the vadose zone.

Practices associated with agricultural land use appear to override the influence of other potentially important factors in this study area. Firstly, clay layers within the vadose zone are sufficiently disseminated throughout the study area that even generally delineated sandy areas are not underlain by ground water of noticeably different quality. Unrestricted downward movement caused by the absence of clay layers probably is an important factor locally but is not a condition that is regionally definable on the basis of current information. Secondly, the characterization of ground-water quality is not substantially dependent on the type of well (irrigation compared to small-yield well) from which samples are obtained. This finding probably reflects lateral transport, within a land-use area of several square miles, of solutes resulting from infiltration of applied chemicals and irrigation water.

SUMMARY AND CONCLUSIONS

A study of the High Plains aquifer in south-central Kansas was made to determine relations between ground-water quality and overlying agricultural (rangeland or irrigated-crop) land use. Sampling design also enabled an evaluation of the effects of generalized vadose-zone lithology and type of well sampled on the characterization of water quality. Samples were collected from randomly selected wells within 22 rangeland areas and 30 irrigated cropland areas. The significance of the sampling results and statistical comparisons using the Wilcoxon-Mann-Whitney rank-sum test are conceptualized as follows:

(1) Application of irrigation water and chemicals in cropland areas have had a discernible effect on the inorganic quality of underlying ground water.

(2) Although most ground-water samples in which atrazine was detected are from irrigated cropland areas, the infrequency of detection probably reflects the effectiveness of degradation and (or) retardation processes in the overlying vadose zone.

(3) The presence of clay layers in the vadose zone is characteristic of much of the study area and probably restricts downward movement of water and chemicals.

(4) Although lateral solute transport is sufficiently slow to identify some relations between water quality and prevailing land use in discrete areas of several square miles, it apparently is sufficiently rapid that, within these discrete areas, water quality directly beneath irrigated fields is not substantially different from water quality away from the fields.

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PLANNED STUDIES OF HERBICIDES IN GROUND AND SURFACE WATER IN THE MIDCONTINENTAL UNITED STATES

By Michael R. Burkart[1], Stephen E. Ragone,[2] E. Michael Thurman[3], and Charles A. Perry[3]

ABSTRACT

This is a plan to study the effects of natural and human factors on the occurrence of herbicides, such as atrazine, in ground and surface waters in the Midwest. The key question to be answered is: "What happens to an herbicide after its application?" To answer this question, procedures are provided that integrate information from a wide variety of deterministic and statistical studies of atrazine--a representative herbicide having widespread use in agricultural areas. These studies range in scale from laboratory and field plots, to regional-scale investigations. The integration of information will lead to the identification of major processes affecting atrazine fate and transport and an understanding of the effect of spatial variability of factors on atrazine in the hydrologic system. Processes, such as chemical decomposition, are physical, chemical, and biological actions that can influence the transformation, transportation, and storage of atrazine. Factors, such as soil pH, are variables that can affect which process plays a dominant role. Processes are normally independent of scale and factors can be scale-dependent. A research matrix is developed that uses a mass-balance concept to account for the distribution of atrazine in the environment and to identify areas of needed research. A geographic information system that will permit interpretation of regional information and evaluation of spatial variability of important natural and human factors, such as atrazine application rates and depth to water, is described. The plan includes use of statistical methods to relate regional patterns of the occurrence of atrazine to a limited number of factors. Full implementation of the plan may take 5 to 10 years or more depending on the availability of information and the need for additional studies. The plan involves an iterative process that uses information from laboratory and field-plot research of natural processes to direct the statistical analysis of the regional distribution of factors. The results of the statistical analysis will be used to identify areas where factors can be measured in more detail and verified. If verification of factors cannot be achieved, additional process research can be initiated in that area. This planned research will be the scientific basis for water-resources managers to develop guidelines for protecting water quality.

INTRODUCTION

Herbicides, insecticides, and other pesticides have contributed to providing an adequate and high-quality supply of food for the Nation and for export. As pesticide usage increases, currently (1988) about 300 thousand megagrams annually (U.S.Department of Agriculture, 1988), the potential for contamination of ground and surface water also increases. Pesticides are present in the ground water of many States (Cohen and others, 1986) and also in streams and large rivers (Hall, 1974; Richard and others, 1974; Wauchope, 1978; Libra and others, 1986 and Squillace and Engberg, 1988). Resource managers need scientific information to improve understanding of the conditions under which pesticides are transported through the hydrologic system and to develop guidelines to protect water quality.

The U.S. Geological Survey, the U.S. Department of Agriculture, and the U.S. Environmental Protection Agency have implemented agreements to better organize research, make appraisals, and develop field and analytical methods to study pesticides. The herbicide study in the midcontinental United States is an important part of this organizational effort by providing a focus for these and other agencies to integrate their expertise into a comprehensive research and appraisal effort. This paper describes the plan for this study.

[1] U.S. Geological Survey, Iowa City, Iowa
[2] U.S. Geological Survey, Reston, Va.
[3] U.S. Geological Survey, Lawrence, Kans.

The midcontinental United States was selected for study (fig. G-22) because the region is dominated by cropland devoted to corn and soybean production where pesticide applications are substantial. The combined pesticide use of the States in the region is about 50 percent of the national total (Gianessi and others, 1986). The region approximately coincides with the Upper Mississippi River basin and much of the northern parts of the Missouri and Ohio River basins. The coincidence of hydrologic boundaries and land use provides an opportunity to examine differences in water quality in distinct land-use regions.

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-s-triazine) was selected as a representative herbicide in this study because:

(1) it is the most widely used triazine herbicide and has the longest history of continuous use; and

(2) its physical and chemical characteristics, such as solubility, are representative of both triazines and acetanilides--the two classes of herbicides accounting for the majority of herbicides used in the midcontinent.

The infiltration of atrazine to ground water may be affected by a variety of natural processes and environmental and human factors. Processes are physical, chemical, and biological actions that can cause atrazine to be stored, transported, or transformed in the various compartments of the hydrologic system and are independent of scale. For instance, the process of degradation will

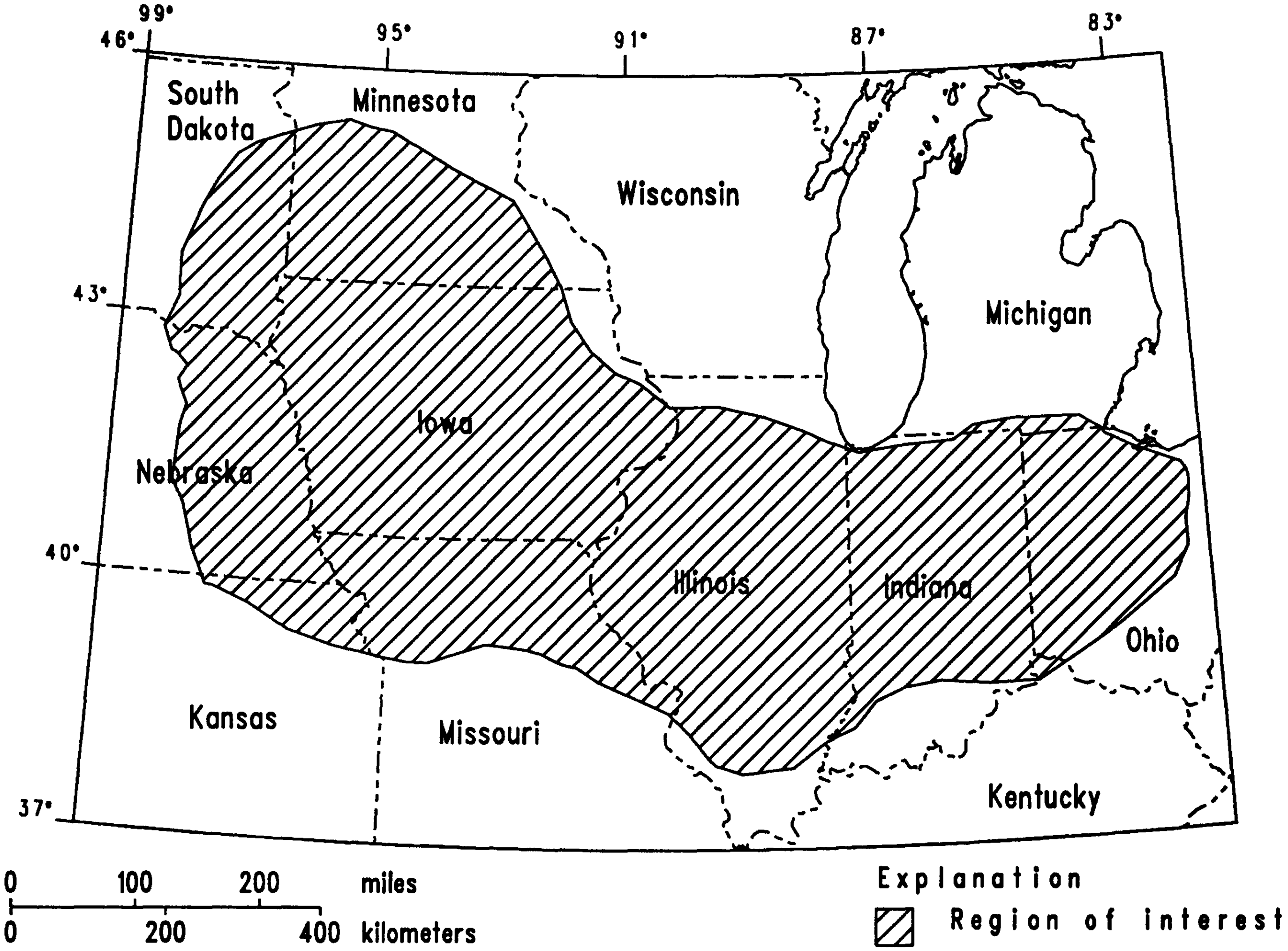

Figure G-22.—Location of midcontinent herbicide initiative.

result in a small sample of atrazine having the same half-life as a large quantity in similar environmental conditions. Factors are variables that can influence which process plays a dominant role. For instance, soil pH is an environmental factor that may retard or accelerate the decomposition of atrazine and thus have a substantial influence on the half-life of pesticides. Human factors include crop type, atrazine application rate, and crop rotation, which can influence the amount of atrazine available to the environment and the rate at which atrazine can be transformed, stored, or transported. All these factors can vary widely, particularly over a large region such as the Midwest.

OBJECTIVES

The overall objective of this study is to improve understanding of the processes and factors that affect the regional distribution of atrazine in ground and surface water. This study will identify the controlling processes and factors, evaluate the sizes of areas or scales within which factor measurements are useful, and relate appropriate factors to the occurrence of atrazine in water. Two specific research objectives will be pursued:

(1) Identify, implement, and integrate deterministic studies of the processes and factors controlling the transformation, transport, and storage of atrazine in the hydrologic system.

(2) Determine the relations between the controlling environmental and human factors and the occurrence of atrazine in ground and surface water to predict the potential for atrazine loading to these waters on a regional scale.

APPROACH

The overall approach is to use deterministic and statistical studies to determine the distribution of atrazine on a regional scale. Deterministic studies of processes will test the effects of environmental and human factor variability. Statistical studies will use regional data bases to determine the significance of natural and human factors on occurrence of atrazine in water. This is an iterative process that consists of two parts. Part 1 involves the identification and interpretation of important physical, chemical, and biological processes that affect the fate of atrazine in the hydrologic system. Part 2 involves studies of the regional variability of factors that control the distribution of atrazine in the environment. The transport of atrazine by ground and surface water connects the parts of the study together.

Part 1--Evaluation of Processes and Factors

This part of the plan provides a procedure to select the appropriate processes and factors that affect the fate of atrazine in the environment, and evaluate the relative importance of the processes and factors that affect the distribution of atrazine in ground and surface water.

Selection of Pertinent Processes and Factors

Selection of information needed to understand the fate of atrazine in the environment is complicated by the potentially large number of processes that affect atrazine. A research matrix (fig. G-23) uses a mass-balance concept (eq. 1) to account for the distribution of atrazine in the various compartments in the hydrologic system.

$$A_{\text{applied}} = A_{\text{transformed}} + A_{\text{transported}} + A_{\text{stored}} \quad (1)$$

where

A = atrazine mass

Processes in the matrix include the major physical, chemical, and biological actions or reactions that transform, transport, or store atrazine in compartments of the hydrologic system. The research matrix will be used at three scales: laboratory, field, and regional. Knowledge gained at one scale may be applicable to corresponding compartments of other scales. For instance, laboratory experiments on chemical transformation of atrazine under simulated saturated zone conditions may be used to explain field-scale transformation where field conditions are similar to the laboratory simulation. The research matrix should allow several questions to be answered, including: What part of the mass of applied atrazine can be accounted for?; and, can any unaccounted mass be explained by measurement inaccuracies or because important processes and factors have not been considered?

Hydrologic System Components

Mass Balance Elements Processes	Atmosphere	Soil/Root Zone	Unsaturated Zone	Saturated Zone	Surface Water
Application					
Transport					
Volatilization					
Plant Uptake					
Diffusion					
Solution					
Capillary Flow					
Macropore Flow					
Macrobiological					
Advection					
Sorption					
Transformation					
Biological					
Chemical					
Photo					
Storage					
Solution					
Sorption					
Bioaccumulation					

Figure G-23.—Matrix of physical compartments and processes for atrazine.

Deterministic Research of Processes

Research on the processes that affect the fate of atrazine in the environment will follow three components of equation 1: transformation, transportation, and storage.

Transformation

Atrazine transformations, including biodegradation, chemical hydrolysis, volatilization and photodegradation, may occur in many compartments of the hydrologic system. In soil, these processes have received considerable attention in field dissipation studies and biodegradation work. Atrazine is degraded into hydroxyatrazine and deethyl and deisopropyl atrazine (Cook, 1987). Our understanding of the mass-balance of atrazine uptake by plants is limited. This gap in our understanding of the mass balance of atrazine may account for an important fraction of the total applied. For example, transpiration by corn may move 30 to 50 percent of the soil water into the atmosphere. Atrazine is soluble, thus much of it may be incorporated by the corn and transformed to hydroxyatrazine by dehalogenation. What becomes of this compound? The partially degraded atrazine could be released into the soil when corn stalks are reincorporated. A major research question is: Are transformation products a major sink of the unaccounted atrazine, especially in plant debris? This is particularly important as the farm practice of minimum tillage becomes more widespread.

How much atrazine and its transformation products is in soil and water? Information is limited about the transformation and fate of atrazine in ground and surface waters. Other important questions are: What is the half-life of atrazine in an aquifer or river?; are the transformation products in these environments similar to those in soil?; are there processes in aquifers or rivers that affect the fate of atrazine but do not operate in soils? and, is atrazine conjugated into the natural organic matter of rivers or aquifers, especially in anaerobic environments?

Volatility of atrazine may not be a topic requiring much research because volatilization of atrazine from soil is not a major transport process, although estimates might be made. The photodecomposition of atrazine in soil has been studied, is of minor significance in ground water, but has not been studied in rivers.

Transportation

Atrazine may be transported in both surface and ground water in the soluble and suspended phase. Rapid removal of herbicides from fields occurs, especially during initial weeks after application (Wauchope, 1978). Thus, the timing of rainfall and herbicide application may control herbicide movement in surface water. Solute transport models, such as CREAMS (Knisel, 1980), will be used to evaluate the timing of pesticide movement. Regional-scale studies, such as one being conducted by Meade and others (R.H. Meade, U.S. Geological Survey, oral commun., 1988) are studying mass balance of herbicides during transport by water, colloids, and other sediment in the Missouri, Illinois, Ohio, and Mississippi Rivers. Suspended sediments, especially colloids, may contain concentrations of 5 to 15 percent organic carbon, an important sorption surface source for herbicides and thus a mechanism for transport of atrazine. The transport of atrazine from ground waters to surface waters is a topic that needs substantial research.

Storage

Storage of atrazine and its transformation products in and on solids such as river sediment, aquifer materials, and organic materials will be considered. Storage by sorption in the unsaturated zone and on aquifer solids is least understood. Deterministic models, such as PRZM (Carsel and others, 1984) and GLEAMS (Leonard and others, 1986), may be useful in predicting the importance of storage of atrazine in the unsaturated zone. Reservoirs may be large repositories of contaminated water and sediments. Large amounts of sediment are stored in flood plains and bottom sediments of rivers. If organic carbon concentrations are large, storage by sorption on sediments may be an important process.

Evaluation of Existing Herbicide-Transport Models

Existing herbicide-transport models will be used to determine the effect of individual or aggregate factors on the fate of atrazine in water. Preliminary use of a steady-state unsaturated-zone transport model, for example, revealed that ground-water contamination potential is very sensitive to deep percolation rate, organic-carbon content in the unsaturated zone, pesticide half-life, and depth to water table (A.T. Rutledge, U.S. Geological Survey, written commun., 1988). More rigorous use of models will reveal more about the factors that affect ground-water contamination potential. Models have been developed for herbicide transport off fields into ground water (PRZM and GLEAMS), and into streams (CREAMS), Knisel and others, 1980). These models may be linked and will be used to verify the efficacy of the models with field data.

Part 2-- Statistical Research-Regional Patterns of Atrazine Occurrence

Part 2 describes a procedure to identify subregions within which representative areas can be defined to study the relations between selected factors and regional patterns of occurrence of atrazine. The approach includes mapping factors known to affect atrazine, selecting subregions that represent a limited range of factor values, and using statistical techniques to relate the factors to patterns of occurrence of atrazine in water.

Mapping Pertinent Factors

Much information is available from literature and ongoing research of factors that may influence the fate and mobility of atrazine. For example, water in aquifers at or near the land surface may contain atrazine or other agricultural chemicals (Libra and others, 1986; Chen and Druliner, 1987; Detroy and others, 1988; and Klaseus and others, 1988). Several general types of hydrogeologic settings may be identified for intensive study and their location mapped. Shallow or surficial aquifers, bedrock aquifers, carbonate aquifers in karst areas, and aquifers beneath thin drift will be considered. Studies of the effects of agriculture on ground water are ongoing in some of these settings and coordination with this research will be important. In addition, subregions where confining materials are hypothesized to be impermeable to the movement of atrazine, will be selected to establish whether the hypothetical aquifer-protection exists.

Information on factors related to land use, climate, hydrology, and soils will be compiled and stored in a Geographic Information System (GIS) to manage, display, and query spatial data. Data bases that are needed include measurements and estimates of atrazine application in agricultural areas, precipitation chemistry, water-table depth, ground-water chemistry, sediment loads in surface water, and chemistry of streams. The software to be used, ARC/INFO[4], is a two-part system that relates attributes or thematic data to geographic location. ARC manages topological data by using a vector format in coverages analogous to two-dimensional maps. INFO is used to organize data in tables that can be related to ARC coverages.

The GIS will use points as well as county data at the largest scale to Landsat data at the smallest scale. It is necessary to determine the accuracy and precision of the data values and location included in the data base. Ground-truth of the estimates will be determined and the variability associated with the estimates will be measured. For example, measurements of the variation in the amount of atrazine applied will be made and compared with the estimated values of atrazine. This procedure will be completed in several subregions representing the full range of values of critical factors, thus allowing a analysis of error associated with the data base. As progress is made toward establishing relations among factors and water quality, the scale and extent of measurements necessary for improved quality of regional data will be identified.

Selection of Representative Subregions for Factor Verification or Further Study

Subregions will be characterized by small spatial variability of pertinent factors compared with that of the entire region. The effect of factor variability within subregions will, in part, be defined by model-sensitivity analysis. Several possible results of this effort are hypothesized:

(1) Subregions cannot be delineated because factor variability is as large in any subregion as in the entire region. In this case, the information needed to make management decisions needs to be obtained for smaller areas;

(2) Subregions may be delineated, but their spatial variability is greater than that defined in model-sensitivity analysis. In this case, information from studies within subregions can be used to formulate management decisions by use of statistical methods;

(3) Subregions may be delineated with spatial variability similar to that allowed in model-sensitivity analysis.

Should subregionalization lead to results (2) or (3), representative subregions and areas will be selected to conduct factor verification or further study (fig. G-24). These studies will include sampling of shallow ground water, streams, and reservoirs for detailed factor measurement or verification of measurements. Information from these studies will further establish the relations between controlling factors and the occurrence of herbicide contamination. The GIS will be used to relate geographic location data to each factor and subdivide the region into subregions having a limited range of factor variability. The number of

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

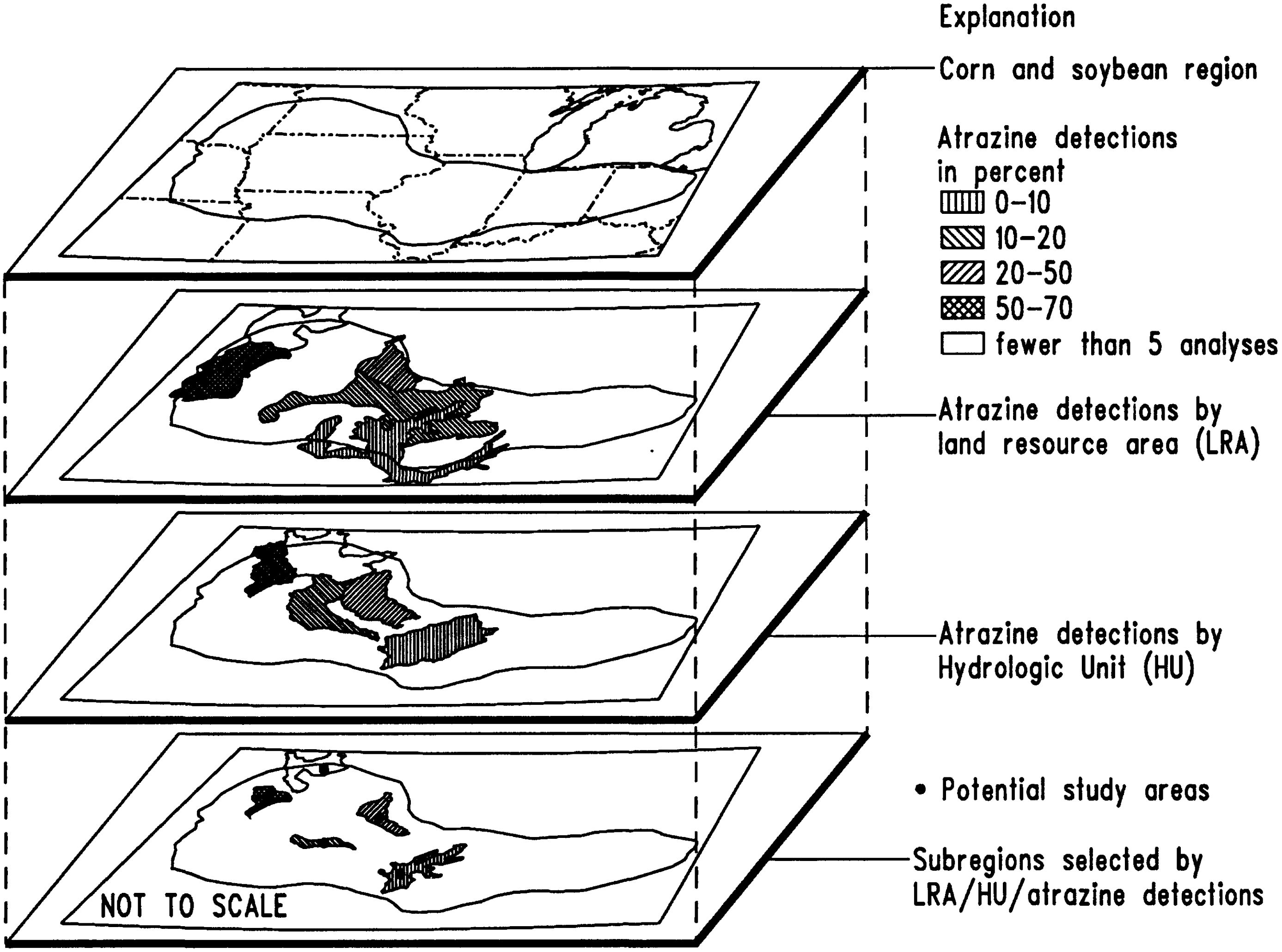

Figure G-24.—Regional, subregional and area delineations for factor verification or further study related by a geographic information system.

areas to be selected for each factor will depend on the range of values and distribution of variability throughout the region.

Use of Statistical Models to Relate Factors and Patterns of Occurrence of Atrazine

Regional water-quality investigations are complicated because of the variable nature of the hydrologic and geologic settings and the variability of chemical sources in space and time. Methods were developed to study these complex problems (Helsel and Ragone, 1984) and applied to a variety of field conditions that ranged in size from several square kilometers to several hundreds of square kilometers. These study results indicate that correlations can be drawn between natural and human factors and the occurrence of selected chemicals in ground water. In the study described in this plan, the concepts used in the previous studies will be applied to a larger region. The key steps in the plan are calibration of statistical models in a control area followed by verification in a similar but independent area. Data obtained from intensive study areas will be used to develop regression models of individual factors and the occurrence of atrazine. From these regression models, multivariate statistical models will be developed to explain the patterns of atrazine contamination. Areas selected at random will be used to test the applicability and veracity of these models.

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PRELIMINARY ASSESSMENT OF THE FATE AND TRANSPORT OF SYNTHETIC ORGANIC AGROCHEMICALS IN THE LOWER MISSISSIPPI RIVER AND ITS TRIBUTARIES

By W.E. Pereira[1], C.E. Rostad[1], and T.J. Leiker[1]

ABSTRACT

The Mississippi River and its tributaries drain about 41 percent of the contiguous United States. The Mississippi River discharges an average of 18,400 cubic meters per second of water into the Gulf of Mexico. This large river basin includes extensive agricultural areas. Millions of pounds of agrochemicals are applied annually in these areas. Therefore, point-source pollution of the river by industrial chemicals may be a relatively minor environmental problem compared with nonpoint-source pollution by synthetic organic agrochemicals transported from these agricultural watersheds. Studies being conducted by the U.S. Geological Survey at 16 different stations along the lower Mississippi River and its tributaries, representing a 1,200-mile reach, have confirmed that these compounds are distributed in water, sediments, and lipid tissue of catfish.

Several triazine and acylamide herbicides and their degradation products were identified in water and suspended sediments. These compounds include atrazine and its degradation products, desethylatrazine and desisopropylatrazine; simazine; metolachlor; and alachlor and its degradation products, 2-hydroxy-2',6'-diethylacetanilide and 2,6-diethylaniline. Preliminary studies have shown that small quantities of these compounds also are associated with silt and clay fractions.

Loads of several herbicides and their degradation products in the lower Mississippi River and its tributaries are reported. Mixing and redistribution of these compounds downstream from major river confluences indicate that many of these compounds exhibit relatively conservative behavior as compared with other hydrophobic compounds. Loads for 2,6-diethylaniline indicate that this compound probably is generated from a point source near St. Louis. More hydrophobic agrochemicals, such as DDT and its degradation products DDE and DDD, and dieldrin, chlordane, hexachlorobenzene, and dacthal are bioconcentrated in the lipid tissue of catfish. Presence of these compounds in stream biota demonstrates the importance of these organisms as sensors and concentrators of hydrophobic organic pollutants. Processes such as sorption, biodegradation, and bioconcentration affect the distributions of synthetic organic agrochemicals in the Mississippi River.

INTRODUCTION

Synthetic organic agrochemicals are being used in increasing amounts to improve crop yields. Each year, new compounds are introduced for agricultural use as pesticides, herbicides, and fungicides as older compounds are phased out of production. Nonpoint-source pollution of surface and ground water by agricultural chemicals is a problem of increasing environmental concern (Humenik and others, 1987). Many synthetic organic agrochemicals applied to crops eventually reach ground and surface water by infiltration of soil or surface runoff and atmospheric deposition.

Water-soluble herbicides such as atrazine, simazine, alachlor, and metolachlor are applied as preemergent and postemergent weed-control agents. It is estimated that millions of pounds of these compounds are used each year (L.P. Gianessi, Resources of the Future, written commun., 1986). Herbicides have half-lives of weeks to several months after application and are degraded in the environment to more water-soluble compounds (Aizawa, 1982). More hydrophobic compounds such as the chlorinated insecticides are refractory and have relatively long residence times in the hydrogeologic environment. Because synthetic organic agrochemicals

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

are used in large amounts, it is reasonable to assume that nonpoint-source pollution of streams and rivers by agrochemicals, transported from agricultural watersheds, is a major factor to be considered in water-quality assessments.

Studies being conducted by the U.S. Geological Survey at different stations along the lower Mississippi River and its major tributaries, representing a 1,200-mile river reach, have confirmed that many of these compounds are distributed in water, sediment, and lipid tissues of catfish. This paper presents the preliminary results of a study to determine (1) the compartmentalization of synthetic organic agrochemicals, (2) mixing and redistribution of agricultural chemicals downstream from major river confluences, and (3) processes that affect the fate and transport of these compounds in the lower Mississippi River and its major tributaries.

MATERIALS AND METHODS

Sample Collection

Representative depth-integrated water samples were collected in July-August and November-December 1987, using a Lagrangian sampling strategy, from 16 stations along the lower Mississippi River and its major tributaries by the methods of Nordin and others (1983) and Meade (1985). Water and suspended sediments (silt and clay fractions) were collected by the methods of Leenheer and others (1989, Proceedings). These samples were chilled on ice and transported to the laboratory for analysis. Catfish were collected in the general vicinity of each sampling station using "hook-and-line" or purchased from commercial fishermen. The fish were chilled on ice for a short time, wrapped in aluminum foil, labeled, and shipped to the laboratory frozen on dry ice.

Sample Preparation and Analysis

For the July-August 1987 trip, water samples from each site were filtered and extracted using the solid phase extraction technique. Eluates from the cartridges were analyzed by gas chromatrography-mass spectrometry (GC-MS). For the November-December 1987 trip, 1 liter water samples were extracted and analyzed by GC-MS using the method of Pereira and others (U.S. Geological Survey, written commun., 1988). Silt and clay fractions were dewatered by the procedure of Leenheer and others (1989, Proceedings). In general, silt and clay fractions were extracted with methylene chloride and analyzed for the presence of hydrophobic organic compounds by GC-MS. Silt and clay fractions collected at St. Louis during the November-December 1987 trip also were analyzed by a modified procedure for herbicides and their degradation products. This procedure consisted of extraction of the sample at pH 8 to 9 with acetone, using a Teckmar Sonic Disruptor[2]. Extracts were analyzed by GC-MS by the method of Rostad and others (U.S. Geological Survey, written commun., 1988).

Catfish samples were prepared for analysis by the following procedure. A 10 gram aliquot of homogenized tissue was mixed with 50 grams of anhydrous Na_2SO_4 and extracted with 100 mL (milliliters) of acetone:hexane (20:80) using a Sonic Disruptor. The extract was passed through a column containing 15 grams of anhydrous Na_2SO_4 and concentrated in a Kuderna-Danish (K-D) device. Prior to concentration, 25 mL of ethyl acetate was added to the K-D to remove all of the hexane from the extract azeotropically. The extract was passed through a gel permeation chromatography (GPC) column containing 45 grams of Bio-Beads SX-3 to remove the bulk of the lipids. The extract was further purified by passage through a column containing 20 grams of florisil. The extract was adjusted to a volume of 10 mL. A 1.0 mL aliquot of extract was analyzed by gas chromatography-electron capture (GC-ECD) analysis. The remainder of the extract was concentrated to a volume of 100 μL (microliters) and analyzed by GC-MS.

RESULTS AND DISCUSSION

Hydrology

Sampling stations for this study along the lower Mississippi River and its tributaries are shown in figure G-25. The hydrologic setting of the sampling trip of July-August 1987 was one of generally low water, punctuated by a surge of sediment-laden water out of the Missouri River basin.

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[2] Any use of trade names is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

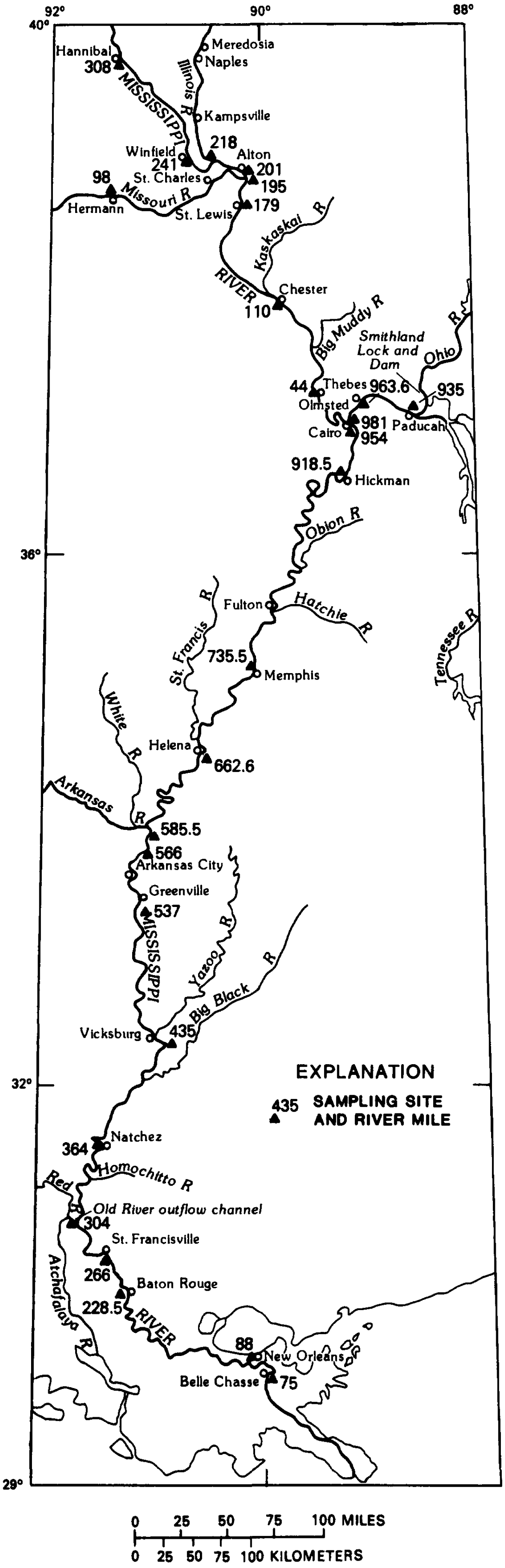

Figure G-25.—Study area and sampling sites.

Because of several periods of delay (2 days for boat repair and 2 days for a detour to sample tributaries), the sampling schedule was not able to keep up with the surge, and the same part of the falling limb, all the way down the river, was not sampled. During the November-December 1987 sampling trip, this type of surge was not encountered, although measured discharges were slightly higher than those of the July-August trip. Also, during the November-December sampling trip, the Red River was relatively high, causing water to back up into the Old River Outflow Channel near Knox Landing. However, the same body of water was sampled throughout the lower Mississippi River during the November-December sampling trip.

Transport of Agrochemicals in the Dissolved Fraction of the Water Column

Several triazine and acylamide herbicides and their degradation products were identified in water samples collected during the July-August sampling trip. These compounds included atrazine and its degradation products, desethyl and desisopropyl atrazine, and simazine, alachlor, and metolachlor. In addition to these compounds, two degradation products of alachlor, 2-hydroxy-2',6'-diethylacetanilide and 2,6-diethylaniline, were identified during the November-December sampling trip. These herbicides and their degradation products were ubiquitous throughout the lower Mississippi River and its tributaries. As expected, concentrations of these compounds were lower during the November-December sampling trip than during the July-August sampling trip. Higher concentrations of these compounds in the water column during the July-August 1987 sampling trip probably were related to the time of sampling (following the field application in spring) and the "flushing effect" caused by the surge of sediment and water out of the Missouri River basin following intense rainfall.

Loads in kilograms per day (concentration × discharge) of water-soluble agrochemicals in the lower Mississippi River and its tributaries, for the July-August 1987 and November-December 1987 sampling trips, are shown as a function of discharge and river miles in figures G-26 and G-27. Because of the surge of sediment-laden water out of the Missouri River basin and the delays mentioned earlier, the same body of water was not sampled all the way downstream during the July-August 1987 sampling trip. These hystereses are reflected in the transport data downstream from major river confluences. According to Federal law, approximately 25 percent of water from the Mississippi River is diverted down the Old River Outflow Channel to the Atchafalaya River. Considering the dynamic nature of the system and errors associated with sample collection, processing, and analysis, loads of atrazine, desethylatrazine, and metolachlor in the Old River Outflow Channel for the July-August 1987 sampling trip are in reasonable agreement with the expected loads of these compounds. The sums of the loads of these compounds at St. Francisville and the Old River Outflow Channel also are in reasonable agreement with their loads at Vicksburg.

Because the same body of water was sampled during the November-December 1987 sampling trip, mixing and redistribution of water-soluble agrochemicals were in closer agreement with calculated values downstream from major river confluences. This is evident from the data for desethylatrazine, simazine, atrazine, alachlor, and metolachlor. The sums of the loads of these compounds in the Mississippi, Illinois, and Missouri Rivers are in reasonable agreement with their loads in the Mississippi River at St. Louis. Similarly, the sums of the loads of these compounds in the Mississippi River at Thebes and the Ohio River at Olmsted are in reasonable agreement with their loads in the Mississippi River at Hickman. During the November-December 1987 sampling trip, the Red River was relatively high, causing water to back up into the Old River Outflow Channel. Despite this problem, the sum of the loads of these compounds in the Mississippi River at St. Francisville and the Old River Outflow Channel near Knox Landing are in reasonable agreement with their loads in the Mississippi River at Vicksburg. These agreements in mixing loads downstream from major river confluences attest to the validity of the equal- transit-rate (equal-width-increment) depth-integration Lagrangian sampling scheme. The data also suggest that several of these agrochemicals exhibit

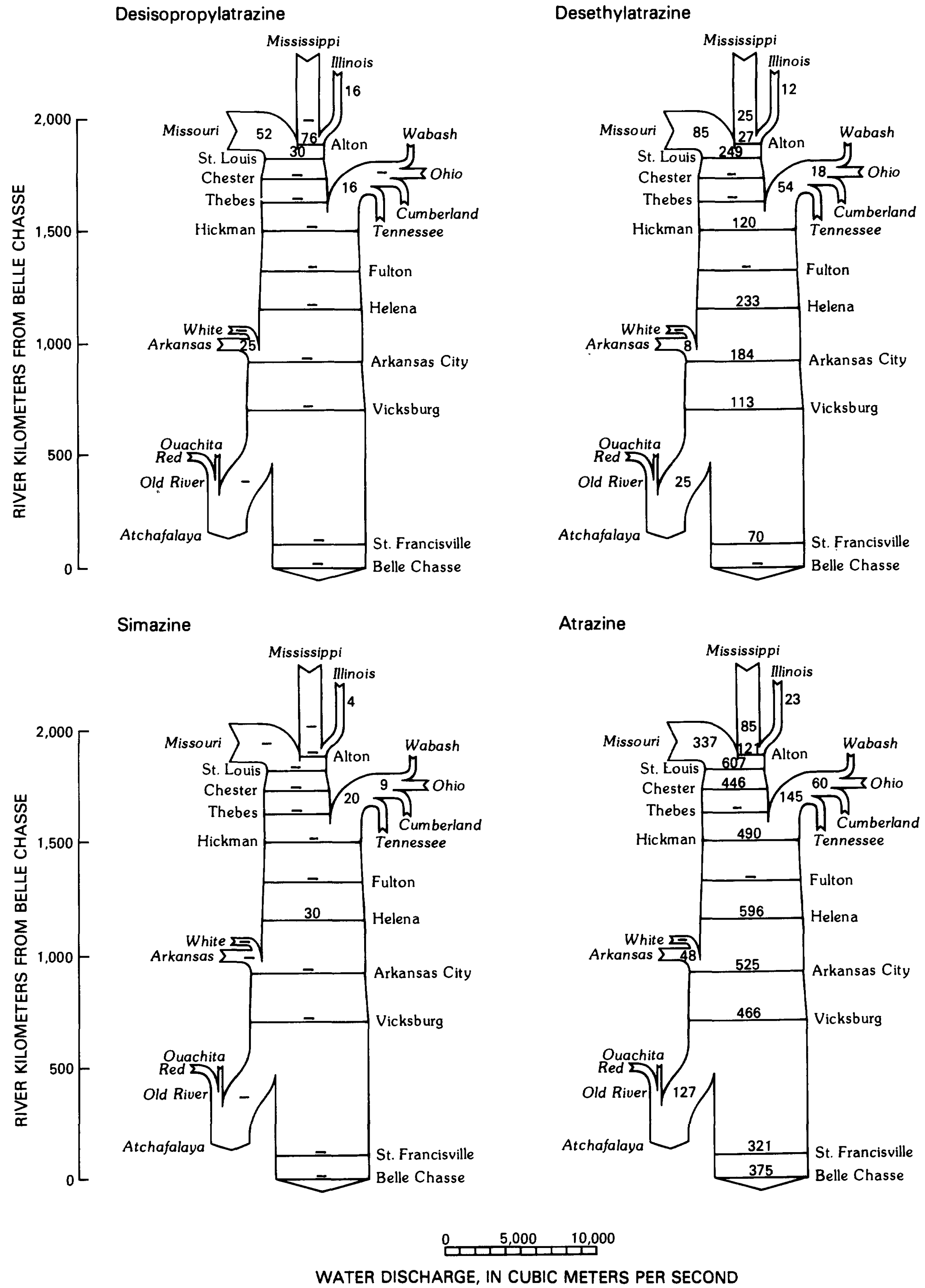

Figure G-26.—Loads in kilograms per day (concentration × discharge), as a function of discharge and river miles, July-August 1987. Numbers represent load of chemical in kilograms per day.

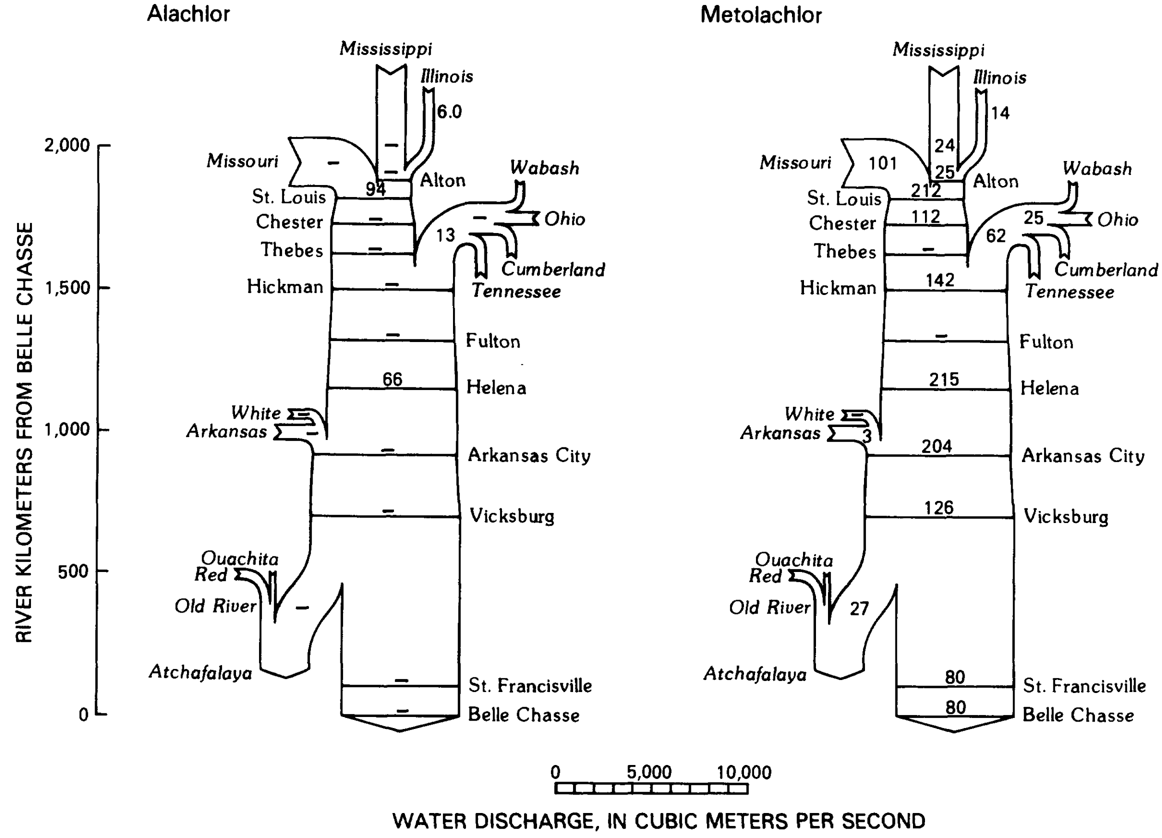

Figure G-26.—Loads in kilograms per day (concentration × discharge), as a function of discharge and river miles, July-August 1987. Numbers represent load of chemical in kilograms per day (Continued).

relatively conservative behavior as compared with other hydrophobic compounds in the lower Mississippi River.

The average atrazine load past Belle Chasse for the July-August and November-December 1987 sampling trips is 287 kg/d (kilograms per day) or 104,755 kg/yr (kilograms per year). Therefore, it is estimated that about 100 metric tons of atrazine enters the Gulf of Mexico every year. Because the average annual production of atrazine is approximately 36 million kilograms, the amount of atrazine that enters the Gulf of Mexico every year represents about 0.3 percent of the annual production of atrazine. The environmental impact of large amounts of herbicides and their degradation products on the offshore environment of the Gulf of Mexico is not known.

Of special interest are the loads for 2,6-diethylaniline identified during the November-December 1987 sampling trip. This compound has been reported to be a degradation product of the herbicide alachlor (Aizawa, 1982). However, the data shown in figure G-27 suggest that 2,6-diethylaniline probably is generated from a point source on the Mississippi River at St. Louis. This compound does not behave conservatively in the Mississippi River. The loads of 2,6-diethylaniline gradually decreased all the way downriver to Belle Chasse, suggesting that this compound is removed from the water column by processes such as sorption, volatilization, biodegradation, and so forth.

Synthetic Organic Agrochemicals in the Silt and Clay Fractions

The clay fraction collected from each site during the July-August 1987 sampling trip was extracted with methylene chloride and analyzed by GC-MS. Because of the small amount of sample available for analysis, the extracts were analyzed by gas chromatography-negative ion chemical ionization mass spectrometry. Trace amounts of dacthal and hexachlorobenzene were found associated with the clay fraction. Dacthal is a commonly used preemergent herbicide, and hexachlorobenzene is used as a fungicide. Concentrations of these compounds in the clay fraction are listed in table G-4.

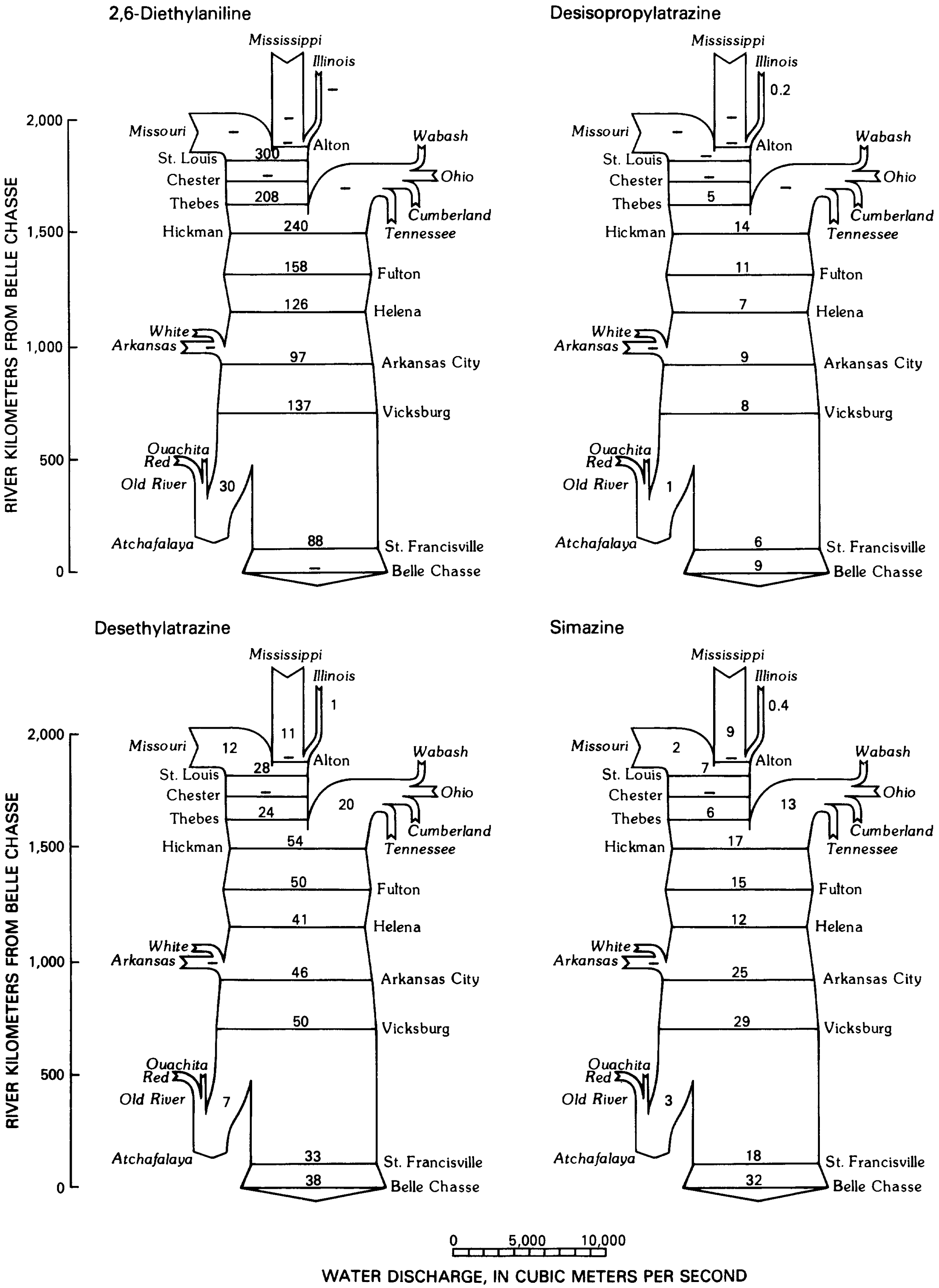

Figure G-27.—Loads in kilograms per day (concentration × discharge), as a function of discharge and river miles, November-December 1987. Numbers represent load of chemical in kilograms per day.

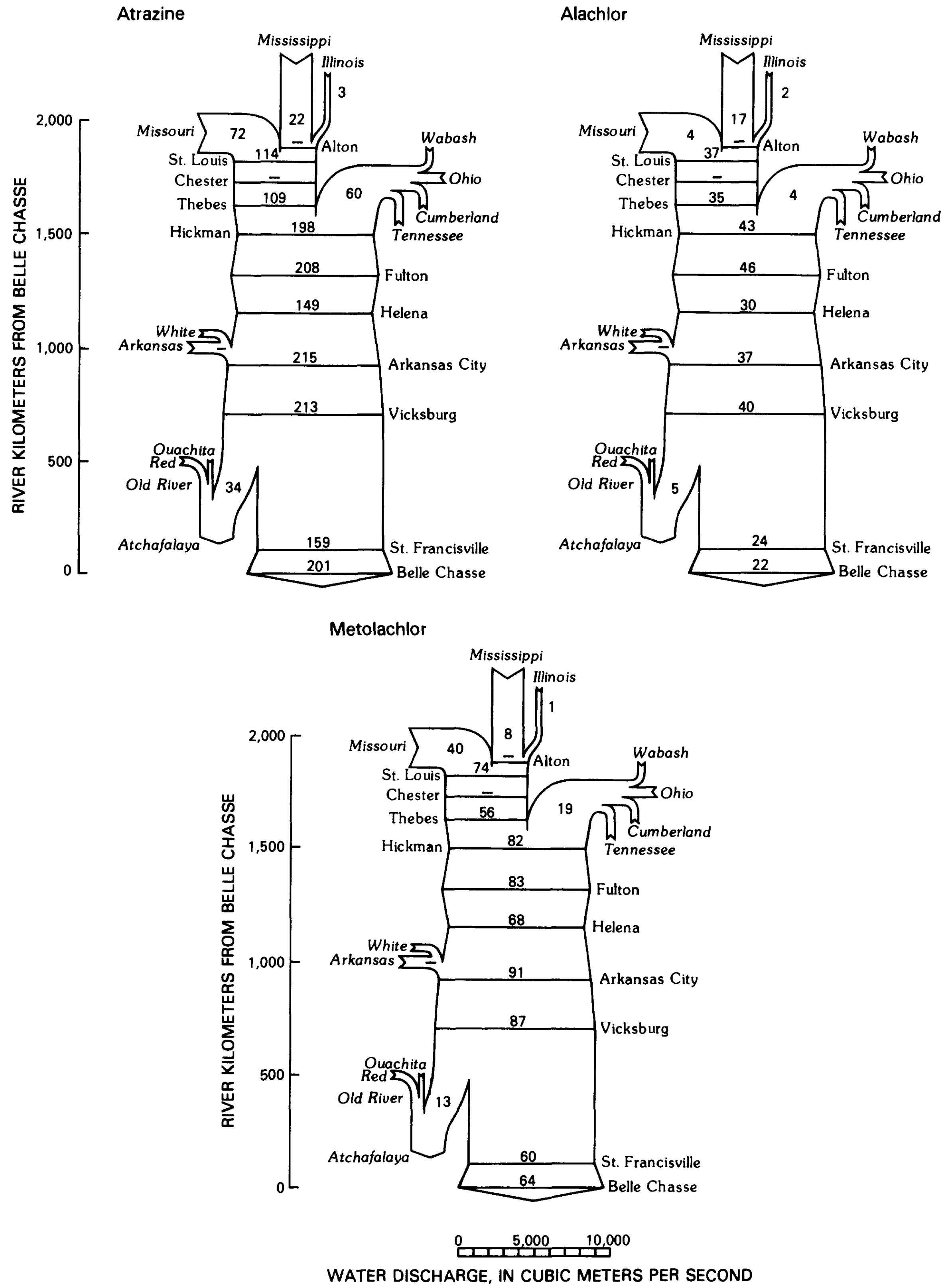

Figure G-27.—Loads in kilograms per day (concentration × discharge), as a function of discharge and river miles, November-December 1987. Numbers represent load of chemical in kilograms per day--continued.

Table G-4.-*Concentrations of hexachlorobenzene and dacthal in the clay fraction from the Mississippi River and tributaries, July-August 1987*

[--, not detected]

Station	Water sample volume (liters)	Amount of clay (grams)	Organic carbon content of clay (percent)	Hexachloro-benzene concentration (picogram per gram dry material)	Dacthal concentration (picogram per gram dry material)
Illinois River at Naples, Ill.	92.0	3.83	5.55	25	933
Mississippi River near Winfield, Mo.	92.0	3.45	5.04	603	--
Missouri River at Hermann, Mo.	58.4	6.12	3.25	35	409
Mississippi River below Alton, Ill.	93.1	1.57	6.07	--	264
Mississippi River at St. Louis, Mo.	85.4	6.43	3.23	102	--
Mississippi River at Chester, Ill.	65.3	5.63	3.18	263	--
Ohio River below Smithland Locks and Dam	86.0	0.63	8.30	--	--
Ohio River at Olmsted, Ill.	82.0	0.48	10.21	505	2,170
Mississippi River at Hickman, Ky.	81.4	2.07	4.95	--	1,800
Mississippi River at Helena, Ark.	104.5	4.72	3.28	--	187
White River at river mile 11.5	96.7	1.10	6.12	175	1,010
Arkansas River at river mile 55.9	87.4	0.41	20.12	--	--
Mississippi River above Arkansas City, Ark.	84.0	3.74	3.31	943	--
Mississippi River at Vicksburg, Miss.	77.8	2.01	4.29	23	--
Old River Outflow Channel near Knox Landing, La.	85.4	3.99	3.00	40	370
Mississippi River at St. Francisville, La.	78.4	2.92	3.09	3	1,330
Mississippi River at Belle Chasse, La.	86.3	2.18	3.36	85	--

Table G-5.-*Concentrations of herbicides and their degradation products in silt and clay fractions from the Mississippi River at St. Louis, November-December 1987*

[--, not detected]

Compound	Concentration (Nanograms per gram dry material)	
	Silt fraction	Clay fraction
2,6-Diethylaniline	1.0	--
Desisopropylatrazine	--	--
Desethylatrazine	1.0	--
Simazine	--	2.0
Atrazine	8.0	14.0
2-Hydroxy-2',6'-diethyl-acetanilide	54.0	--
Alachlor	13.0	30.0
Metolachlor	6.0	24.0

Table G-6.—*Concentrations of synthetic organic agrochemicals in catfish from the lower Mississippi River and its major tributaries, July-August 1987*

[Units in nanograms per gram wet tissue (nanograms per gram lipid); ND, not detected; D, detected, not quantitated]

Station	Number of fish	Hexa-chloro-benzene	Argochemical						DDT+DDD DDE
			Dacthal	Chlordane	Dieldrin	DDT	DDD	DDE	
Illinois River at Naples, Ill.	1	D	2.6 (260)	11 (1,120)	ND	14 (1,440)	2.6 (260)	18 (1,780)	0.96
Mississippi River near Winfield, Mo.	4	D	3.9 (58)	61 (916)	ND	19 (356)	8.2 (112)	53 (833)	0.52
Missouri River at Hermann, Mo.	1	ND	ND	64 (3,121)	ND	19 (932)	3.6 (175)	50 (2,437)	0.45
Mississippi River below Alton, Ill.	3	D	8.8 (46)	48 (400)	75 (374)	8.5 (58)	4.7 (46)	38 (371)	0.35
Mississippi River at St. Louis, Mo.	1	ND	ND	2.8 (101)	ND	ND	ND	7.8 (280)	--
Mississippi River at Chester, Ill.	3	D	1.7 (26)	45 (1,136)	31 (167)	16 (321)	8.1 (177)	32 (750)	0.74
Mississippi River at Thebes, Ill.	1	ND	ND	ND	ND	ND	ND	ND	--
Ohio River at Cumberland River	4	3.8 (38)	ND	16 (154)	ND	ND	16 (53)	16 (124)	1.00
Ohio River at Olmsted, Ill.	2	ND	ND	151 (820)	ND	ND	ND	51.8 (294)	--
Mississippi River at Hickman, Ky.	2	D	ND	19 (166)	ND	ND	3.8 (37)	19 (178)	0.2
Mississippi River at Fulton, Tenn.	1	ND	ND	24 (176)	ND	ND	1.8 (13)	82 (589)	0.02
Mississippi River at Helena, Ark.	2	D	ND	84 (1,756)	13 (132)	54 (756)	49 (784)	202 (3,548)	0.51
Mississippi River at White River	2	D	ND	170 (1,174)	59 (513)	27 (234)	34 (252)	133 (802)	0.46
White River 6 mi upstream from Mississippi River	2	ND	ND	54 (851)	ND	5.8 (59)	373 (3,884)	269 (3,313)	1.41
Mississippi River above Arkansas City, Ark.	1	ND	ND	46 (1,751)	12 (438)	29 (1,094)	1.9 (72)	252 (9,509)	0.12
Mississippi River at Greenville, Miss.	2	ND	ND	54 (696)	ND	179 (2,297)	160 (2,057)	159 (1,695)	2.13
Mississippi River at Old River Outflow Channel	1	11.3 (70)	ND	130 (798)	45 (276)	81 (498)	62 (381)	143 (879)	1.00
Mississippi River at St. Francisville, La.	1	1.5 (27)	ND	17 (306)	ND	ND	3.2 (58)	16 (284)	0.2
Mississippi River at Belle Chasse, La.	1	D	ND	9.3 (52)	ND	ND	1.3 (7.2)	9.4 (128)	0.14

Silt and clay fractions from the St. Louis site were collected during the November-December 1987 sampling trip and analyzed by extraction with acetone, followed by GC-MS. Several herbicides and their degradation products were identified. Concentrations of these compounds in the silt and clay fractions from St. Louis are listed in table G-5. These preliminary experiments indicate that both hydrophilic and hydrophobic agrochemicals are associated with the silt and clay fractions. Additional work is planned for future sampling trips to study the transport of agrochemicals associated with silt and clay fractions from the Mississippi River and its tributaries.

Biconcentration of Hydrophobic Synthetic Organic Agrochemicals

Hydrophobic organic compounds, such as chlorinated pesticides and herbicides, often are present in water at concentrations below analytical detection limits. Bottom feeders, such as catfish, are good biomonitors for detecting these trace organic compounds. Phytoplankton bioconcentrate hydrophobic organic contaminants. Zooplankton that feed on phytoplankton, in turn, transfer these compounds to bottom feeders, such as catfish. Therefore, hydrophobic organic compounds can bioaccumulate in fish lipid tissue, either by consumption of contaminated food or by gill processing of large volumes of water containing ultra-trace levels of these compounds (Oliver and Niimi, 1985).

A reconnaissance of several species of catfish (blue, flathead, black bullhead, and channel) collected along a 1,200-mile reach of the lower Mississippi River and its major tributaries indicated that this whole waterway is contaminated by trace amounts of many chlorinated synthetic organic agrochemicals and their degradation products. Concentrations of these compounds are listed in table G-6.

Data in table G-6 indicate that three sections of the lower Mississippi River are more highly contaminated by chlorinated pesticides (using catfish as bioindicators) than are other sections of the river. These three sections are (1) from Winfield to Alton, (2) at Chester, and (3) from Hickman to Greenville. Because this initial attempt was a reconnaissance study only, catfish were not sampled statistically. However, the data suggest that these compounds are bioavailable and probably have affected every trophic level in the lower Mississippi River basin. The ratio of (DDT + DDD)/DDE, which gives an indication of the degradation of DDT to DDD and DDE, has decreased significantly with time, following the ban of DDT in 1972. Additional studies are in progress to assess water quality in the lower Mississippi River basin.

SUMMARY

Preliminary water-quality studies on the lower Mississippi River and its major tributaries indicate that the entire river reach is contaminated by trace amounts of synthetic organic agrochemicals. The loads of water-soluble agrochemicals downstream from major river confluences suggest that many of these compounds are relatively conservative as compared with other hydrophobic compounds. More hydrophobic compounds, such as the chlorinated pesticides, are bioconcentrated in the tissue of catfish. Contaminant transport by suspended sediment is being investigated by the U.S. Geological Survey. Additional studies are needed to determine temporal, spatial, and seasonal variations of these compounds in the Mississippi River.

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ASSESSMENT OF POTENTIAL FOR CONTAMINATION OF THE UPPER FLORIDAN AQUIFER FROM DRAINAGE-WELL RECHARGE IN THE ORLANDO AREA, CENTRAL FLORIDA

By Edward R. German[1]

ABSTRACT

The Orlando area, in central Florida, was selected for study of the potential for contamination of ground water from drainage-well inflow. Presently, about 400 drainage wells are used for stormwater-runoff disposal and regulation of lake stage.

The Upper Floridan aquifer in the Orlando study area can be viewed conceptually as a continuously stirred tank reactor for conservative constituents, recharged by drainage from disposal of stormwater runoff. According to this concept, a conservative constituent injected at constant concentration would presently (1988) be at about 70 percent of the equilibrium concentration in the aquifer of the study area. This conservative constituent equilibrium concentration is estimated to be about 30 percent of the average concentration in the drainage-well inflow.

A comparison of water quality between an undeveloped control area and the Orlando urban area indicated significantly greater concentrations of most major constituents and nutrients in the urban area. The greater concentrations of ammonia and total organic carbon in the urban area compared to the control area probably are attributable to the drainage-well inflow. The greater concentrations of the major constituents in the urban area compared to the control area probably are the result of differences in geochemical and hydrologic factors. Frequency of detection of trace elements and volatile organic compounds was not statistically greater in the urban area than in the control area at a probability significance level of 0.05.

INTRODUCTION

Drainage wells, which induce surface waters into the Floridan aquifer system by gravity, are widely used in several urban areas in Florida. Early uses of drainage wells included disposal of domestic sewage and industrial wastewater, but present use is mostly for stormwater runoff disposal and regulation of lake stage.

The Orlando area, in central Florida, was selected for study of potential contamination of ground water from drainage-well inflow, under the Toxic Waste--Ground-Water Contamination Program of the U.S. Geological Survey. The study area includes about 87 mi^2 (square miles) within Orlando and adjacent suburbs (fig. G-28).

Drainage wells function as direct conduits for water from the land surface to the Floridan aquifer system, bypassing the surficial aquifer and the intermediate confining unit which together are about 150 feet thick (fig. G- 29). The freshwater part of the Floridan aquifer system is about 1,500 feet thick in central Florida, and consists of the Upper Floridan and Lower Floridan aquifers, separated by a less permeable unit that functions as a semiconfining layer. Drainage wells are cased either into the intermediate confining unit or into the Upper Floridan aquifer, whereas most public supply wells within the study area are cased through the Upper Floridan aquifer and the semiconfining unit and are completed in the Lower Floridan aquifer. Some public supply wells outside the central part of the study area are completed in the Upper Floridan aquifer.

There are about 400 drainage wells in the Orlando area. The wells are not evenly distributed over the area but are mostly concentrated in the central part. Overall drainage-well density averages about five wells per square mile, but is about 15 wells per square mile in the central part of the area. About 50 percent of the drainage wells receive stormwater runoff directly from streets and other impervious areas, 30 percent receive overflow from lakes, 15 percent

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

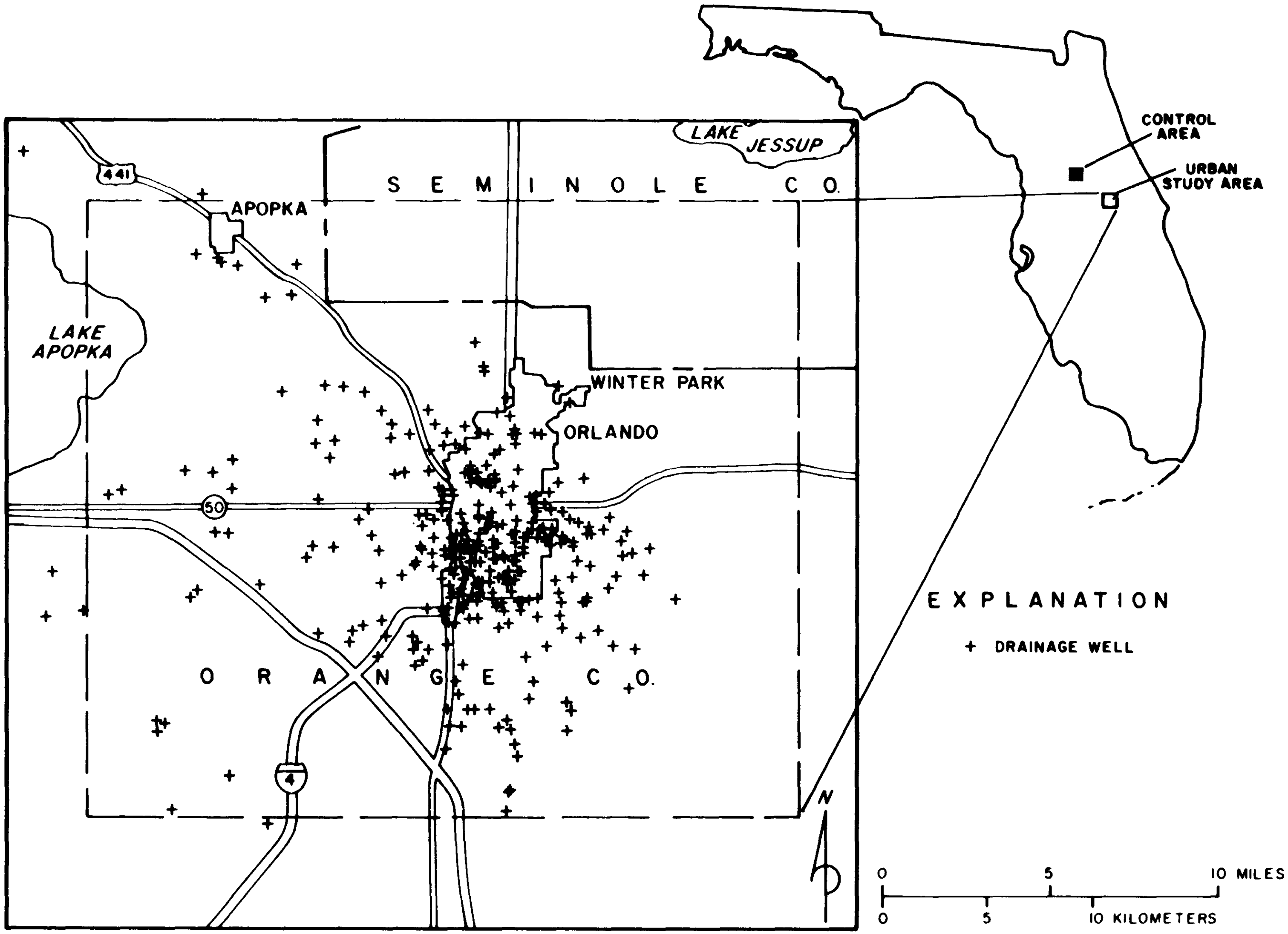

Figure G-28. –Location of the central area and the urban study area.

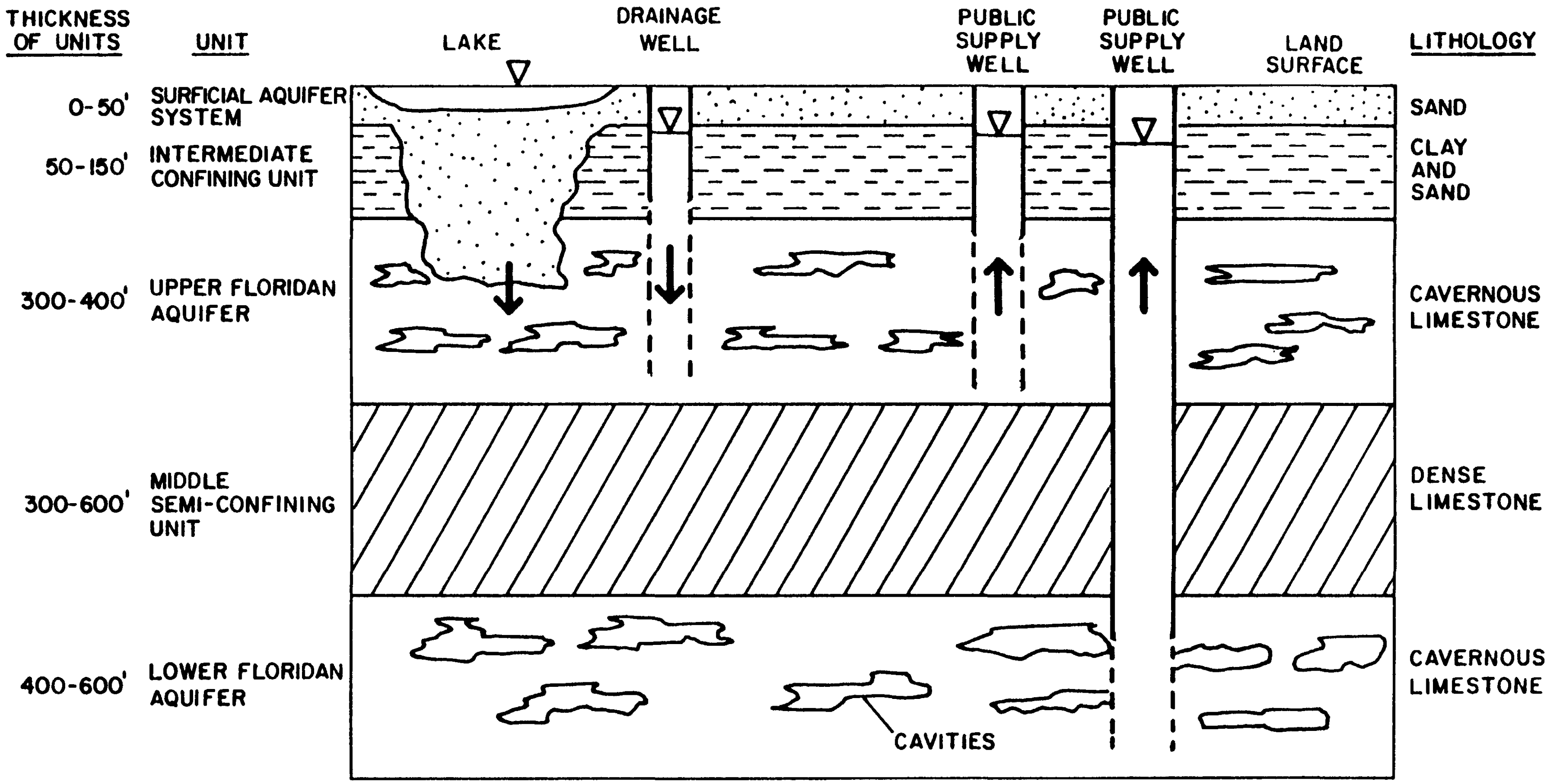

Figure G-29.—Generalized geohydrologic section, Floridan aquifer system, Orlando area. (Arrows indicate direction of water flow.)

receive outflow from wetlands, and the remaining 5 percent either currently receive air-conditioning return water or were previously used to dispose of wastes.

The earliest known drainage well was drilled in about 1904; by 1945, more than half of the 400 drainage wells had been drilled. Regulations prohibiting installation of new drainage wells became effective in 1974, and only replacement wells have been installed since then.

The potential for contamination of the Floridan aquifer system induced by drainage wells arises from the contaminants in stormwater runoff. These include metals related to traffic, especially lead and zinc, and organic compounds associated with vehicular operation. Widely used pesticides in residential areas also may contribute to possible contamination. Previous studies have documented the contaminant content of stormwater. German (in press) found median total-recoverable lead and zinc concentrations of 120 $\mu g/L$ (micrograms per liter) in stormwater runoff to lakes controlled by drainage wells in the Orlando area. German also reported the presence of 24 organic compounds in stormwater runoff or drainage-well inflow. These compounds, mostly pesticides, phthalates, or polynuclear aromatics, were very sporadic in occurrence.

A CONCEPTUAL MODEL OF EFFECTS OF DRAINAGE-WELL INFLOW

The potential effect of the drainage-well injection of stormwater-borne contaminants into the Upper Floridan aquifer depends on the magnitude of the input loading in relation to the capacity of the aquifer to dilute and assimilate the contaminants. The processes of assimilation are complex and difficult to simulate. Transport modeling of the system would be difficult and highly dependent on accuracy of definition of the heterogeneous karstic system and on quality and quantity of the drainage-well inflow. However, a simple conceptual approach to modeling the drainage-well injection of a hypothetical conservative contaminant from the surface helps to describe the potential for pollution by answering two questions: (1) Is the drainage-well- inflow load large enough, considering the regional flow rates, to cause any significant local buildup of contaminants in the Floridan aquifer system? (2) What is the time required for contaminant levels to approach equilibrium levels?

The model considers the Upper Floridan aquifer as a continuously stirred tank reactor (CSTR) (Metcalf and Eddy, Inc., 1972, p. 395), in which injected material is mixed instantaneously throughout the Upper Floridan aquifer. Inflow to the CSTR is from three sources: (1) natural recharge through the confining bed, (2) lateral flow from upgradient areas (west of Orlando), and (3) drainage-well inflow. Outflow from the CSTR is downward to the Lower Floridan aquifer, and laterally to the downgradient areas (east of Orlando). The differential equation describing this CSTR has the following solution:

$$X_i = [B*C_i/A][1-(1-A*X_{io}/(B*C_i))*\exp(-A*T/B)]$$

where

X_i = the amount of material "i" in the CSTR,

X_{io} = the amount of material "i" in the CSTR at time = 0,

A = rate of water inflow (= rate of water outflow),

B = CSTR volume (product of aquifer length, width, thickness, and porosity), or 160,000 million cubic feet,

C_i = sum of loadings of constituent "i" in all inflow components, and

T = time.

The rate of water inflow is the sum of natural recharge from the surficial aquifer, drainage-well inflow, and lateral inflow from the Upper Floridan aquifer upgradient from the study area. Rutledge (1987) estimated that natural recharge to the Upper Floridan aquifer from the surficial aquifer system is 12 in/yr (inches per year), and that the drainage-well inflow is 7 in/yr. Lateral inflow from upgradient can be estimated from the Darcy equation. If transmissivity is 280,000 ft^2/d (feet squared per day) (Tibbals, 1981), hydraulic gradient is 0.8 ft^2/mi (square feet per mile)

(Rutledge, 1987), and thickness of the Upper Floridan aquifer is 330 feet (Rutledge, 1987), the lateral flow rate is equivalent to recharge of about 3 in/yr. This estimated water budget indicates that the drainage-well inflow (7 in/yr) is a substantial part (about 30 percent) of the total quantity of water moving through the Upper Floridan aquifer in the study area (about 22 in/yr).

Application of the CSTR equation indicates the timeframe of the buildup of a hypothetical conservative tracer, present in constant concentration in drainage-well inflow (fig. G-30). At the present time (1988), concentration of a conservative contaminant induced by drainage wells probably would not yet have reached equilibrium. If it is assumed that the drainage-well inflow rate has been proportional to the number of drainage wells, the present concentration of a conservative tracer would be about 70 percent of the equilibrium concentration (fig. G-30). The

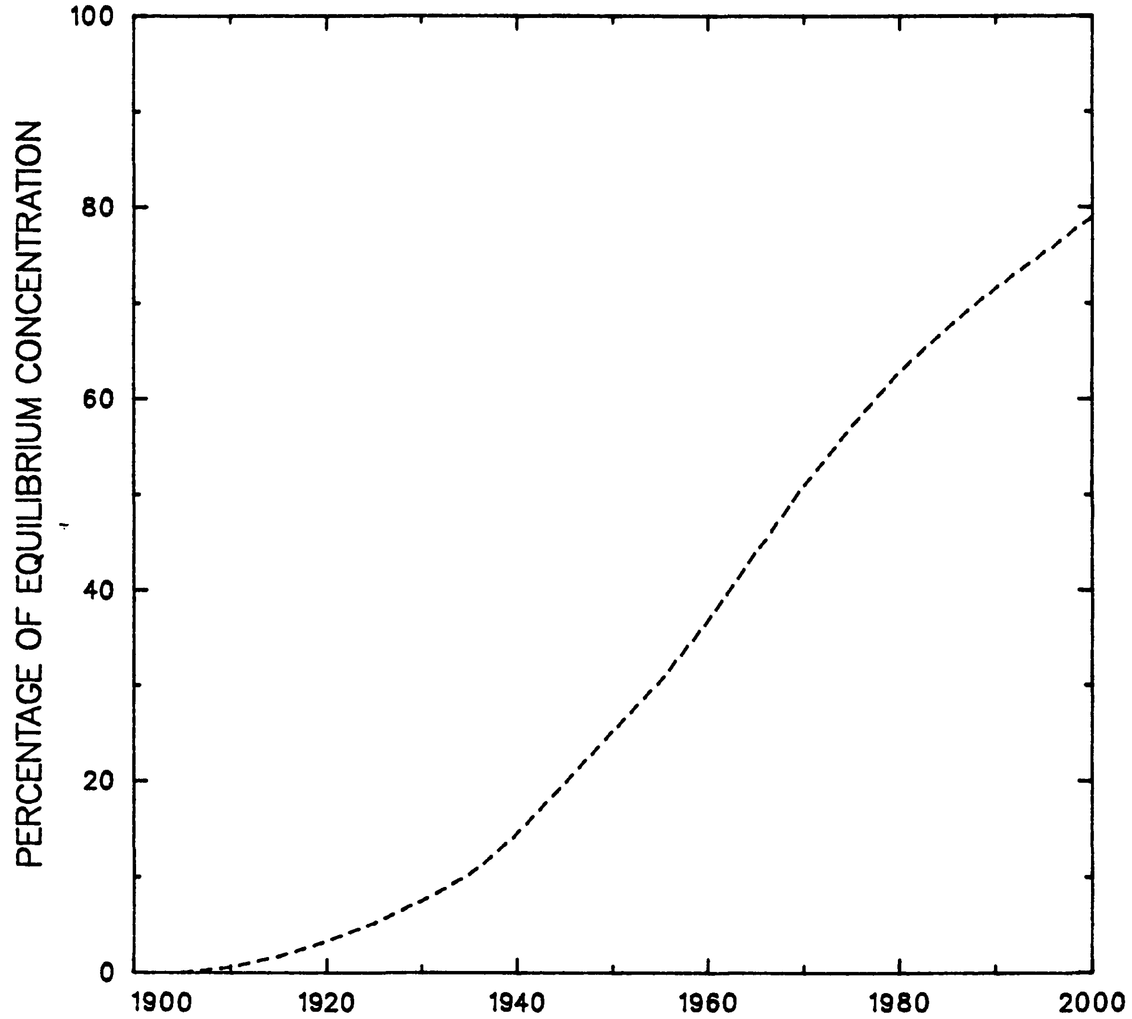

Figure G-30.—Simulated response of the Upper Floridan aquifer to injection of a conservative tracer.

equilibrium concentration would be about 30 percent of the concentration in the drainage-well inflow, assuming drainage-well inflow is 30 percent of the total inflow.

Although the potentially toxic organic compounds and trace metals in stormwater runoff induced through drainage wells are not conservative and, thus, not predictable using this CSTR conceptualization, the model does indicate that effects of drainage-well inflow on water quality in the Upper Floridan aquifer could now be apparent. However, maximum effects would not occur for several more decades.

COMPARISON OF WATER QUALITY BETWEEN CONTROL AREA AND URBAN AREA

Water-quality data from 11 wells completed in the Upper Floridan aquifer in an undeveloped (control) area in the Ocala National Forest about 50 miles north of Orlando were compared with data from 22 observation or supply wells in the Orlando area to determine if differences in water quality could be attributable to the drainage-well inflow. The samples were collected during 1984-87, generally once at each well.

The comparison of major constituent and nutrient concentrations between the two areas was made using a nonparametric statistical analysis (Wilcoxon rank-sum test). All constituents except magnesium, nitrate, and phosphorus were present in significantly greater concentrations in the urban area than in the control area, at a significance level of 0.05 (table G-7).

The greater concentrations of ammonia and total organic carbon in water from wells in the urban area probably are attributable to drainage-well inflow, because stormwater runoff and lake overflow waters generally have greater concentrations of these constituents than water in the Floridan aquifer system. German (in press) reported a median total nitrogen concentration of 0.67 mg/L (milligrams per liter) in 15 samples of inflow to 2 drainage wells, and a median total nitrogen concentration of 2 mg/L in 7 samples of stormwater runoff. German (1983, p. 52) reported a median total organic carbon concentration of 21 mg/L in stormwater runoff from a residential area, and a median total organic concentration of 26 in 18 samples of stormwater runoff from highways. These values are much greater than the median total nitrogen

Table G-7.-*Comparison of major constituents and nutrients between control area and urban area*
[Probability computed by Wilcoxon rank-sum test. All concentrations are in milligrams per liter]

Constituent	Interquartile range				Probability of no difference
	Control area		Urban area		
Calcium	26	37	38	47	0.04
Magnesium	6.6	9.2	6.6	9.4	[1].44
Sodium	3.6	5.2	8.4	12	.0006
Potassium	.6	.8	1.5	2.1	.0006
Alkalinity	80	110	110	130	.05
Chloride	6.3	9.6	12	18	.004
Sulfate	.2	5.8	5.6	19	.01
Ammonia	.02	.07	.26	.98	.0008
Nitrate	<.02	.05	<.02	<.02	[1].35
Phosphorus	.04	.06	.08	.21	[1].06
Organic carbon	.2	1.1	3.0	4.3	.0001

[1] Not significant at the 0.05 probability level.

concentration (0.05 mg/L) and median total organic carbon concentration (1.0 mg/L) for Floridan aquifer water from 9 wells in the control area. The greater concentrations of the major constituents in water from wells in the the urban area probably are not the result of the drainage-well inflow. Rather, these differences likely are the result of differences in age of water in the aquifer.

The frequency of detection of trace elements and volatile organic compounds in water from the wells was compared between the control area and the urban area (table G-8). A nonparametric comparison, Fisher's exact test, was used to make the comparison (Schweitzer and Black, 1985.) Of the five trace elements (cadmium, chromium, lead, zinc, and selenium), all but zinc were detected more frequently in the urban area than in the control area. However, the frequency of detection was not significantly different at a significance level of 0.05.

Water samples from 10 wells in the control area and 21 wells in the urban area were analyzed for volatile compounds. Thirteen volatile organic compounds were detected in at least one sample (table G-8). Benzene was the most frequently detected compound in the urban area, but neither benzene nor any of the other compounds were detected frequently enough to be statistically more likely to be present in one area than the other. However, large concentrations of benzene (65 and 210 μg/L) were present in two wells located within about 1,000 feet of one another in downtown Orlando. These large concentrations are thought to originate from a coal-gasification plant operated there in the 1940's. Runoff from

Table G-8.—*Comparison of detection frequencies of trace elements and volatile organic compounds in control area and urban area*

[Probability computed by Fisher's exact test on number of detections in each area]

Element or compound	Control, percentage detected	Urban, percentage detected	Probability of no difference
Cadmium	36	62	0.20
Chromium	18	50	.11
Lead	18	46	.15
Zinc	91	71	.06
Selenium	0	4	.70
Benzene	0	18	.20
Toluene	30	14	.26
Chloroform	20	5	.22
Ethylbenzene	10	9	.78
1,2-Trans-dichloroethylene	0	9	.47
1,2-Dichloropropane	0	5	.68
Chlorobenzene	0	5	.68
1,4-Dichlorobenzene	0	5	.68
Dichlorodifluoromethane	0	5	.68
Tetrachloroethylene	0	5	.68
Trichloroethane	0	5	.68
Trichloroethylene	0	5	.68
Vinyl chloride	0	5	.68

the plant could have reached the Upper Floridan aquifer through drainage wells or by seepage through the surficial aquifer system.

SUMMARY

The potential for contamination of the Upper Floridan aquifer by conservative constituents in drainage-well inflow probably has reached about 70 percent of the maximum potential, based on an estimated 7 in/yr inflow rate for drainage wells. Larger concentrations of ammonia and total organic carbon in the urban area, compared to the undeveloped control area, probably are the result of drainage-well inflow. Trace elements and volatile organic compounds do not occur more frequently in the urban area than in the control area. However, maximum effects of the contaminants induced by drainage wells may not occur for several more decades.

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STATISTICAL COMPARISON OF GROUND-WATER QUALITY IN FOUR LAND-USE AREAS OF STRATIFIED-DRIFT AQUIFERS IN CONNECTICUT

By Stephen J. Grady[1]

ABSTRACT

Chemical data for water samples collected from 83 wells in undeveloped, agricultural, residential, and mixed industrial and commercial areas that overlie four stratified-drift aquifers in Connecticut were statistically compared to determine if land use affects ground-water quality. Analysis of variance on the ranks of constituent concentrations and contingency-table analysis of the frequency of detections of highly censored constituents indicate that 26 water-quality variables differ at the 0.05--significance level for one or more of the land uses. For most constituents, concentrations or detections are smallest in the undeveloped areas. In agricultural areas fertilizer and pesticide use significantly increase the specific conductance and the concentration or detection frequency of calcium, magnesium, hardness, sulfate, nitrate plus nitrite, ammonia, dissolved solids, strontium, boron, lithium, methylene-blue-active substance, l,2-dichloropropane, and atrazine. A variety of nonpoint sources in residential and (or) industrial and commercial areas contribute to significantly elevated water temperature plus higher concentrations or detection frequencies of all of the aforementioned constituents (except l,2-dichloropropane and atrazine), as well as sodium, chloride, beryllium, chromium, iron, manganese, trichloroethylene, tetrachloroethylene, l,l,l-trichloroethane, chloroform, and acid- and base- neutral extractable organic compounds compared to ground-water samples from undeveloped and (or) agricultural land-use areas.

INTRODUCTION

In 1984, the U.S. Geological Survey Toxic Waste--Ground-Water Contamination Program initiated regional studies of the effects of land use on the quality of ground water in 14 areas of the Nation (Ragone, 1984). Each study endeavors to relate present ground-water quality to the hydrologic, climatic, and land-use characteristics of that region, and by so doing, to provide a basis for appraising ground-water quality in other areas of the Nation that have similar characteristics (Helsel and Ragone, 1984). The regional appraisal in Connecticut is focused on stratified-drift aquifers typical of the glaciated northeastern United States.

A primary goal of this study is to determine if the quality of water in stratified-drift aquifers can be related to the overlying land use using statistical comparisons. This paper presents the interim (1988) findings for four land-use categories common to four stratified-drift aquifers in Connecticut.

Methods

Existing data on aquifer characteristics, ground-water quality, and land use were compiled and evaluated. New ground-water-quality data were collected, emphasizing trace elements and organic compounds that may be derived principally from human sources. Nonparametric statistical procedures were used to test the hypothesis that land use affects ground-water quality. The hypothesis is accepted if significant differences in the concentrations or frequency of detection of chemical constituents exist for data segregated by land-use category. Grady and Weaver (1988) have described the methodology used to relate land use to observed water-quality conditions in stratified-drift aquifers in Connecticut.

Hydrogeology of Stratified-Drift Aquifers

Stratified-drift aquifers in the Pootatuck, Pomperaug, Farmington, and Hockanum River valleys (fig. G-31) were selected for this study because their hydrogeologic characteristics and state of development are typical of southern New England. They are composed of interbedded layers of generally well-sorted gravel, sand, silt, and clay deposited in the valleys and lowlands occupied by glacial meltwater streams and

[1] U.S. Geological Survey, Hartford, Conn.

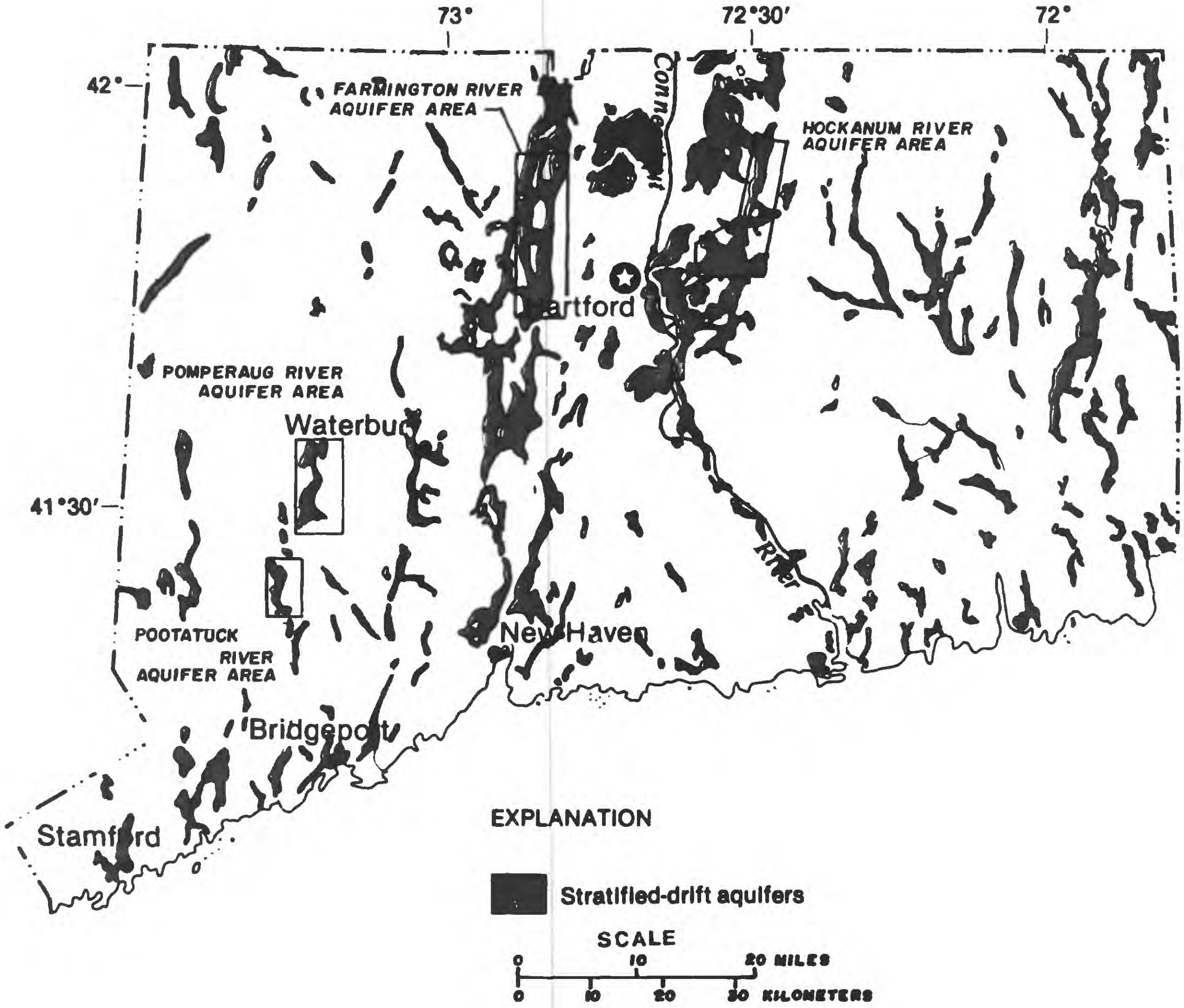

Figure G-31.—Location of stratified-drift aquifers.

proglacial lakes. The aquifers are elongate (5 to 25 miles long), narrow (200 to 5,000 feet wide), and thin (10 to 300 feet thick).

Stratified-drift deposits are unconsolidated and exhibit abrupt changes in texture that reflect their complex depositional environment. However, except for lake deposits, the stratified drift contains little silt and clay, and the sand and gravel beds are moderately to highly permeable. Hydraulic conductivity in the horizontal direction ranges from 60 to 170 ft/d (feet per day) for large parts of the aquifers (Grady and Weaver, 1988). Consequently, stratified-drift aquifers yield large quantities of water (0.07 to 2.9 Mgal/d (million gallons per day) to wells (Meade, 1978), and are the most productive aquifers in the region. Their high hydraulic conductivities, unconfined conditions, and shallow water tables also make them highly susceptible to contamination.

Natural recharge is primarily through infiltration of precipitation that falls directly on the surface of the aquifer, although some water enters as inflow from adjacent till and bedrock uplands. Mean annual recharge ranges from 19 to 25 inches (Handman, 1986 p.12). Ground-water circulation within stratified-drift aquifers is restricted, both laterally and below, by the relatively impermeable till and bedrock, and by the hydraulic boundary formed by a major perennial stream. Flow paths generally are a few hundred to a few thousand feet in length. Because ground-water velocities in the permeable sand and gravel layers are relatively high (1-3 ft/d), the residence time is short, commonly less than 1 year to several years, and at most a few decades (Grady and Weaver, 1988). Hence, ground-water quality would be expected to reflect recent land-use history.

Land Use

This study statistically compares ground-water quality data for undeveloped, agricultural, residential, and industrial and commercial land-use areas. The 1970 Connecticut Land-Use Inventory (Connecticut Office of Policy and Management, 1970) was updated using 1985 aerial photography, local land-use maps, and field reconnaissance. Land use was differentiated into categories consistent with Level II of Anderson and others (1976), then aggregated into four broad categories to facilitate statistical analysis of the limited water-quality data.

Undeveloped lands generally occupy areas along the periphery of the aquifers and often consist of public reservoir watersheds, parks, and wildlife preserves, or private woodland recreational areas. They are predominantly forested and commonly contain surface-water bodies and wetlands. Some low-density residential development, secondary roadways, and minor agricultural land use also are present in this category.

Agricultural lands generally occupy the flood plains and adjacent terraces. Tilled cultivation of silage corn and vegetables predominates, but other agricultural uses (hay and alfalfa, pasture, sod farms and nurseries, as well as golf courses and recreational fields) also are in this category. Residential land use includes sewered and unsewered areas with three housing densities--less than 1 dwelling per acre, 1 to 2 dwellings per acre, and 3 to 8 dwellings per acre. The unsewered areas typically have lower population densities and include more open land and have little industrial or commercial development. The sewered areas are more densely populated and commonly include some industrial and commercial development.

The mixed industrial and commercial land-use category contains a variety of trades and services, including gas stations, repair shops, dry cleaners, restaurants, shops, and offices, as well as light-industrial facilities for electronic-equipment manufacturing, metal plating, food processing, warehousing, and distribution. Typically, they are clustered into industrial parks, the central business districts of the towns, or along principal transportation corridors. Minor residential, institutional, open space, and other land uses are within the industrial and commercial land-use category.

Data Collection

Little historical ground-water-quality information existed for the selected aquifers (Grady and Weaver, 1988). The availability of only incomplete and largely outdated chemical analyses necessitated collection of new water-quality data. Consequently, 83 wells were installed in the Pootatuck, Pomperaug, Farmington, and Hockanum aquifers (table G-9). Each well is within or immediately downgradient from a distinct and extensive land-use area. The wells are shallow (average depth of 21.4 feet) with 2-foot screens open to the upper part of the saturated zone (average depth below the water table of 12.6 feet). All wells were constructed of 2-inch diameter, stainless-steel (type 304) casing with wire-wound screens, and were cleaned prior to installation. The wells were augered to the water table, then driven into undisturbed aquifer materials. These construction features were designed to maximize the possibility of detecting nonpoint-source pollutants that may infiltrate through the thin unsaturated zone beneath the surrounding land-use area.

Ground-water samples were collected during three sampling periods: April 1985, July through September 1986, and June through September 1987. Samples were collected using a stainless-steel and Teflon[2] positive-displacement, gas-bladder pump pressurized with an oilless air

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

Table G-9.—*Number of wells in four land-use areas of four stratified-drift aquifers in Connecticut*

Aquifer	Land-use area: Undeveloped	Agricultural	Residential	Industrial and commercial	Number of wells per aquifer
Pootatuck	0	1	2	3	6
Pomperaug	3	8	6	6	23
Farmington	7	9	8	6	30
Hockanum	5	5	6	8	24
Number of wells per land use	15	23	22	23	

compressor. Standard sample-collection and preservation methods were used (Wood, 1976; Skougstad and others, 1979; Classen, 1982; Wershaw and others, 1987).

COMPARISON OF GROUND-WATER QUALITY IN FOUR LAND-USE AREAS

Water-quality data for the 83 wells were segregated by land use and compared by use of two nonparametric statistical procedures. If 80 percent or more of the observations for a constituent were at or above the analytical detection limit, then analysis of variance (ANOVA) on the ranks of the concentration data was used to determine if water quality differed among land-use categories (Sokal and Rohlf, 1969; Conover and Iman, 1981; Helsel, 1983). If the data were strongly censored (greater than 20 percent of the observations below detection limits), then contingency-table analysis was used to compare the frequency of detection of a constituent among the four land-use areas (Conover, 1980; Helsel and Ragone, 1984). The significance level (alpha), which defines the probability of falsely detecting differences that are the result of chance rather than the tested effect, was chosen as 0.05 (equal to a 95-percent confidence level) for all statistical tests. For any well where more than one measurement of a water-quality variable was available, the median value was used.

Table G-10 identifies 26 water-quality variables that differed significantly for one or more of the land-use areas. Differences observed in the concentration or frequency of detection of these variables in relation to land use and possible nonpoint sources are shown in table G-10 and discussed in the following sections.

ANOVA Results

Results of the ANOVA on data ranks for water-quality variables that are not highly censored show that 14 variables, including most of the major inorganic constituents and physical properties, plus three trace elements, and methylene-blue-active substance (MBAS), differ significantly by land use at the 95-percent confidence level. Land-use effects are highly significant (at or above the 99.98-percent confidence level) for nine constituents--specific conductance, calcium, magnesium, sodium, chloride, nitrogen, hardness, dissolved solids, and strontium.

Where the ANOVA results indicate a significant land-use effect, a multiple-comparison procedure, Tukey's honest significant difference test (Sokal and Rohlf, 1969; Stoline, 1981), has been used to discriminate the land uses that differ. The Tukey test results are shown in table

Table G-10.—Statistical summary of data for 26 water-quality variables that demonstrate the effects of land use

[Asterisk indicates statistic estimated for censored data sets using method of Helsel and Gilliom (1985). Dashes indicate insufficient data to calculate statistic. Populations are designated by letter symbols "A", "B", "AB", "BC", or "C" based on results of ANOVA and Tukey's test or on contingency-table analysis. Sample populations sharing the same letter are not significantly diferent at the 95-percent confidence level. Units: µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; < indicates "less than"]

Water-quality variable, units, and statistic	Land-use area			
	Undeveloped	Agricultural	Residential	Industrial and commercial
VARIABLES COMPARED BY ANOVA				
Temperature, degrees Celsius				
Number of wells	14	23	20	23
Number of detections	14	23	20	23
Median	11.6	13.0	13.9	14.5
Interquartile range	3.3	1.5	2.0	2.5
Population	A	AB	AB	B
Specific conductance, µS/cm				
Number of wells	15	23	22	23
Number of detections	15	23	22	23
Median	99	170	232	342
Interquartile range	58	98	102	199
Population	A	B	BC	C
Calcium, mg/L				
Number of wells	15	23	22	23
Number of detections	15	23	22	23
Median	9.2	16	24	25
Interquartile range	8.9	15	17	25
Population	A	B	B	B
Magnesium, mg/L				
Number of wells	15	23	22	23
Number of detections	15	23	22	23
Median	1.5	4.4	3.8	4.7
Interquartile range	1.0	3.8	2.8	5.4
Population	A	B	B	B
Hardness as CaCO3, mg/L				
Number of wells	15	23	22	23
Number of detections	15	23	22	23
Median	32	71	74	79
Interquartile range	26	52	46	78
Population	A	B	B	B
Sodium, mg/L				
Number of wells	15	23	22	23
Number of detections	15	23	22	23
Median	4.6	5.6	13	14
Interquartile range	4.8	3.6	8.5	23
Population	A	A	B	B
Chloride, mg/L				
Number of wells	15	23	22	23
Number of detections	15	23	22	23
Median	7.1	12	18	27
Interquartile range	15	6.2	22	24
Population	A	A	B	B
Nitrate plus nitrite as N, mg/L				
Number of wells	14	23	22	23
Number of detections	8	22	20	19
Median	.1	3.3	3.2	2.9
Interquartile range	.6*	5.2	3.8	3.5
Population	A	B	B	B
Sulfate, mg/L				
Number of wells	14	23	22	23
Number of detections	14	23	22	23
Median	10	17	16	18
Interquartile range	6.1	16	10	11
Population	A	B	B	B
Dissolved solids, mg/L				
Number of wells	15	23	22	23
Number of detections	15	23	22	23
Median	64	113	156	229
Interquartile range	40	75	91	144
Population	A	B	BC	C
Iron, µg/L				
Number of wells	15	23	22	23
Number of detections	14	22	22	23
Median	37	9	22	29
Interquartile range	169	11	76	87
Population	B	A	AB	B
Manganese, µg/L				
Number of wells	15	23	22	23
Number of detections	15	21	22	23
Median	45	14	67	67
Interquartile range	215	35	238	128
Population	AB	A	B	B
Strontium, µg/L				
Number of wells	15	23	22	23
Number of detections	15	23	22	23
Median	37	59	91	88
Interquartile range	25	28	69	53
Population	A	B	B	B
Methylene-blue-active substance, mg/L				
Number of wells	15	22	21	22
Number of detections	15	21	21	22
Median	.03	.04	.05	.05
Interquartile range	.02	.04	.02	.02
Population	A	B	B	B

Water-quality variable, units, and statistic	Land-use area			
	Undeveloped	Agricultural	Residential	Industrial and commercial
VARIABLES COMPARED BY CONTINGENCY-TABLE ANALYSIS				
Ammonia as N, mg/L				
Number of wells	13	23	22	23
Number of detections	4	14	15	18
Median	.002*	.01	.03	.03
Interquartile range	.008*	.04*	.13*	.04
Population	A	B	B	B
Beryllium, µg/L				
Number of wells	15	23	22	23
Number of detections	1	2	3	8
Median	<.5	<.5	.19*	.36*
Interquartile range	<.5	<.5	.24*	.61*
Population	A	A	A	B
Boron, µg/L				
Number of wells	14	23	22	23
Number of detections	3	15	17	19
Median	<20	20	30	40
Interquartile range	<20	21*	20	40
Population	A	B	B	B
Chromium, µg/L				
Number of wells	15	23	22	23
Number of detections	3	1	3	6
Median	.42*	<1.0	.11*	.35*
Interquartile range	.64*	<1.0	.41*	1.05*
Population	AB	A	AB	B
Lithium, µg/L				
Number of wells	15	23	22	23
Number of detections	2	11	8	10
Median	<4.0	4.0*	3.2*	4.0*
Interquartile range	<4.0	2.1*	2.9*	4.0*
Population	A	B	AB	B
Acid- and base-neutral extractable organic compounds				
Number of wells	15	23	22	23
Number of detections	1	5	9	7
Median	--	--	--	--
Interquartile range	--	--	--	--
Population	A	AB	B	B
Atrazine, µg/L				
Number of wells	14	23	20	23
Number of detections	0	5	0	2
Median	<.1	.07*	<.1	<.1
Interquartile range	<.1	.04*	<.1	<.1
Population	A	B	A	AB
Chloroform, µg/L				
Number of wells	14	23	20	23
Number of detections	2	2	9	5
Median	<.2	<.2	.18*	.07*
Interquartile range	<.2	<.2	.31*	.29*
Population	A	A	B	AB
1,2-Dichloropropane, µg/L				
Number of wells	14	23	20	23
Number of detections	1	3	1	0
Median	<.2	<.2	<.2	<.2
Interquartile range	<.2	<.2	<.2	<.2
Population	AB	B	AB	A
Tetrachloroethylene, µg/L				
Number of wells	14	23	20	23
Number of detections	0	0	6	9
Median	<.2	<.2	.09*	.07*
Interquartile range	<.2	<.2	.16*	.29*
Population	A	A	B	B
1,1,1-Trichloroethane, µg/L				
Number of wells	14	23	20	23
Number of detections	0	2	7	7
Median	<.2	<.2	.11*	.03*
Interquartile range	<.2	<.2	.26*	.27*
Population	A	A	B	B
Trichloroethylene, µg/L				
Number of wells	14	23	20	23
Number of detections	1	0	2	6
Median	<.2	<.2	<.2	.04*
Interquartile range	<.2	<.2	<.2	.22*
Population	AB	A	AB	B

G-10 by letters (A, AB, B, BC, C) that identify each sample population. Populations that share the same letter are not significantly different.

Specific conductance and dissolved solids are particularly sensitive indicators as they are the only variables to show three distinct sample populations (designated by letters A, B, and C in table G-10). Median specific conductance and dissolved solids for industrial and commercial areas are about three times greater than for undeveloped areas, and about twice that for agricultural areas. This observation is believed to represent a progressive increase in the release of inorganic chemicals to the environment from undeveloped to agricultural to industrial and commercial land use. Specific conductance and dissolved solids in residential areas appear to be transitional between agricultural and industrial and commercial areas, but are statistically indistinguishable.

Agricultural, residential, and industrial and commercial areas have significantly greater concentrations of calcium, magnesium, sulfate, and nitrogen than undeveloped areas. In agricultural areas, the sources are most likely fertilizers and pesticides, whereas in residential and industrial and commercial areas, the most probable source is waste disposal. Sodium and chloride concentrations, however, are significantly greater in residential and industrial and commercial land-use areas. In ground water from agricultural areas, sodium and chloride concentrations are comparable to those of undeveloped areas, reflecting the general absence of septic systems and roadways that receive deicing chemicals. Median concentrations and population variance (as indicated by the interquartile range) generally are greatest in the industrial and commercial areas with respect to the major inorganic constituents, with the exception of nitrogen. The use of nitrogen fertilizers on agricultural lands increases nitrate plus nitrite concentrations in the ground water so that 13 percent of the observations exceed the 10 mg/L (milligrams per liter) National primary drinking-water regulation (U.S. Environmental Protection Agency, 1986).

Other water-quality variables including water temperature, hardness, iron, manganese, and strontium differ significantly for some land uses. Water temperature is higher in the industrial and commercial areas than in undeveloped areas. Distributions of hardness and strontium are similar to those of the calcium and magnesium--smaller in the undeveloped areas than in the other three land-use areas. Iron and manganese concentrations are greater in industrial and commercial areas (and for manganese, also in the residential areas) than in agricultural areas.

The only organic water-quality variable that differs significantly among the land uses when compared by ANOVA was MBAS. Although low concentrations of MBAS are commonly observed in ground water from natural processes, elevated concentrations may indicate the presence of synthetic organic compounds related to land use. Differences in MBAS concentrations are small but significant in agricultural, residential, and industrial and commercial land-use areas compared to the undeveloped areas. Sources for MBAS in agricultural areas may include surfactants used to disperse pesticide compounds, whereas the likely source is detergents in residential and industrial and commercial areas.

Results of Contingency-Table Analysis

Data for ammonia, most of the trace elements, and all of the organic constituents (except MBAS) are strongly censored. A categorical statistical method, contingency-table analysis (Conover, 1980; Helsel and Ragone, 1984), therefore, was used to compare the frequency of detection of these constituents in each of the land-use areas. The results of this analysis for 12 constituents that demonstrate the effects of land use are shown in table G-10. Significant differences in the percentage of wells in which a constituent was detected are indicated in a manner analogous to the Tukey test results--as letter symbols (A, AB, B). Populations for which the frequency of detection is similar have a common letter; those that are significantly different have a unique letter.

Four trace elements--boron, lithium, chromium, and beryllium--demonstrate the effects of land use. Boron was detected more frequently in ground water beneath agricultural, residential, and industrial and commercial areas than in undeveloped areas. Median boron concentrations were greatest--40 μg/L (micrograms per liter) in the industrial and commercial land-use areas. The frequency of lithium detections was similar to boron, but residential areas could not be differentiated from the undeveloped areas statistically. Anthropogenic sources of boron and lithium include inorganic fertilizers and pesticides used on agricultural lands, and the use and disposal of certain soaps, cleaners, bleach, and chemicals in residential and industrial and commercial areas. Chromium and beryllium, conversely, primarily are associated with industrial and commercial land use. These elements have applications in electronics and metallurgical processes and may enter the ground water through industrial leaks, spills, or wastewater discharges. The concentrations of chromium and beryllium in ground water from industrial and commercial areas were low (maximum observed concentrations of 5.0 and 1.5 μg/L, respectively), indicating that nearby point-source pollution is not a likely contributing factor. No land-use effect was observed for several trace elements (arsenic, cadmium, lead, mercury, and silver) commonly associated with industrial contamination.

Ammonia nitrogen was detected more frequently in agricultural, residential, and industrial and commercial areas than in undeveloped areas. Although median concentrations were small (0.01 to 0.03 mg/L) in the affected land-use areas, concentrations as great as 1.7 mg/L were measured in the industrial and commercial areas.

Four volatile organic compounds detected in a significant number of wells in residential or industrial and commercial areas, or both, were rare or absent in ground water beneath undeveloped and agricultural lands. Tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene are common industrial solvents and degreasers that also have numerous domestic uses. Concentrations as high as 150, 63, and 19 μg/L, respectively, were observed in samples from two wells in industrial and commercial areas and one well in a residential area. The fourth compound, chloroform, was detected most frequently in ground water from residential areas (45 percent of the wells) where generally low concentrations (0.2 to 1.0 μg/L) may originate from chlorination of natural water supplies that contain dissolved organic carbon or from disposal of chlorine bleach in septic systems (Thurman, 1985, p. 226).

Acid- and base-neutral extractable organic compounds were detected more frequently in the residential and industrial and commercial areas than in undeveloped areas. The gas-chromatography/flame-ionization detection analytical method used does not identify the specific compounds that are present in the sample but rather indicates the presence of unknown organic compounds that are extracted from the water samples by that particular laboratory procedure. The number of unidentified acid- and base-neutral extractable compounds that were detected in the samples varied from one to as many as seven, and concentrations ranged from 1.0 to 130 μg/L.

Only two pesticide compounds have been detected in a sufficient number of wells to demonstrate a relation to land use. The volatile organic compound 1,2-dichloropropane (DCP)--a soil fumigant used for control of nematodes and other pests in root vegetable cultivation--and the triazine herbicide atrazine--widely used for preemergence weed control in silage corn--were detected in significantly more wells in agricultural areas than in one or more of the other land-use areas. DCP was observed in 13 percent of the agricultural wells at concentrations of 0.9 to 41 μg/L. Atrazine was more frequently detected (in 23 percent of the agricultural-area wells), but at lower concentrations (0.1 to 0.2 μg/L). The greatest atrazine concentration, 2.0 μg/L, was unexpectedly detected in an industrial and commercial area where the herbicide may have been applied to control grassy weeds along a highway. The herbicides propazine, prometone, and simazine also have been detected at low concentrations in a few wells, but no significant land-use effects are evident. The carbamate pesticide compounds, including aldicarb, and the soil fumigant 1,2-dibromoethylene, that have previously been found to be widely distributed in ground water beneath potato- and tobacco-growing regions of Connecticut and neighboring States, were not detected in any of the samples from wells in this study.

CONCLUSIONS

The quality of water in four stratified-drift aquifers in Connecticut has been degraded by nonpoint-source, inorganic and organic contaminants that can be related to land use. Statistically significant differences in the concentration or frequency of detection of 26 water-quality variables have been observed in sample populations from undeveloped, agricultural, residential, and mixed industrial and commercial land uses. Concentrations, variance, and detection frequencies typically are lowest in undeveloped areas where ground-water quality is most representative of natural conditions. Use of agricultural chemicals, including inorganic and organic fertilizers and pesticides, has resulted in a significant increase in the concentration or frequency of detections of 13 water-quality variables (specific conductance, calcium, magnesium, hardness, sulfate, nitrate plus nitrite, ammonia, dissolved solids, strontium, boron, lithium, MBAS, and atrazine) in ground water beneath agricultural lands compared to undeveloped areas. Also, the frequency of 1,2-dichloropropane detection is greater in agricultural areas than in industrial and commercial areas.

A variety of sources contribute to the degradation of ground-water quality beneath residential and industrial and commercial land use. They include effluent from domestic septic systems and leaky sanitary sewer lines; runoff that infiltrates from roadways and parking lots; leaks, spills, and discharges of industrial chemicals, hydrocarbons, and wastewater; deicing chemicals used on streets and walkways; lawn and garden chemicals; and domestic animal wastes. As a result, there is a significant increase in the water temperature and the concentration or frequency of detection of 23 water-quality variables (specific conductance, calcium, magnesium, hardness, sodium, chloride, sulfate, nitrate plus nitrite, ammonia, dissolved solids, strontium, boron, lithium, beryllium, chromium, iron, manganese, MBAS, tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, chloroform and acid- and base- neutral extractable organic compounds) in residential and industrial and commercial land use compared to undeveloped and (or) agricultural areas. Statistically, there are no differences between ground water in residential and industrial and commercial areas at the 0.05-significance level except for beryllium, although median concentrations, variance, and detection frequency generally are greatest in the industrial and commercial areas.

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CHAPTER H – RESEARCH METHODS AND TECHNIQUES

(p. 485 follows)

A COMPARISON OF INSTRUMENTAL DEWATERING METHODS FOR THE SEPARATION AND CONCENTRATION OF SUSPENDED SEDIMENTS

By Arthur J. Horowitz[1], Kent A. Elrick[1], and Ronald C. Hooper[1]

ABSTRACT

A comparison involving field and laboratory trials was performed to evaluate the utility of two continuous-flow centrifuges and a tangential-flow filtration system for dewatering suspended sediments for trace-element analysis. Although recovery efficiencies for the various devices differed, the analytical results from the separated suspended sediments indicate that any of the tested units can be used effectively and precisely for dewatering. Further, the three devices appear to concentrate and dewater suspended sediments in such a manner as to be equivalent to that which could be obtained by in-line filtration.

The continuous-flow centrifuges can process whole water at an influent feed rate of 4 liters per minute; however, if (1) suspended-sediment concentrations are low (less than 30 milligrams per liter), (2) small volumes of whole water are to be processed (30 to 40 liters), or (3) suspended sediment mean grain size is very fine (less than 10 micrometers), influent feed rates of 2 liters per minute may be more efficient. Tangential-flow filtration can be used to process samples at the rate of 1 liter per minute.

INTRODUCTION

Suspended sediment plays an important role in the transport and geochemical cycling of trace elements in aquatic systems (Gibbs, 1967; Kharkar and others, 1968; Turekian and Scott, 1976; Forstner and Wittmann, 1981; Salomons and Forstner, 1984). The sampling and subsequent chemical analysis of suspended sediment has been used to locate ore deposits, to identify long- and short-term trends in water quality, and to identify sources of anthropogenic pollution.

The standard procedure for the concentration and separation of suspended sediment for subsequent chemical analysis entails in-line filtration using preweighed 0.45-5 μm (micrometer) membrane filters (see for example, Etchebar and Jouanneau, 1980; Horowitz, 1986). Commonly, this procedure is used if limited sample masses are sufficient to meet study goals or if sample numbers are limited (Horowitz, 1986). However, if large-scale studies are undertaken that entail numerous sampling sites, high sampling frequencies, or both, the analytical costs and manpower demands of in-line filtration can become prohibitive. Recent side-by-side studies comparing in-line filtration with standard laboratory centrifugation have shown that centrifugation is a viable alternative to in-line filtration for the dewatering of suspended sediment for subsequent trace element analysis (Horowitz, 1986). However, laboratory centrifugation would not be the method of choice if suspended-sediment concentrations were very low (less than 30 mg/L)(milligrams per liter), or if large sediment masses were needed, because of the large amount of water that would have to be processed.

At present, two procedures potentially could be used to process large volumes of water: flow-through centrifugation and tangential-flow filtration (Etchebar and Jouanneau, 1980; Savile, 1980; Ongley and Blachford, 1982; Merriman, 1987). Either method can be used in the field to permit sample processing and stabilization at or near the time of collection. Field dewatering would reduce sample volumes and processing delays, and also would reduce the logistical problems associated with the shipment of large-volume samples.

The purpose of this study was to evaluate the effectiveness and utility of two flow-through centrifuges: an Alfa-Laval or Sedisamp system[2] (A.L.FTC) (Ongley and Blachford, 1982), and a Westfalia system (W.FTC) (Savile, 1980); and a Pellicon (manufactured by Millipore) tangential-flow filtration system (P.TFFS) for dewatering suspended sediments for subsequent chemical analysis. The chemical concentrations

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

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

determined for material dewatered by these three devices were compared to the same constitutents determined for material dewatered by laboratory centrifugation, which already has been shown to be comparable to in-line filtration. The comparisons entailed laboratory and field trials.

ANALYTICAL METHODS

Dewatered suspended sediment slurries were refrigerated until they could be frozen usually within 8 hours of collection, and were freeze-dried prior to analysis. The freeze-dried suspended sediments were analyzed for Fe, Mn, Al, Ti, Cu, Zn, Pb, Cd, Cr, Ni, Co, As, Sb, and Se, following the procedures of Horowitz and Elrick (1985) and Elrick and Horowitz (1986). Precision and bias (usually better than ±10 percent) were monitored by replicate analyses and by the concomitant digestion and analysis of National Bureau of Standards and U. S. Geological Survey reference materials. Total organic carbon (TOC) was determined using a Leco Carbon Analyzer after pretreatment with 10-percent HCl (Wershaw and others, 1987).

Suspended-sediment concentrations in the influent and effluent samples were determined by vacuum filtering 250-mL (milliliter) sample aliquots through tared 0.45 μm membrane filters (Nuclepore). Actual masses of dewatered suspended sediments were determined by weighing in tared vials immediately after freeze drying. Practical recovery (PR) (in percent) was calculated on the basis of suspended-sediment influent concentrations and the mass of dewatered freeze-dried sediment actually recovered from the various devices, as follows:

$$\text{PR (in percent)} = \frac{\text{recovered mass of suspended sediment}}{(\text{input concentration})(\text{volume processed})}(100)$$

LABORATORY AND FIELD TRIALS

To permit direct comparison of the various dewatering techniques, all tests had to be based on a single, large, homogeneous batch of whole water that could be subsampled effectively. This was accomplished, both in the laboratory and in the field, through the use of 40-liter, churn-type sample splitters that effectively homogenize whole water samples if the particle size of the solids is less than 63 μm (Meade, 1985).

In the laboratory, homogeneous samples were prepared by placing known weights of freeze-dried, less than 63-μm sediment into known volumes of deionized water in a 40-liter churn splitter. After homogenization, and while agitation continued, the material was either passed through a dewatering device or collected for laboratory centrifugation. In the field, five 40-liter splitters were used. At each site, 160 liters of whole water were obtained with a submersible pump; the whole-water sample was prescreened through a 63-μm polyester mesh and retained in four of the five 40-liter splitters. A composite whole-water sample was then generated by withdrawing equal volume aliquots from each of the four splitters and pouring it into the fifth splitter. This procedure was repeated four times to obtain three 32-liter representative whole-water samples for field dewatering and one 36-liter sample for laboratory centrifugation. The three field devices (A.L.FTC, W.FTC, P.TFFS) processed 31 liters of whole water. Prior to dewatering, 1 liter was withdrawn from the composite churn to obtain a suspended-sediment concentration. The 36-liter sample was split into two 13- to 15-liter aliquots for subsequent laboratory centrifugation by alternately filling equal volume containers from the composite churn splitter.

The various devices/techniques were field tested at five different locations. Each site was sampled twice, on different days, and at least a week apart, to test the equipment under both high and low suspended sediment loads. The selected sites are characterized by different hydrologic and land-use conditions.

The laboratory trials were designed to develop precision measurements on each device or technique, and to examine the potential gains or losses obtained by altering the feed rates to the two flow-through centrifuges. Precision measurements were made on whole-water slurries manufactured in the laboratory by placing known weights of freeze-dried, less than 63-μm sediment in known volumes of deionized water in churn splitters. Three different materials were used to create separate slurries. Slurries of two different concentrations (50 mg/L and 200 mg/L) were dewatered by each device five times. Influent and recovered sediment concentrations were determined.

During the field trials and the laboratory precision study, the flow-through centrifuges were run at feed rates of 4 L/min (liters per minute) based on manufacturer's/designer's recommendations (Savile, 1980; Ongley and Blachford, 1982). The centrifuges were tested at slower feed rates to determine if significant gains in sediment recovery could be achieved at the expense of slower processing times. These tests were carried out using slurries of the same materials and at the same concentrations as used in the precision study.

RESULTS AND DISCUSSION

Field Trials

The churn-splitter methodology produced highly consistent suspended-sediment concentrations, the consistency of which improved as sediment concentration increased. Even in the worst case, in which the mean concentration was 31±2.6 mg/L, the relative standard deviation (RSD) was only 8.5 percent. At higher concentrations, the RSD's improved to 2.9 percent at 170 mg/L, and to 0.9 percent at 884 mg/L.

The PR data indicate that as suspended-sediment concentrations increase, recovery efficiencies (percent recovery as opposed to mass of sediment recovered) improve, regardless of the device or technique used (table H-1). On the basis of the PR calculated for each device from the 10 field trials, the data indicate that differences exist between the various techniques. If the average percentage recoveries are considered (at the 95-percent confidence limit), using mean recoveries and standard errors of the mean, calculated according to Mendenhall and Schaeffer (1973), are:

W.FTC (95±3 percent) > swing-bucket centrifuge
(91±4 percent) > fixed-anglehead centrifuge
(91±3 percent) > A.L.FTC (90±3 percent) >
P.TFFS (85±5 percent).

However, if the standard errors are considered, most of the recovery percentages overlap.

A more rigorous statistical analysis based on a test for two population means yields slightly different results depending on the confidence limit selected. At the more conservative 99 percent confidence limit, the null hypothesis that recoveries for all the techniques are equivalent holds except for those of the W.FTC and the P.TFFS systems. At the less conservative 95 percent confidence limit, recoveries for the W.FTC system were higher than those of the A.L.FTC, P.TFFS, and fixed-anglehead systems, and the recovery efficiencies for the two laboratory centrifuges were higher than those for the P.TFFS system. Considering the relatively limited size of the data set and the large number of associated sampling and analytical variables, the recovery differences for the various techniques were relatively small.

Selected chemical data for dewatered suspended sediments collected at two sites are presented in table H-1. As can be seen, sediments dewatered with the A.L.FTC indicate contamination by copper, lead, and antimony. With these exceptions, the great majority of trace element data are comparable (within the analytical errors of the methods employed) for each technique. By extension, they also are comparable to in-line filtration, because in-line filtration has been shown to be equivalent to laboratory fixed-anglehead centrifugation (Horowitz, 1986). This conclusion is based on a comparison of chemical concentrations determined from material dewatered by the fixed-anglehead centrifuge with that obtained by other techniques.

During the precision trials, slurry volumes were reduced to 16 liters to reduce processing times. In addition, after each dewatering run, the resultant concentrates were centrifuged. This added an extra step to the dewatering process and probably increased the likelihood of additional sediment losses. However, the field trials indicated that dewatered concentrates were likely to range in volume from 2 to 7 liters. This amount of fluid could represent logistical and storage problems if a large number of samples were collected, or if all the concentrates had to be shipped to a central point for later processing and analysis. A final concentrate volume on the order of 250 to 500 mL would be more manageable. Laboratory centrifugation, which was the most viable technique to effect the volume reduction, was carried out by using the large-volume (6 liters per run), swing-bucket centrifuge.

Laboratory Studies

The precision data obtained during laboratory trials indicate that all the tested techniques are highly precise (table H-2). With only one exception, precision was ±5 percent , or better. The exception was the P.TFFS system with the 50 mg/L Ducktown sample (table H-2). The imprecision resulted from the use of two sets of filters, one was entirely new and the other was used during part of the field trials.

Table H-1—*Analytical results for selected dewatered sediments*

[<, less than; conc, concentration; mg/kg, milligrams per kilogram; mg/L, milligrams per liter]

	Sediment conc. mg/L	Recovery, in percent	Concentrations mg/kg										Weight percent				
Device	Input	PR[1]	Cu	Zn	Pb	Cd	Ni	Co	Cr	As	Sb	Se	Fe	Mn	Al	Ti	TOC[2]
Sweetwater Creek at Austell, Ga. (08/18/87)																	
A.L.FTC[3]	116	84	300	490	250	0.5	48	24	105	8.3	1.4	0.5	5.1	0.30	13.6	0.55	2.8
W.FTC[4]	110	90	135	500	78	.4	44	25	99	8.3	.7	.4	5.2	.40	14.5	.54	2.8
P.TFFS[5]	112	78	135	450	66	.3	42	28	91	8.0	.6	.4	5.1	.40	14.4	.54	2.8
S.B.[6]	109	90	130	500	62	.3	40	27	93	8.4	.7	.4	5.1	.50	14.4	.53	2.6
F.A.[7]	109	92	130	540	63	.4	42	28	95	8.4	.6	.4	5.4	.50	14.8	.55	2.7
Sweetwater Creek at Austell, Ga. (08/26/87)																	
A.L.FTC	86	87	500	470	280	<1	49	28	81	9.7	2.8	.6	6.0	.40	13.6	.58	3.0
W.FTC	86	90	135	460	65	<1	44	29	82	9.1	.8	.8	6.0	.40	13.3	.55	2.6
P.TFFS	87	82	140	470	66	<1	40	31	73	9.2	.8	.6	6.1	.40	12.7	.58	3.2
S.B.	86	87	140	530	70	<1	38	32	75	9.4	.8	.6	6.2	.50	12.3	.62	2.8
F.A.	86	92	140	590	66	<1	37	31	77	9.7	.7	.6	6.2	.50	12.6	.57	2.7

Table H-1.—*Analytical results for selected dewatered sediments --Continued*

	Sediment conc. mg/L	Recoveries percent	Concentrations mg/kg										Weight percent				
Sample	Input	PR[1]	Cu	Zn	Pb	Cd	Ni	Co	Cr	As	Sb	Se	Fe	Mn	Al	Ti	TOC[2]
Broad River at Bell, Ga. (07/28/87)																	
A.L.FTC	164	84	280	300	530	1.5	44	23	85	5.0	0.8	0.4	4.9	.20	8.0	0.63	3.1
W.FTC	169	98	43	210	49	.9	41	24	91	4.8	.4	.4	5.0	.20	8.7	.61	2.8
P.TFFS	176	82	41	190	37	.8	38	31	80	4.8	.4	.4	5.1	.20	9.0	.60	2.7
S.B.	170	92	38	190	34	.4	35	24	80	5.0	.4	.4	5.2	.20	9.0	.67	2.7
F.A.	170	90	38	210	36	.5	37	27	83	4.7	.4	.4	5.1	.20	9.0	.63	2.7
Broad River at Bell, Ga. (10/01/87)																	
A.L.FTC	181	95	105	150	100	<0.5	33	20	74	5.0	.7	.4	4.4	.25	13.5	.55	2.7
W.FTC	177	98	38	135	49	<.5	30	20	72	4.7	.4	.3	4.3	.25	14.0	.57	2.7
P.TFFS	176	93	44	145	43	<.5	31	20	72	4.5	.4	.4	4.4	.30	14.5	.59	2.9
S.B.	178	88	37	140	42	<.5	30	21	73	4.8	.4	.4	4.4	.30	14.5	.62	2.6
F.A.	178	90	38	150	46	<.5	31	21	72	5.0	.4	.3	4.5	.30	14.0	.59	2.9

[1] PR - Practical recovery
[2] TOC - Total organic carbon
[3] A.L.FTC - Alfa-Laval flow-through centrifuge
[4] W.FTC - Westfalia flow-through centrifuge
[5] P.TFFS - Pellicon tangential-flow filtration system
[6] S.B. - Swing-bucket laboratory centrifuge
[7] F.A. - Fixed-anglehead laboratory centrifuge

Table H-2. —*Results for the precision studies performed on three separate samples*
[mg/L; milligrams per liter]

	Ducktown		Keg Creek		Mined kaolin	
	50 mg/L[1]	200 mg/L[2]	50 mg/L	200 mg/L	50 mg/L	200mg/L
Device	P.R.[3]	P.R.	P.R.	P.R.	P.R.	P.R.
W.FTC[4]	83±2	91±1	73±1	82±1	83±2	92±1
A.L.FTC[5]	75±3	93±1	71±3	80±2	70±3	77±3
P.TFFS[6]	71±11	89±2	67±4	80±2	60±5	88±5
Lab Centrifuge[7]	84±1	93±1	82±3	84±2	92±4	96±4

[1] 50 mg/L --measurements on influent samples indicated an input concentration of 49±1 mg/L
[2] 200 mg/L --measurements on influent samples indicated an input concentration of 196±6 mg/L
[3] P.R. --practical recovery, mean and standard deviation (see text).
[4] W.FTC --Westfalia flow-through centrifuge
[5] A.L.FTC --Alfa-Laval flow-through centrifuge
[6] P.TFFS --Pellicon tangential-flow filtration system
[7] Lab centrifuge --large volume swing-bucket centrifuge

Table H-3. —*Practical recoveries for selected samples of the flow-through centrifuges at different influent rates, in percent*

[mg/L, milligrams per liter; L/min, liters per minute]

	Ducktown					
	50 mg/L[1]			200 mg/L[2]		
Device	4 L/min	2 L/min	1 L/min	4 L/min	2L/min	1L/min
W.FTC[5]	[3]83±2	[4]ND	84±3	91±1	ND	93±0
A.L.FTC[6]	75±3	89±5	87±0	93±1	ND	91±4
	Keg Creek					
W.FTC	73±1	81±0	80±1	82±1	ND	82±2
A.L.FTC	71±3	80±5	83±2	80±2	ND	82±2
	Mined kaolin					
W.FTC	83±2	96±1	97±1	92±1	98±0	98±1
A.L.FTC	70±3	87±1	92±1	77±3	92±0	93±0

[1]50 mg/L - measurements on influent samples indicated an input concentration of 49±1 mg/L

[2]200 mg/L - measurements on influent samples indicated an input concentration of 200±6 mg/L

[3]83±2 - mean and standard deviation of recoveries in percent from five separate runs for 4 L/min and two separate runs for 2 L/min and 1 L/min.

[4]ND - not determined because no significant difference was detectedbetween 4-L/min and 1-L/min influent rates

[5]W.FTC - Westfalia flow-through centrifuge

[6]A.L.FTC - Alfa-Laval flow-through centrifuge

The old set (used three of the five times) had a PR of 80±2 percent, while the new set had a PR of 57.5 ±4 percent; this disparity produced the combined PR of 71 + 11 percent (table H-2). These results indicate that a P.TFFS filter stack should be conditioned by passing a quantity of whole water through the system prior to initial field use. Subsequent precision runs, using both sets of filters support this conclusion inasmuch as the latter runs show a more typical precision of ±5 percent (table H-2).

Designer or manufacturer recommendations for both the A.L.FTC and the W.FTC systems suggest a whole-water influent rate of 4 L/min (Savile, 1980, Ongley and Blachford, 1982). To investigate the effect of reduced influent feed rates on the PR of the continuous-flow centrifuges, a series of comparative studies were carried out using the same three samples and the same two concentration ranges (in 16-liter volumes of deionized water) that were used during the precision studies. Data on recoveries at 4 L/min were already available from the precision studies (table H-2). A series of dewatering runs (two per sample per concentration) were made at an influent feed rate of 1 L/min. No further work was done for that device/sample type/concentration unless a significant improvement in PR occurred compared to the 4-L/min run. If an improvement in PR was observed, a second set of runs were made at 2 L/min (table H-3). The data show that improvements in PR occurred in 7 out of the 12 flow-rate-study segments when influent feed rates were reduced to 2 L/min. A reduction in feed rates produced the greatest effect on PR at low suspended-sediment concentrations; five of the seven improved cases occurred for the 50-mg/L concentrations (table H-3). Slower feed rates also were important when the mean grain size of the suspended sediment was very small (2 μm), regardless of concentration, as shown in the results for all the mined kaolin runs (table H-3). In all cases, where slower feed rates led to improved recoveries, maximum recoveries for the W.FTC system were achieved when the rate was reduced to 2 L/min. For the 200-mg/L concentrations, the A.L.FTC system also achieved maximal recoveries at feed rates of 2 L/min (table H-3). However, for two of the three 50-mg/L concentrations, the A.L.FTC system did not reach maximum efficiency until the feed rate dropped to 1 L/min. These results indicate that unless a user has prior knowledge of suspended-sediment concentrations or mean grain size before sampling and dewatering, it may be prudent to use feed rates of 2 L/min for the continuous-flow centrifuges.

CONCLUSIONS

On the basis of testing and comparisons carried out during this study, and despite some differences in recovery efficiency, any of the three devices tested could be used successfully for the initial dewatering of suspended sediments for subsequent trace-element analysis (except the A.L.FTC for copper, lead, and antimony). If large programs are undertaken that entail numerous samples, a second dewatering step may be required, using standard laboratory centrifugation, to reduce the initial concentrate volumes down to a more manageable size. Experience gained with the various devices in both the laboratory and the field indicates that flow-through centrifugation probably is simpler and faster to use than tangential-flow filtration. Although subject to the disadvantages of comparatively long processing times and large initial concentrate volumes, tangential-flow filtration systems, because of their portability, may be easier to use than flow-through centrifuges in rough terrain where access by powered vehicles is limited.

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(p. 495 follows)

COMPARISON OF WELL-PURGING CRITERIA FOR SAMPLING PURGEABLE ORGANIC COMPOUNDS

By Jacob Gibs[1] and Thomas E. Imbrigiotta[1]

ABSTRACT

Ground-water-sampling protocols generally recommend that a well be purged prior to sampling. This recommendation is based on the assumption that the water quality of the water standing in the casing is not the same as that in the aquifer. Two criteria that generally have been used to determine when a well has been purged sufficiently to yield "representative" water-quality samples are (1) flushing a recommended number of casing volumes, usually a minimum of three, and (2) flushing the well until field water-quality characteristics--temperature, pH, specific conductance and dissolved oxygen--in the purge water are stable. The primary purpose of this study was to evaluate the effectiveness of these criteria in sampling for purgeable organic compounds.

The results indicate that (1) purgeable organic compound concentrations stabilized when three casing volumes were purged in only 55 percent of the cases evaluated in this study, and (2) purgeable organic compound concentrations did not consistently follow the temporal variation of, nor stabilize at the same time as, the measured field water-quality characteristics. The conclusion from these data is that neither of the previously recommended criteria for purging a well can be reliably applied to collecting a "representative" sample for purgeable organic compounds.

INTRODUCTION

Ground-water-sampling protocols generally recommend that a well be purged prior to sampling (New Jersey Department of Environmental Protection, 1986; U.S. Environmental Protection Agency, 1986). This recommendation is based on the assumption that the water quality of the water standing in the well casing is not "representative" of that in the aquifer. This may be particularly true when sampling for purgeable organic compounds (POCs), because POCs in well water can (1) volatilize into the well-head space, (2) partition between the aqueous phase and the well casing and screen materials, or (3) be transformed into different compounds or reduced in concentration by biological activity. Another consideration in obtaining a "representative" sample is that the sample constituent concentrations and properties should be reproducible so that replicate samples can be collected. This aspect is gaining increased emphasis with the requirement of quality-assurance plans as part of ground-water sampling protocols (New Jersey Department of Environmental Protection, 1986; U.S. Environmental Protection Agency, 1986). Given the necessity of purging a well prior to sampling, it is important to have some basis for determining the length of time and volume of water that needs to be flushed from a casing.

Two criteria that generally have been used to determine when a well has been purged sufficiently to yield "representative" water-quality samples are (1) flushing a recommended number of casing volumes, usually a minimum of three, (Schuller and others, 1981; New Jersey Department of Environmental Protection, 1986; U.S. Environmental Protection Agency, 1986; Robin and Gillham, 1987; Unwin and Maltby, 1988), and (2) flushing the well until traditional field water-quality characteristics--temperature, pH, specific conductance and dissolved oxygen--in the purge water become stable (Wood, 1976; Claassen, 1982; Wilson and Rouse, 1983; Barcelona and others, 1985; New Jersey Department of Environmental Protection, 1986.)

This paper presents the results of the study to determine which of two criteria would provide a more representative sample for POC analysis: purging a well until the field water-quality characteristics stabilized or removing an arbitrary three-casing volumes. A secondary goal of the study was to determine whether two other field measurements--ultraviolet (UV) absorbance at 254 nm (nanometers) and measurement of chloride-ion concentration--could be used to indicate POC concentration stabilization more

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

accurately than traditional field water-quality measurements. A final goal was to determine if overpurging of wells occurred (that is, if a well could be pumped too long).

METHODS

Wells at 6 sites were sampled during a total of 10 purging experiments in this study. Two experiments were conducted at four of the six sites. Because all the wells were screened in unconsolidated sand-and-gravel aquifers, they could be pumped by an electric submersible pump continuously with the drawdown always less than 2 feet. Additionally, in 9 out of the 10 experiments, the pumping rate was matched to the casing volume so that 10 minutes of pumping represented purging one to two casing volumes.

The standard field water-quality measurements--temperature, pH, specific conductance, and dissolved oxygen--were measured in the field according to procedures described by Wood (1976). Either individual meters or a multiparameter instrument was used. The probes were located in a flow-through chamber connected to the discharge line of the submersible pump to make these measurements.

Grab samples were collected from the purged water for two other field measurements--chloride and UV absorbance. Chloride was investigated because it is a more conservative water-quality characteristic than specific conductance or pH. The latter two properties may be significantly affected by changes in dissolved-gas equilibria during sampling; chloride concentrations are not similarly affected. UV absorbance at 254 nm is characteristic of aromatic organic compounds (Allinger and others, 1971). Therefore, this measurement was tested as an indicator of the organic content of the purge water. Samples for this measurement were filtered through a 0.45-μm (micrometer) filter prior to measuring the UV absorbance.

All POC samples were concentrated by the purge and trap technique and analyzed for purgeable priority pollutant concentrations by gas chromatography with the following detectors; either a photoionization detector in series with a "Hall" [2] electrolytic conductivity detector (J.A. Kammer and Jacob Gibs, 1989) or a mass spectrometer. This corresponds to U.S. Environmental Protection Agency methods 601 and 602, or 624, respectively (Longbottom and Lichtenberg, 1982).

All field water-quality measurements and POC concentrations were tabulated and plotted as a function of time and of the number of casing volumes removed for each well purging experiment. The casing volume was defined as the volume from the top of the water column before pumping begins, to the bottom of the casing, including the screened part and the tail piece or sediment trap, if one exists. To determine when stability occurred, the change between successive values of a measurement per unit time or casing volume was calculated. When the absolute value of this rate of change in a measurement fell below a predetermined maximum acceptable rate of change for three consecutive observations, the water-quality measurement was considered to have attained stability. The maximum acceptable rate of change was defined as twice the precision of the instrument (usually coefficient of variation) over a 10-minute period. The average time between the first and second of the three consecutive observations was designated as the time to stability; this value was converted into number of casing volumes to stability.

Medians were used to summarize the data because the data set was not normally distributed, and contained several "greater than" values. A two-factor analysis of variance on ranks was used to compare the median number of casing volumes to reach a stable measurement for chlorinated alkane and alkene POCs, relative to aromatic POCs, and for field measurements, relative to all POCs at a statistical significance level of 95 percent (Zar, 1974). Both analyses had purging experiment as the second factor.

RESULTS AND DISCUSSION

Comparison of Well-Purging Criteria

During most of the well purgings, the values of field water-quality measurements initially decreased sharply, and then gradually reached a stable value as purging progressed. As an example, the data for the Gibbstown, N.J. no. 7- I well are presented in figure H-1. Water temperature, pH, and specific conductance all followed this decreasing pattern during purging. However,

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

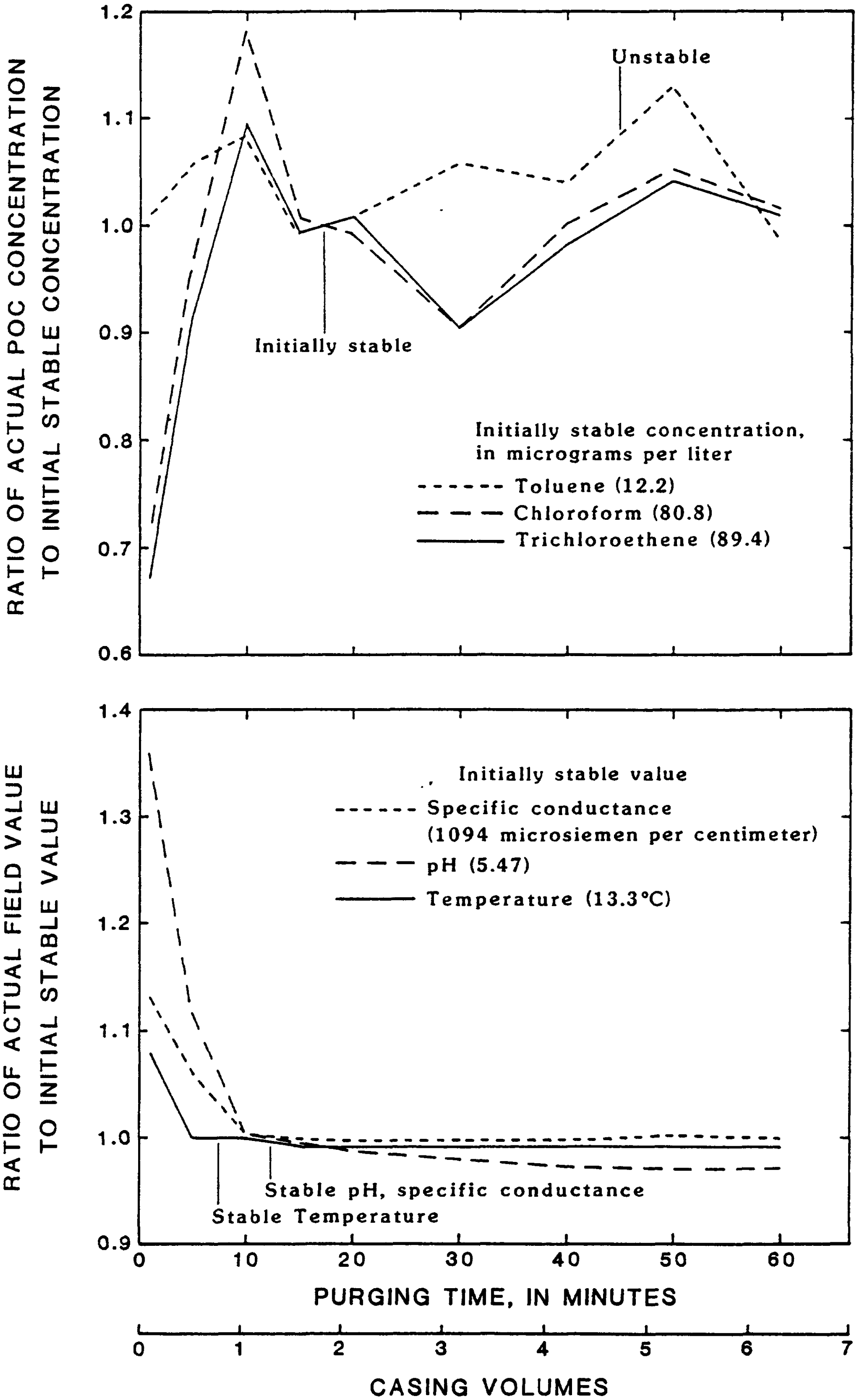

Figure H-1.—Relative variation of selected water-quality measurements during purging of the Gibbstown no. 7-I well.

the three POCs plotted, chloroform, trichloroethylene, and toluene, do not vary in the same fashion. This was typical of the results found throughout this study. In addition, all the field water-quality measurements typically stabilize before all the POC concentrations stabilize.

The number of casing volumes removed to achieve stability for all field water-quality characteristics and POC concentrations are summarized in table H-4. The median number of casing volumes to stable POC concentration for the aromatic POCs was 3.25, whereas that of the chlorinated alkane and alkene POCs was 3.0. A two-factor analysis of variance by ranks (Zar, 1974) determined that the medians of the two classes of POCs were not significantly different and, thus, could be grouped together. Another two-factor analysis of variance by ranks then determined that the median number of casing volumes to stability for field water-quality measurements, 1.7, and all POC concentrations, 3.0, were significantly different. Therefore, the onset of stable values for field water-quality measurements did not reliably predict the onset of stable POC concentration values during purging.

It was determined that 90 percent of all field water-quality measurements became stable at less than or equal to three casing volumes removed during purging. However, only 55 percent of all POC concentrations became stable at less than or equal to three casing volumes removed during purging. Thus, the use of three casing volumes works with a reasonable degree of reliability for field water-quality measurements but only about half the time for POC concentrations. The differing numbers of casing volumes before stabilization occurred at the six wells in this study appear to be related to the hydrogeologic characteristics of each well location, the well construction, and the nature and extent of the POC contamination.

At three of the four sites where duplicate experiments were run, the overall medians for each duplicate experiment were not statistically different. The two experiments at the Picatinny, N.J., site were statistically different because the pumping rate used in each differed by a factor of approximately 10. This finding indicates that replicate purgings of a well will result in a reproducible median number of casing volumes to stable measurements for all water-quality measurements and concentrations during purging in unconsolidated sand-and-gravel aquifers, if a well is purged at a similar pumping rate and the same criteria of field water-quality measurement stability are used.

Evaluation of Other Field Measurements as Indicators of Stability

The number of casing volumes removed prior to stabilization of chloride concentrations was not similar to those needed for stabilization of POC concentrations and thus no better than the other field water-quality measurements for indicating stabilization of POC concentrations. Chloride ion is not affected by the presence of ferrous iron, and, therefore, may be a better indicator of stable water quality than specific conductance when determined for water in wells with steel casings.

The UV absorbance at 254 nm stabilized at casing volumes (1.7 and 3.5) very close to those for the aromatic compounds, benzene, toluene,

Table H-4.—*Median number of casing volumes to a stable measurement for the field water-quality characteristics and purgeable organic compounds.*

[$\underbrace{\qquad}$ not significantly different at 95-percent confidence level;
( ) = number of data points.]

Field measurements	Purgeable organic compounds	
	Chlorinated alkanes and alkenes	Aromatics
1.70 (43)	3.00 (49)	3.25 (18)
	$\underbrace{\qquad\qquad\qquad}_{3.00\ (67)}$	

ethylbenzene, and chlorobenzene (median = 1.7 and 3.5) during the two purging experiments at the Logan Township, N.J., well. The total purgeable aromatic concentration exceeded 300 $\mu g/L$ (micrograms per liter) and the associated UV absorbance exceeded 0.490. In contrast, during the first purging experiment at the Camden, N.J., well, UV absorbance did not stabilize at a similar number of casing volumes (2.1) as it did for chlorobenzene (5.9). However, the total purgeable aromatic concentration was only 1.8 $\mu g/L$ and the associated UV absorbance was 0.066. Therefore, the usefulness of UV absorbance as a POC indicator appears to have limitations at concentrations less than 150 $\mu g/L$.

Overpurging

In this study, overpurging occurred when a measurement achieved a stable value during purging, and then as purging continued, the value subsequently changed more than the maximum acceptable value. This occurred 11.6 percent of the time for field water-quality measurements and 34.3 percent of the time for POC concentrations. Thus, overpurging occurred almost three times more frequently for POC concentrations than it did for the field water-quality measurements. However, if one POC at a well was overpurged, it did not indicate that other POCs were similarly affected. An example of such a case is shown in figure H-1. Toluene, which stabilized after 1.75 casing volumes were purged, became unstable after 4.7 casing volumes were purged, while the chloroform and trichloroethylene remained stable.

SUMMARY

Monitoring field water-quality measurements for stability is not a reliable indicator of when to collect a representative sample for POCs. Purging three casing volumes stabilizes field water-quality measurements 90 percent of the time, but stabilizes POC concentrations only 55 percent of the time. Thus, neither of the two purging criteria, monitoring for stable field water-quality measurements and purging three casing volumes, evaluated in this study can be applied reliably to sampling for POC.

Replicate purgings of the same well using approximately the same pumping rate and criteria of monitoring field water-quality measurements until stability, resulted in a reproducible number of casing volumes to sampling. The different numbers of casing volumes purged before water-quality measurements stabilized at the six wells in this study appear to be related to differences in hydrogeologic characteristics, well construction, and in the nature and extent of the POC contamination.

Although chloride was found to be a reliable indicator of stability of field water-quality measurements and may be advantageous to use when sampling wells with steel casings, it was not a reliable indicator of POC stability. UV absorbance at 254 nm was found to be a reliable indicator of stability of aromatic POC concentrations during purging. However, its disadvantages are that samples must be filtered before measurement and the method is not sensitive to total aromatic POC concentrations less than 150 $\mu g/L$.

Overpurging of wells was documented. Well overpurging occurs much more frequently for POC than for field water-quality measurements (34.3 and 11.6 percent of the time, respectively). Overpurging of a well might cause a loss of stability in concentration of one POC, but not necessarily others in the same samples. The occurrence of overpurging was not predictable.

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SAMPLING, FRACTIONATION, AND DEWATERING OF SUSPENDED SEDIMENT FROM THE MISSISSIPPI RIVER FOR GEOCHEMICAL AND TRACE-CONTAMINANT ANALYSIS

By J.A. Leenheer[1], R.H. Meade[1], H.E. Taylor[1], and W.E. Pereira[1]

ABSTRACT

The Mississippi River and its major tributaries were sampled at 17 sites located just upstream from St. Louis, Missouri, downstream to New Orleans, Louisiana, during two sampling trips in July-August 1987 and November-December 1987. Approximately 100 liters of water and suspended sediment were representatively sampled at each site in a Lagrangian sampling pattern. Suspended sediment was separated by size at each site into sand by sieving, silt was separated by gravitational settling or continuous-flow centrifugation, and clay was separated by tangential-flow ultrafiltration. Various aliquots of the water-sample and suspended-sediment-size fractions were split among 17 researchers for determinations of suspended-sediment concentration, particle and mineralogical characteristics, radionuclide content, and organic geochemistry of natural constituents. Sampling and fractionating equipment was custom fabricated to ensure compatibility and prevent sampling contamination for all analyses. Recoveries of suspended sediment ranged from 72 to 94 percent; recovery was directly related to suspended-sediment concentration. The clay fraction had 1.5 to 5 times the organic-carbon content of the silt fraction; the carbon-to-nitrogen ratio of the clay fraction was 6 to 9, whereas the ratio of the silt fraction was 9 to 14.

INTRODUCTION

The Mississippi River research project is composed of a number of projects with diverse objectives. Robert Meade, Herbert Stevens, and John Moody are studying the movement and storage of sediment in the Mississippi River. Howard Taylor, John Garbarino, and Terry Brinton are studying the transport of trace metals in water, sediment, and biota. Wilfred Pereira, Colleen Rostad, and Tom Leiker are investigating the partitioning of trace organic contaminants among water, sediments, and biota. Terry Rees and James Ranville are investigating the chemistry and physics of colloid interactions. Robert Stallard is determining the inorganic geochemistry and nutrient chemistry of water and sediment; Jerry Leenheer, Ted Noyes, and Patricia Brown are studying the organic geochemistry of the dissolved and colloid fractions of organic matter in the river. The objective of this paper is to relate how a program for sampling, fractionating, and dewatering of suspended sediment was devised to be compatible with the research objectives of each project.

SAMPLING OF WATER AND SEDIMENT

The basic sampling approach that was followed involved repeated trips, which began upstream from St. Louis, Mo., to collect samples from cross sections of the main stem and principal tributaries, in downstream sequence to New Orleans, La. (fig. H-2). Two such trips, each requiring 3 to 4 weeks, have been completed to date (April 1988) – July-August 1987 and November-December 1987. Additional trips are planned about two times each year for 4 to 5 years. Trips will be timed so that samples are collected at different periods of the annual flow hydrograph. With such a Lagrangian sampling pattern, and with additional 9 to 12 seasonal samplings spaced more or less evenly through the year, data can be obtained that describe average seasonal and annual routings, water budgets, sediment, other constituents, and contaminants.

An important sampling consideration was the total quantity of suspended sediment required for analysis by the various research projects. Five grams of suspended sediment were sufficient for the combined needs of all research projects, with the exception of the project studying organic contaminants; this project needed 50 grams for solvent extraction of organic contaminants. Recovery of 5 grams of suspended sediment for study required the collection of about 100 liters of river water, based on the estimated minimum

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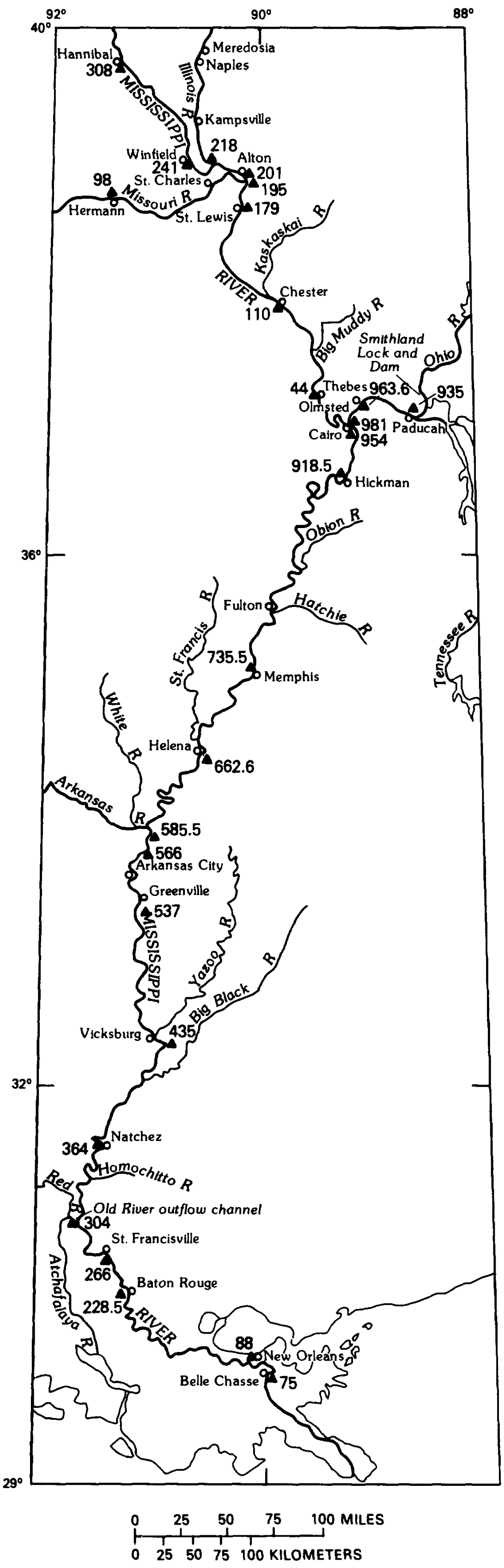
[1] U.S. Geological Survey, Denver, Co.



EXPLANATION

Stations sampled/measured from R/V **Acadiana** during sampling trips of July-August 1987 and November-December 1987

Station name	**River mile**[2]
Mississippi River near Winfield, Mo.	UM 239.2
Illinois River below Meredosia, Ill.	IL 67.2
Mississippi River at Hartford, Ill.	UM 197.7
Missouri River at Hermann, Mo.	MO 97.9
Missouri River at St. Charles, Mo.	MO 28.1
Mississippi River at St. Louis, Mo.	UM 179.3
Mississippi River at Chester, Ill.	UM 108.9
Mississippi River at Thebes, Ill.	UM 43.9
Ohio River below Smithland Locks and Dam, Ill.-Ky.	OH 919.2
Ohio River at Olmsted, Ill.	OH 965.0
Mississippi River below Hickman, Ky.	LM 916.8
Mississippi River at Fulton, Tenn.	LM 777.3
Mississippi River at Helena, Ark.	LM 663.9
White River at mile 11.5, Ark.	WH 11.5
Arkansas River at mile 55.9, Ark.	AR 55.9
Mississippi River above Arkansas City, Ark.	LM 566.0
Yazoo River at mile 10, Miss.	YZ 10.0
Mississippi River below Vicksburg, Miss.	LM 433.4
Old River Outflow Channel near Knox Landing, La.	---
Mississippi River near St. Francisville, La.	LM 266.4
Mississippi River below Belle Chasse, La.	LM 73.1

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[2] UM, Upper Mississippi River miles measured upriver of confluence with Ohio River.

IL, Illinois River miles measured upriver of confluence with MississippiRiver (UM 218.0).

MO, Missouri River miles measured upriver of confluence with Mississippi River (UM 195.3).

OH, Ohio River miles measured downriver of Pittsburgh, Pa. (Ohio-Mississippi confluence is at Ohio River mile 981.5 and Lower Mississippi River mile 953.8).

LM, Lower Mississippi River miles measured upriver of Head of Passes, La.

WH, White River miles measured upriver of confluence with Mississippi River (LM 598.8).

AR, Arkansas River miles measured upriver of confluence with Mississippi River (LM 581.5).

YZ, Yazoo River miles measured upriver of confluence with Mississippi River (LM 437.2).

Figure H-2. – Mississippi River, major tributaries, and sampling locations.

suspended-sediment concentrations. The sampling procedure follows the method developed in the large rivers of South America (Nordin and others, 1983; Meade, 1985; Richey and others, 1986) for collecting large-volume, discharge-weighted samples. For the Mississippi River research project, further modifications were added to avoid contamination and to separate several size fractions of the suspended matter.

Essential sampling equipment included a boat, hydraulic winch, collapsible-bag sampler, and microwave positioning equipment. The boat used was the research vessel *Acadiana*, which is 57 feet in length, has a draft of 4 feet, and is owned and operated by Louisiana Universities' Marine Consortium (LUMCON). With the addition of a trailer-type van to its open fantail, *Acadiana* has two compact laboratories and sleeping accommodations for two crew and seven scientists. The hydraulic winch and collapsible-bag sampler enable collection of discharge-weighted, depth-integrated samples by the equal-width-increment (equal-transit-rate) method. Each river cross section is sampled at 10 to 30 equally spaced verticals – as few as 10 verticals in smaller tributaries and 30 or more verticals in main-stem cross sections. The hydraulic winch was designed by C.C. Cranston (now retired from the U.S. Geological Survey) for use on the Columbia River. The winch design enables sensitive control and consistency in the vertical integrating velocity. The collapsible-bag sampler, modified after the original design by Stevens and others (1980), enables integrated samples to be collected throughout the full range of depths in the river. It consists of an 8-liter plastic outer support bottle, which is perforated on its base and shoulders so that water can surround the outside of the collapsible bag. The bag is held in place in the bottle by screwing on a threaded cap, which also is a support for the isokinetic sampling nozzle. In the configuration used, the bag sampler can collect a volume of about 6.5 liters without overfilling. Positioning across the river and maintaining fixed positions during sampling are accomplished by continuous references to microwave positioning equipment that is placed on the riverbanks at the beginning of each day's sampling.

The principal modification of this procedure to meet the needs of the Mississippi River research project involved finding materials for sampling and equipment for sample processing that had appropriate chemical and physical properties required for trace-organic, trace-metal, and suspended-sediment analyses. Various hydrocarbon rubbers and plastics were unsuitable for trace-organic analyses because of release of plasticizers and stabilizers into water samples. Common metals and alloys were unsuitable because of the potential for contamination of the samples by various metals.

The most critical material need was a flexible and durable bag for the depth-integrating sampler developed by Stevens and others (1980). Aluminum-coated Mylar[3], linear polyethylene, and fluorinated ethylene propylene (FEP) Teflon[3] were evaluated. The aluminum-coated Mylar bags were eliminated from consideration because they did not have sufficient flexibility for the bag sampler. The linear polyethylene and FEP Teflon bags were evaluated for sorption of and contamination by trace-organic constituents by equilibrating the bags with water solutions that contained 250 μg/L (micrograms per liter) of d_9-acridine, d_{10}-biphenyl, d_8-dibenzothiophene, d_4-1,4-dichlorobenzene, d_5-phenol, and d_{10}-pyrene.

The linear polyethylene bag contaminated the water solutions with plasticizers and sorbed substantial quantities of the organic contaminant standards as determined by gas chromatography-mass spectrometry (GC-MS) analyses. The FEP Teflon bag indicated no substantial sorption or contamination; therefore, it was selected as the material of choice for the bag sampler. Bag thicknesses of 0.050, 0.025, and 0.012 mm (millimeters) were evaluated for flexibility and durability in the depth-integrating sampler; the 0.025-mm bag thickness had the best combination of flexibility and durability, which was maintained even at the near-freezing water temperatures that occurred during the second sampling trip (November- December 1987). The FEP Teflon bag also had exceptional nonstick characteristics, which enabled suspended sediment to be transferred more efficiently than with the linear polyethylene bag. The isokinetic sampling

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

nozzles for the bag sampler also were fabricated from FEP Teflon.

PROCESSING THE SAMPLE

As soon as the sampler bottle was brought aboard the boat at each vertical, it was rinsed with deionized water to remove the sand particles and detritus that may have adhered to the outside of the collapsible bag. The sample of water and suspended sediment then was poured into a graduated glass cylinder so that the volume could be measured and recorded. As part of this step, the sample was poured through a nickel-wire 63-μm (micrometer) sieve to remove all sand. The collapsible bag then was removed from the sampler bottle, and its remaining contents were washed through the sieve and into the glass cylinder. As the sampling progressed, the suspensions that passed through the sieve were composited into 20-liter churn splitters (usually three churn splitters per composite). At the end of the sampling period, proportional fractions from the 20-liter splitters were combined into 8-liter splitters from which aliquots were drawn for various analyses.

During the first two sampling trips, two separate composite samples were collected at each cross section. Separate sampling bottles, collapsible bags, sieves, graduated cylinders, and churn splitters were used to completely separate the two composites. Samples collected as verticals 1, 3, 5, and so on, were designated "composite A," and samples collected at verticals 2, 4, 6, and so on, were designated "composite B." The separation of composites served two purposes. First, the samples for one composite could be processed (usually the most time-consuming step in the sample-collection procedure) while those for the other composite were being collected. Second, comparisons of aliquots from the two composites allowed assessment of the sampling error for constituents such as suspended sediments (fig. H-3).

FRACTIONATION AND DEWATERING OF SUSPENDED SEDIMENT

The procedures used to separate water and suspended sediment for the November-December 1987 sampling trip are shown in the flow chart of figure H-4. Gravitational settling in 46-liter glass carboys was used to separate the silt and clay fractions for the July-August 1987 sampling trip, and continuous-flow centrifugation is planned for use to separate clay from silt on the May-June 1988 sampling trip.

The nickel-wire sieve to separate sand was a compromise solution after considering sieves made of polypropylene, stainless steel, Teflon, glass fiber and titanium. Polypropylene sieves increased the adsorption and contamination problem for trace-organic solutes, and stainless steel was unsuitable for trace-metal studies. Teflon sieves were tested, but water would not flow through the sieve because of the hydrophobic nature of Teflon. Glass-fiber sieves were unsuitable because the fibers deformed during use, giving nonuniform pore size. Titanium-wire sieves were unavailable in 63 μm size because small-diameter titanium wire cannot be fabricated. The nickel-wire sieve was selected because it contaminated the water sample with only a single element, and had sturdy mechanical characteristics. The sieve was Heleoarc welded into a stainless-steel ring holder, 76.2 mm in diameter, which was coated with FEP Teflon.

The churn splitters were custom fabricated from stainless-steel vessels; the 20-liter splitter dimensions were 311 mm in diameter by 330 mm in height. The dimensions of the 8-liter-churn splitter were 203 mm in diameter by 228 mm in height. The close-fitting steel cover and the churn assembly were fabricated to conform closely with those used in the standard U.S. Geological Survey polycarbonate splitter.

All steel surfaces that contacted water were coated with FEP Teflon, and an FEP-Teflon pushbutton valve near the bottom of the vessel was used to withdraw the samples during churning.

The whole-water aliquots provided to the various projects are given in footnote 1 of figure H-4. The aliquots that R.H. Meade received were filtered, dried, and weighed; when the sand weight was added, a total suspended-sediment concentration was determined.

During the July-August 1987 sampling trip, settling, tangential-flow ultrafiltration, and XAD-8 column-adsorption steps (composite B, in figure H-4) were performed in a land-based mobile field laboratory that rendezvoused with the *Acadiana* near the sampling sites. The composited samples in 46-liter glass carboys (400 mm in diameter by 400 mm in height) were transferred from the boat to the laboratory, and silt was permitted to settle overnight (6-12 hours);

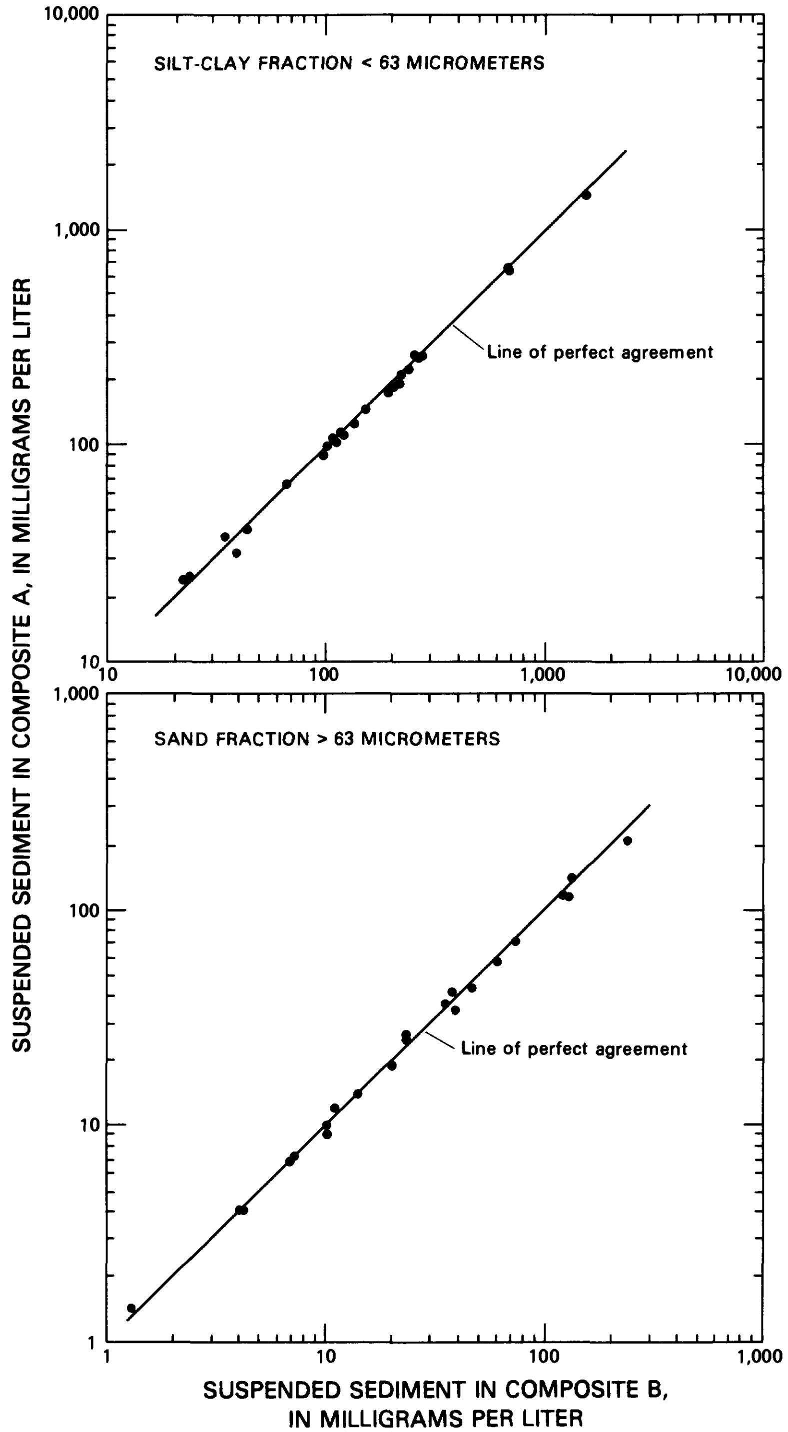

Figure H-3.—Comparisons of concentrations of suspended silt and clay and suspended sand in alternating composite samples collected simultaneously in cross sections of the Mississippi River and principal tributaries, July-August and November-December 1987. Between composites, silt-clay concentrations usually agreed within 3 percent, and sand concentrations usually agreed within 5 percent.

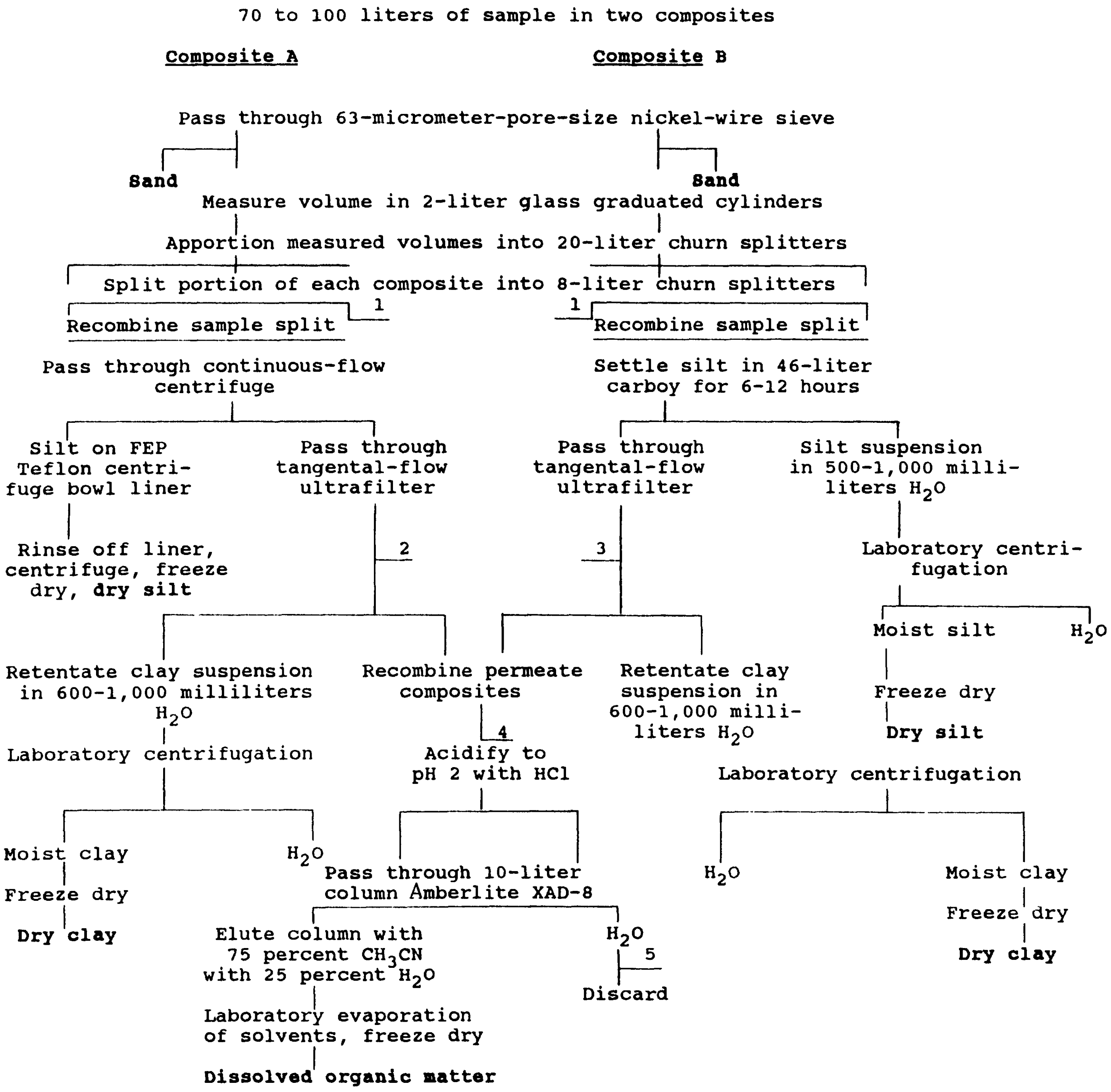

Figure H-4.—Flow chart of procedures for water and suspended-sediment fractionation, November-December 1987 sampling trip.

the time elapsed depended on the work schedule. On the November-December 1987 sampling trip, the silt in composite B was settled in a carboy suspended in a custom-fabricated gimbal on the boat. The gimbal minimized the rocking motion of the boat, and an air-filled plenum on which the carboy was placed minimized the vibration of the boat. The effective particle-size break between silt and clay for a particle of clay-mineral density was calculated to range from 2 to 4 μm for the settling procedure. The remaining supernatant suspension was removed from the carboys by siphoning.

Tangential-flow ultrafiltration was used to isolate the clay fraction (and low-density organic materials of larger size) from water. Two systems were evaluated for use.

A tangential-flow ultrafiltration system built by Dorr-Oliver was selected because the filter membranes were heat-sealed to the filter plates rather than glued with polyurethane as were the membranes in the alternative system. The polyurethane was anticipated to cause bleed problems for organic-contaminant analysis, and it also caused adjacent filter membranes to stick together and tear when the unit was disassembled for cleaning. All tubing in the Dorr-Oliver system was replaced with perfluorinated alkoxy (PFA) Teflon, and the end plates were made from ultrahigh-molecular-weight polypropylene. The ultrafiltration membranes were heat bonded to polypropylene plate supports, and the flow plates between filters were made of polysulfone. The gaskets between filter-plate units were silicon rubber. The pump used for the system was a Wilden MI/UP/TF/TF/TF diaphragm pump constructed of PFA Teflon. The pump was driven by compressed air.

A pore size of 0.005 μm (about 30,000 daltons for organic substance, molecular-weight retention) was selected for the particle size of the ultrafilter membranes, based on particle-size distributions for organic carbon and the series of metals that occur in the upper Mississippi River (Eisenreich and others, 1980). The distribution of carbon, cadmium, copper, lead, manganese, and iron concentrations by sequential ultrafiltration in a number of samples in the upper Mississippi among particle size was bimodal, and 0.005-μm diameter particles were near the minimum concentrations in these bimodal distributions.

Ultrafiltration membranes were tested for trace-organic sorption and contamination and for trace-metal sorption and contamination. Membranes tested were made from polysulfone and regenerated (deacetylated) cellulose. The filters were equilibrated with the same organic-compound mixture as was used to test the Teflon bags, and the solutions were analyzed after equilibration by GC-MS. Rutin, an organic surrogate for dissolved humic substances, was analyzed by ultraviolet spectroscopy after equilibration. The polysulfone membrane adsorbed 1.2 to 6.0 times more the deuterated organic-test compounds than the regenerated cellulose membrane. Conversely, the polysulfone released 6.5 times more organic contaminants into the solution (based on total ion-current chromatogram) than did the regenerated cellulose. Eighteen percent of the rutin was adsorbed on the polysulfone and 3 percent on the regenerated cellulose.

A trace-metal test solution that contained a mixture of about 50 μg/L each of lithium, beryllium, boron, aluminum, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc,

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Footnotes for figure H-4

[1] The following sample splits were collected: (1) 600 mL (milliliters) of each composite for suspended silt and clay (Meade); (2) 600 mL of each composite particle-characteristic analyses (Rees); (3) 750 mL of each composite for nutrients (Stallard); (4) 500 mL of each composite for trace-metal analyses (Taylor); and (5) 1,000 mL of combined composite for organic-contaminant analyses (Pereira).

[2] The following sample splits were collected: (1) 250 mL for trace-metal analyses (Taylor); and (2) 100 mL for particle-characteristic analyses (Rees).

[3] A 100-mL sample was collected for particle-characteristic analyses (Rees).

[4] The following sample splits were collected: (1) 250 mL for trace-metal analyses (Taylor); (2) 100 mL for particle-characteristic analyses (Rees); and (3) 1,000 mL for radionuclide analyses (Tom Kramer, U.S. Geological Survey, Reston, Va.)

[5] Twenty liters of sample at selected sites were collected for radionuclide analyses (Brent McKee, LUMCON, Cocodrie, La.).

arsenic, selenium, strontium, molybdenum, cadmium, barium, lanthanum, cesium, mercury, titanium, and lead, and 2.5 mg/L (milligrams per liter) each of calcium, sodium, and magnesium was equilibrated with the regenerated cellulose and polysulfone membranes for 2 hours. Test solutions were analyzed by inductively coupled plasma-mass spectrometric techniques. Neither membrane adsorbed any trace metal. The concentrations of aluminum, vanadium, chromium, zinc, arsenic, and lead in solution increased for the regenerated cellulose membrane test and the concentrations of aluminum, vanadium, chromium, copper, zinc, arsenic, cesium, mercury, and lead increased for the polysulfone membrane test. Tests performed by Dorr-Oliver indicated that metal contaminants could be removed by a pH 3.0 to 3.5 nitric acid rinse of the regenerated cellulose filters. The organic-solute experiments and trace-metal experiments clearly indicated that the regenerated cellulose membrane was superior to the polysulfone membrane filters.

During the July-August 1987 sampling trip, a stack of 15 regenerated cellulose filters (0.005--μm porosity) was used to process each 70- to 100- liter sample. The filters were rinsed with 90 liters of reagent water before use, and the filters were reused at each site after cleanup until holes were worn into the membranes. The filters could be reused 5 to 10 times before they were discarded. The filters were cleaned and the clay was recovered by placing a filter plate in a FEP Teflon bag (the same bag as was used in the depth-integrating bag sampler), by pouring about 100 mL of retentate sample water into the bag, and then by gently massaging the clay from the filter membrane with the Teflon film of the bag, as a stream of retentate water from a FEP Teflon bottle was directed onto the area being cleaned. With a stack of 15 filters, the total retentate volume that contained the clay was 2 to 3 liters.

During the November-December 1987 sampling trip, the filter stack was decreased to three filters to decrease the retentate volume containing the clay and to enable new filters to be used at each site; this procedure decreased the possibility of contamination.

The filters were rinsed with 10 liters of pH 3.0 to 3.5 high-purity nitric acid for 30 minutes, and then rinsed with 20 liters of reagent water. All handling of the filter plates after disassembly and during cleaning was by personnel wearing FEP Teflon gloves. The final retentate volume containing the clay was 600 to 1,000 mL, using three filter plates. The retentate solution was stored in 1-liter Teflon bottles at 4 °C (degrees Celsius), and 0.5 mL of chloroform was added as a preservative. Final dewatering of the clay was performed in Denver by centrifuging the retentate suspensions in 250-mL polycarbonate bottles lined with FEP Teflon bags at 5,000 r/min (revolutions per minute) in a Sorvall RC5B supercentrifuge. The clay was separated at this relatively slow centrifuge speed because the water chemistry of the Mississippi River is such that clay flocculates at relatively high clay concentrations in the retentate water. The clay was easily removed from the FEP Teflon bag liner because of the nonstick characteristics of Teflon. Finally, the moist clay was freeze-dried to a powder that was tractable for handling. Freeze-dried powder was blended and subsampled by conventional cone and quartering techniques.

For both sampling trips, silt-plus-clay recovery values for the settling and ultrafiltration procedures ranged from 72 to 94 percent, normalizing on total silt-plus-clay values determined by membrane filtration of the aliquot collected earlier (footnote 1 of fig. H-4). The silt-plus-clay recovery for the July-August 1987 trip decreased as the suspended-sediment concentration decreased, as indicated in figure H-5; the recovery also decreased as the percentage of clay increased. Silt-plus-clay recovery data for the November-December 1987 trip was approximately the same as for the July- August 1987 trip, which indicates that the ultrafiltration membranes were not a significant cause of loss of sediment because of the different number of membrane plates used on each trip. Sediment loss most likely occurs during laboratory centrifugation of the retentate concentrate from the ultrafilter. The smallest and lightest particles probably are not efficiently recovered by laboratory centrifugation.

One purpose of the November-December 1987 trip was to evaluate if continuous-flow centrifugation was a faster and more complete method than gravitational settling for dewatering the fine sediment fractions. A Sharples Model AS-12 continuous-flow supercentrifuge was borrowed from the Great Lakes Research Institute of the University of Wisconsin and was installed on the *Acadiana* at Alton, Ill. The bowl of the centrifuge is a stainless-steel cylinder, 10.5 cm (centimeter) in diameter by 71.1 cm in length. The bowl spins at 15,000 r/min, and water passes through the vertically mounted bowl from bottom to top. The centrifuge weighed 227 kg (kilograms) and was powered by a 2-hp (horsepower) (or 1.49 kW (kilowatt)) motor that used 3-phase, 220-volt power. The bowl interior and all metal centrifuge surfaces that contact the sample were coated with FEP or PFA Teflon. Before each run, a 0.25-mm-thick FEP Teflon liner was inserted into the bowl so that the recovered sediment could easily be removed from the liner at the end of the run. Gravitational flow from a 15-liter glass-funnel reservoir mounted about 1 meter above the centrifuge through FEP Teflon lines to the centrifuge was used to pass water through the centrifuge. Flow rate was controlled by a stopcock at the outlet of the reservoir and by control of the hydraulic head of the reservoir, which could be raised or lowered by a compressed-air piston. Flow rate was maintained at 2 L/min (liters per minute) except at the last three sites when an airlock developed in the line below the stopcock, and the flow rate decreased to 1.0 to 1.5 L/min. The particle-size cutoff (for a clay mineral of hydrated density of 1.6 g/mL (grams per milliliter) was calculated to be 0.2 μm for a flow rate of 2 L/min (Jackson, 1956). This particle-size cutoff is an order of magnitude less than was recovered by the gravitational-settling procedure. Processing time for composite A fraction (fig. H-4) through the centrifuge was about 30 minutes.

A comparison of the quantity of suspended-sediment recovered by gravitational settling and by continuous-flow centrifugation are summarized in table H-5. These data indicate consistently larger recoveries of suspended sediment by the centrifugation procedure, compared to gravitational settling, principally because of the much smaller particles recovered by centrifugation. Conversely, the total recoveries for the centrifugation-plus-ultrafiltration procedure are commonly less than the total recovery for the settling plus ultrafiltration procedure. At the end of the sampling trip, a deposit of coarse silt was discovered in a self-sealing bowl-bottom device that prevents water from draining out of the bowl; this accumulation may explain the smaller total recoveries for the centrifuge-plus-ultrafiltration procedure. The White and Yazoo River samples contained larger percentages of clay-size particles than did the Mississippi River samples, and the percentage recoveries of suspended

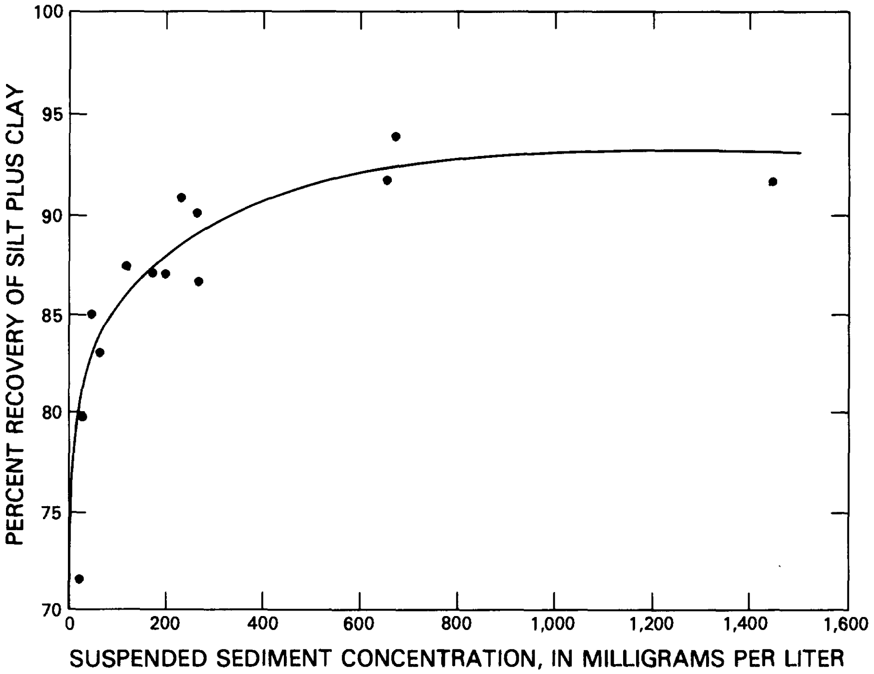

Figure H-5. – Relation of suspended-sediment recovery data to suspended- sediment concentration, July-August 1987 sampling trip.

Table H-5. —*Suspended-sediment recoveries by gravitational settling and continuous-flow centrifugation, November-December 1987 sampling trip*

Sampling site	Suspended-sediment recovery[1] by: Gravitational settling (percent)	Centrifugation (percent)	Ultrafiltration after settling (percent)	Ultrafiltration after centrifugation (percent)
Mississippi River at Thebes, Ill.	65.2	74.1	19.7	9.4
Ohio River at Olmsted, Ill.	54.1	85.3	35.3	7.1
Mississippi River below Hickman, Ky.	53.5	71.4	25.0	10.8
Mississippi River at Fulton, Tenn.	66.5	67.4	24.4	10.4
Mississippi River at Helena, Ark.	58.1	72.0	27.2	10.8
White River at river mile 11.5	42.5	52.6	44.2	24.3
Mississippi River above Arkansas City, Ark.	53.6	58.1	32.5	12.4
Yazoo River at mile 10	31.2	42.1	56.0	35.5
Mississippi River below Vicksburg, Miss.	49.0	[2]50.2	31.9	[2]7.1
Old River Outflow Channel near Knox Landing, La.	61.2	[2]68.0	29.5	[2]6.3
Mississippi River near St. Francisville, La.	52.5	[2]62.2	27.3	[2]4.8

[1] Recovery figures do not include sand-sized fraction.

[2] Centrifuge flow rate decreased to 1.0 to 1.5 liters per minute.

sediment for the ultrafilter are much larger for these tributary rivers. The data in table H-5 clearly indicate the necessity of tangential-flow ultrafiltration to recover the fine suspended sediment that is not recovered by gravitational settling or continuous-flow centrifugation.

Differences in organic composition between the silt and clay fractions of suspended sediment from the July-August 1987 sampling trip are listed in table H-6. Organic carbon and nitrogen percentages are consistently greater in the clay fraction than in the silt. Atomic carbon-nitrogen ratios are consistently less in the clay fraction than in the silt fraction. These consistent differences occur throughout a wide range of organic carbon compositions from 1.5 to 20.1

Table H-6. —*Organic compositional differences between silt and clay fractions of suspended sediment from the Mississippi River and tributaries, July-August 1987 sampling trip*

Sample site	Silt fraction: Percent organic carbon	Percent nitrogen	Carbon-nitrogen atomic ratio	Clay fraction: Percent organic carbon	Percent nitrogen	Carbon-nitrogen atomic ratio
Mississippi River near Winfield, Mo.	3.22	0.44	8.54	5.04	0.74	7.95
Illinois River at Naples, Ill.[1]	2.64	.34	.07	5.55	.79	8.20
Mississippi River at Hartford, Ill.	3.08	.41	8.80	6.07	.96	7.38
Missouri River at Hermann, Mo.	2.37	.23	12.03	3.25	.42	9.03
Mississippi River at St. Louis, Ill.	2.07	.21	11.50	3.23	.46	8.20
Mississippi River at Chester, Ill.	2.15	.22	11.38	3.18	.48	7.76
Ohio River below Smithland Locks and Dam	3.01	.38	9.23	8.30	1.21	8.00
Ohio River at Olmsted, Ill.	3.27	.34	11.24	10.21	1.64	7.24
Mississippi River below Hickmann, Ky.	2.03	.20	11.87	4.95	.76	7.60
Mississippi River at Helena, Ark.	2.40	.24	11.65	3.28	.51	7.51
White River at river mile 11.5	1.49	.27	6.48	6.12	1.14	6.27
Arkansas River at river mile 55.9	5.95	.81	8.57	20.12	3.73	6.29
Mississippi River above Arkansas City, Ark.	1.48	.14	10.67	3.31	.49	7.88
Old River Outflow Channel near Knox Landing, La.	1.86	.18	12.07	3.00	.43	8.13
Mississippi River near St. Francisville, La.	2.08	.17	14.24	3.09	.52	6.93
Mississippi River at Belle Chasse, La.	2.20	.23	11.16	3.36	.56	7.00

[1] Sample collected from boat and personnel from the Illinois District Office, U.S. Geological Survey.

percent and organic nitrogen compositions from 0.2 to 3.7 percent. The small carbon-to-nitrogen ratios in the clay fraction are caused by large amounts of phytoplankton and related low-density organic matter that coisolates with the clay-sized inorganic material. These large compositional differences between the silt and clay fractions present a strong argument for fractionating suspended sediment for studies of contaminant transport and of biogeochemical processes in the river.

FUTURE RESEARCH

The Mississippi River research group for the sampling trip planned for May-June 1988 intends to develop a pumping sampler to be directly coupled with the continuous-flow centrifuge. The objective of this arrangement is to process enough water to isolate 40 to 50 grams of suspended sediment to conduct trace-organic contaminant analyses. The pump sampling will be conducted simultaneously with the depth-integrated sampling by the bag sampler. The pump-sampling strategy will be designed to collect a representative discharge-weighted sample of the silt and clay fractions but not the sand fraction.

Certain components of the ultrafilter are being modified to minimize contaminants for trace-organic analysis. The silicon-rubber gaskets that seal the flow plates are being coated with FEP Teflon to eliminate polysiloxane contaminants, and the polysulfone flow plates are being replaced with FEP Teflon flow plates to minimize contamination and adsorption and to facilitate suspended-sediment recovery from the filter assembly. The research group also plans to process 400 to 500 liters of water at three or four sites to determine if enough clay-sized material can be isolated from the ultrafilter for trace organic-contaminant analyses.

The Mississippi River research project plans to conduct two to three sampling trips per year through 1992. These additional trips are needed to study comprehensively the seasonal and areal variations in sediment transport and sediment chemistry. Improvements to the methods described in this report will be made for sampling, fractionation, and dewatering of suspended sediment during these trips.

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CHARACTERIZATION OF COLLOIDS IN THE MISSISSIPPI RIVER AND ITS MAJOR TRIBUTARIES

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

ABSTRACT

Colloids collected from the Mississippi River and its major tributaries during sampling cruises during the summer and winter of 1987 have been characterized as to colloid concentration, particle-size distribution, mineralogy, and electrophoretic mobility. Colloid concentrations generally correlated with main stream velocity. Particle-size distributions were generally unimodal, with larger particles in the Mississippi main stem than in the tributaries. Mineralogy of the colloids was dominated by clays, with lesser amounts of quartz, rutile, and organic material. Electrophoretic mobilities ranged from -1.27 to -2.88 x 10^{-8} meters squared per second per volt, and were generally more negative in the summer than in the winter.

INTRODUCTION

The Mississippi River drains approximately 40 percent of the conterminous United States and discharges into the Gulf of Mexico an average of 18,400 m^3/s (cubic meters per second). This discharge carries an average of about 210 million metric tons of sediment per year (Milliman and Meade, 1983; Meade and Parker, 1985). In 1987, the U.S. Geological Survey began an interdisciplinary study of the Mississippi River that includes study of this sediment flux, and the role that these sediments play in the transport of metals and organic contaminants. Part of this research entails the quantification of the amounts and types of colloidal particles that are present, and the contaminants most strongly associated with colloidal materials.

A colloid is any particle, droplet, or gas bubble that has at least one dimension in the range of 0.001 μm to approximately 5 μm. A colloid is larger than most individual molecules, but is generally too small to be seen by optical microscopy. Because of the small size of colloidal particles, surface-free energy dominates bulk-free energy, making their surfaces very reactive toward a variety of metals and hydrophobic organic materials. Many investigators now believe colloidal material may be a major transport control for anthropogenic contaminants in surface and ground waters. This paper describes the methods used to collect, concentrate, and characterize colloidal materials suspended in the Mississippi River and its major tributaries.

EXPERIMENTAL

Samples used in this study were collected during two sampling cruises of the Research Vessel *Acadiana*. The first was a low-discharge, warm-temperature cruise from July 19 to August 7, 1987. The second was a low-discharge, cold-temperature cruise from November 29 to December 21, 1987. Samples on both cruises were collected at numerous locations on the main stem of the Mississippi River beginning north of the confluence of the Illinois River and continuing downriver to south of New Orleans at Belle Chasse, La. Samples were also collected from the Illinois, the Missouri, the Arkansas, the White, the Yazoo, and the Old Rivers. Figure H-6 is a map of the Mississippi River drainage showing river miles relative to cities along its banks. Precise sampling locations are given in table H-7.

Discharge-weighted suspended-sediment samples were collected by isokinetic bag samplers as described in Nordin and others (1983), using Teflon[2] bags. Depending on river width, mean velocities, and discharge, between 10 and 36 individual vertically integrated samples were composited. After compositing, silt-sized particles (5 to 63 μm) were allowed to settle under gravity for approximately 8 hours before the supernatant suspension containing the colloidal materials was siphoned off. The colloids were then concentrated using a Dorr-Oliver crossflow ultrafiltration system equipped with 0.005 μm membranes. Colloidal material retained on the membranes was gently removed by placing

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

[2] Use of brand or trade names is for identification purposes only and does not constitute endoresement by the U.S. Geological Survey.

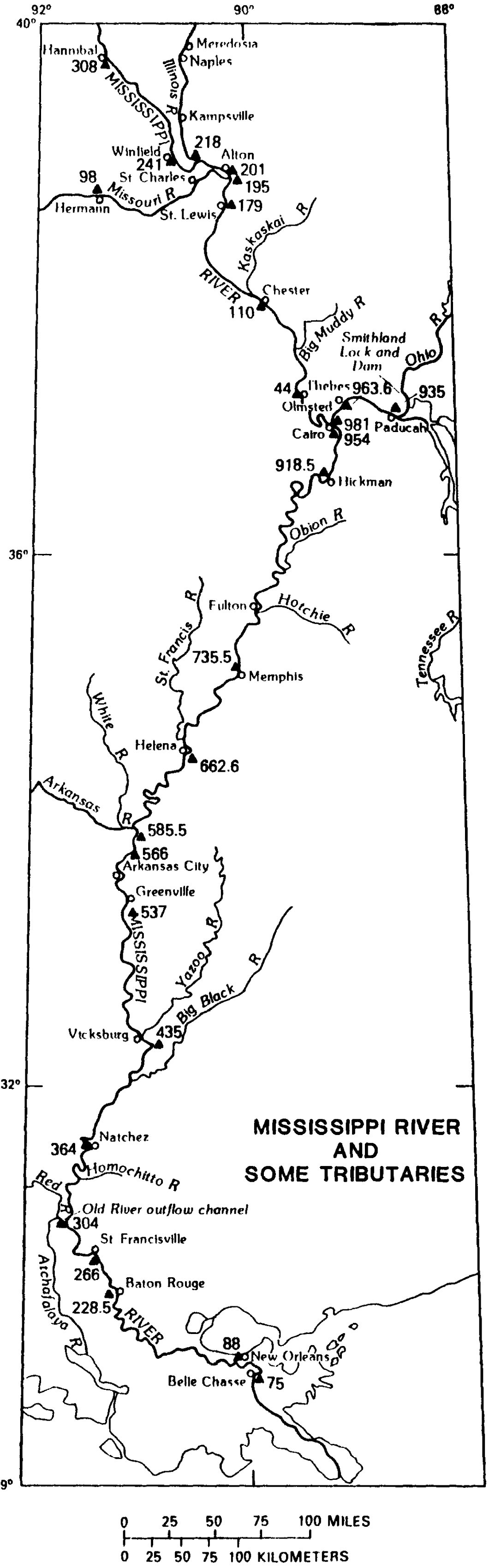

Figure H-6.—Sample locations along the Mississippi River and its major tributaries.

Table H-7.—*Locations of sampling locations on the Mississippi River and its tributaries*

Station name	River mile[1]
Mississippi River near Winfield, Mo.	UM 239.2
Illinois River below Meredosia, Ill.	IL 67.2
Mississippi River at Hartford, Ill.	UM 197.7
Missouri River at Hermann, Mo.	MO 97.9
Missouri River at St. Charles, Mo.	MO 28.1
Mississippi River at St. Louis, Mo.	UM 179.3
Mississippi River at Chester, Ill.	UM 108.9
Mississippi River at Thebes, Ill.	UM 43.9
Ohio River below Smithland Locks and Dam, Ill.-Ky.	OH 919.2
Ohio River at Olmsted, Ill.	OH 965.0
Mississippi River below Hickman, Ky.	LM 916.8
Mississippi River at Fulton, Tenn.	LM 777.3
Mississippi River at Helena, Ark.	LM 663.9
White River at mile 11.5, Ark.	WH 11.5
Arkansas River at mile 55.9, Ark.	AR 55.9
Mississippi River above Arkansas City, Ark.	LM 566.0
Yazoo River at mile 10, Miss.	YZ 10.0
Mississippi River below Vicksburg, Miss.	LM 433.4
Old River Outflow Channel near Knox Landing, La.	
Mississippi River near St. Francisville, La.	LM 266.4
Mississippi River below Belle Chasse, La.	LM 73.1

[1] UM, Upper Mississippi River miles measured upriver of confluence with Ohio River.
IL, Illinois River miles measured upriver of confluence with Mississippi River (UM 218.0)
MO, Missouri River miles measured upriver of confluence with Mississippi River (UM 195.3).
OH, Ohio River miles measured downriver of Pittsburg, Pa. Ohio-Mississippi confluence is at Ohio River mile 981.5 and Lower Mississippi River mile 953.8.
LM, Lower Mississippi River miles measured upriver of Head of Passes, La.
WH, White River miles measured upriver of confluence with Mississippi River (LM 598.8).
AR, Arkansas River miles measured upriver of confluence with Mississippi River (LM 581.5).
YZ, Yazoo River miles measured upriver of confluence with Mississippi River (LM 437.2)

the membrane plate into a Teflon bag, adding a small amount of the colloid concentrate suspension into the bag, and gently massaging the membrane with the Teflon bag until all visible residue was removed. After removing the membrane plate, the resulting suspension was combined with the ultrafiltration concentrate to give the final concentrated colloid suspension.

The colloid concentrations in the riverwater were determined gravimetrically from the mass of colloid collected from the concentration step and the volume from which they were collected. Particle-size distributions were determined using photon correlation spectroscopy (PCS), photosedimentation analysis (PSA), and scanning electron microscopy (SEM). Surface charge was determined using electrophoretic light scattering (ELS). Mineralogy was determined using X-ray diffraction. For a more detailed description of PCS and ELS, see Rees (1987). Photosedimentation determines particle-size distributions by the differential optical transmission of a solution in a centrifugal field. The other analytical techniques are standard procedures.

RESULTS AND DISCUSSION

Colloid concentrations for the two cruises are given in tables H-8 and H-9. Summer colloid concentrations were approximately twice those found during the winter. Lowest colloid concentrations were in the Ohio and the Arkansas Rivers and the Mississippi River at Winfield and Belle Chasse. Concentrations were highest in the

Missouri River. During Cruise 1, there was a clear trend in the Mississippi main stem of increasing colloid concentrations with increasing mean velocity (see fig. H-7). Only the St. Louis and Helena sections were off this trend. This concentration trend was also present during the cold-water cruise (see fig. H-8), when colloid concentrations in the Yazoo River and the Mississippi River at Helena were statistically off the trend.

Selected particle-size distributions for disaggregated samples collected during Cruise 1 are given in figures H-9 and H-10 (complete particle-size distribution analyses are not yet completed for Cruise 2). Distributions were generally unimodal, peaking at approximately 0.4 μm in the Mississippi main stem, and at a slightly smaller 0.3 μm in the tributary rivers. SEM analyses of filters collected on the second cruise of unconcentrated, unsonicated riverine particles indicates that colloids in the rivers were mostly aggregated. Disaggregated colloids dominate the SEM-determined distributions only in the Yazoo River. The aggregates from the other rivers are very fragile, and may be disrupted by the simple handling procedures such as pipetting, centrifugation, and filtration (Gibbs and Konwar, 1982). Special care was taken to minimize disruption of these aggregates for this SEM study.

Mineralogical analysis indicated that the colloids collected during Cruise 1 were

Table H-8. — *Colloid concentrations in the Mississippi River and its major tributaries — Cruise 1: July 19 through August 7, 1987*

[m^3/s, cubic meters per second; m/s, meters per second; g/L grams per liter]

Location[1]	Discharge m^3/s	Mean velocity m/s	Colloid conc. g/L
IL 67.2	300	(2)	0.022
MO 97.9	2,600	1.23	.126
OH 965.0	2,100	.42	.009
WH 11.1	330	.67	.014
AR 55.9	790	.65	.006
UM 239.2	1,370	(2)	.0375
UM 197.7	1,550	.54	.0169
UM 179.3	3,900	1.10	.350
UM 108.9	4,300	1.12	.091
LM 916.8	6,300	1.02	.029
LM 663.9	6,900	1.44	.054
LM 566.0	7,600	.78	.056
LM 433.4	7,700	.95	.036
Old River	2,100	.97	.056
LM 266.4	6,200	.81	.040
LM 73.1	(2)	(2)	.030

[1] UM, Upper Mississippi River miles measured upriver of confluence with Ohio River.
IL, Illinois River miles measured upriver of confluence with Mississippi River (UM 218.0).
MO, Missouri River miles measured upriver of confluence with Mississippi River (UM 195.3).
OH, Ohio River miles measured downriver of Pittsburgh, Pa. Ohio-Mississippi confluence is at Ohio River mile 981.5 and Lower Mississippi River mile 953.8.
LM, Lower Mississippi River miles measured upriver of Head of Passes, La.
WH, White River miles measured upriver of confluence with Mississippi River (LM 598.8).
AR, Arkansas River miles measured upriver of confluence with Mississippi River (LM 581.5).
YZ, Yazoo River miles measured upriver of confluence with Mississippi River (LM 437.2)

[2] Not able to measure this parameter.

Table H-9. – *Colloid concentrations in the Mississippi River and its major tributaries – Cruise 2: November 19 through December 21, 1987*

[m^3/s cubic meters per second, m/s meters per second, g/L, grams per liter]

Location[1]	Discharge m^3/s	Mean velocity m/s	Colloid conc. g/L
IL 67.2	260	(2)	0.022
MO 28.1	2,800	1.25	.083
OH 965.0	4,200	.57	.013
WH 11.5	520	.75	.045
YZ 10.0	200	.34	.083
UM 239.2	2,000	.64	.010
UM 179.3	5,400	1.33	.092
UM 43.9	5,200	1.35	.063
LM 916.8	8,800	1.17	.042
LM 777.3	8,900	1.22	.0218
LM 633.9	8,800	1.55	.048
LM 566.0	9,900	.98	.047
LM 433.4	10,500	1.10	.053
Old River	1,800	.65	.033
LM 266.4	8,200	.96	.042
LM 73.1	[3]9,600	.62	.0060

[1] UM, Upper Mississippi River miles measured upriver of confluence with Ohio River.
IL, Illinois River miles measured upriver of confluence with Mississippi River (UM 218.0).
MO, Missouri River miles measured upriver of confluence with Mississippi River (UM 195.3).
OH, Ohio River miles measured downriver of Pittsburgh, Pa. Ohio-Mississippi confluence is at Ohio River mile 981.5 and Lower Mississippi River mile 953.8.
LM, Lower Mississippi River miles measured upriver of Head of Passes, La.
WH, White River miles measured upriver of confluence with Mississippi River (LM 598.8).
AR, Arkansas River miles measured upriver of confluence with Mississippi River (LM 581.5).
YZ, Yazoo River miles measured upriver of confluence with Mississippi River (LM 437.2)

[2] Not able to measure this parameter.

[3] Discharge may be affected by tidal currents.

principally clays with lesser amounts of other minerals and organic material. Illite and kaolinite were major components and montmorillonite was a minor component in all the rivers. Smectites were major mineral components in the Missouri, and in the main stem of the Mississippi River below the confluence of the Missouri. The Ohio, the White, and the Arkansas Rivers had only traces of smectite in suspension. Significant amounts of vermiculite were identified in the Arkansas River. Quartz and rutile were ubiquitous minor minerals in all the rivers.

Mean electrophorectic mobilities ranged from -1.27 to -2.88 x 10^{-8} $m^2/s/v$ (meters squared per second per volt) using an ELS field strength of 15 V/cm (volts per centimeter). Mobilities were significantly lower during the winter. Colloids from the Missouri and the Ohio Rivers had the highest mobilities, whereas those from the Yazoo, the Illinois, and the White Rivers had the lowest. Mobilities of colloids in the Mississippi main stem appear to be dominated by inflow from the Missouri and the Ohio Rivers.

SUMMARY

Colloids collected from the Mississippi River and its tributaries show distinct differences in concentration, size distributions, mineralogy, and electrophoretic mobility depending upon in which season they were collected, and the river from which they came. Further work is planned by this, and other projects, to further characterize the nature of contaminants associated with these colloidal materials.

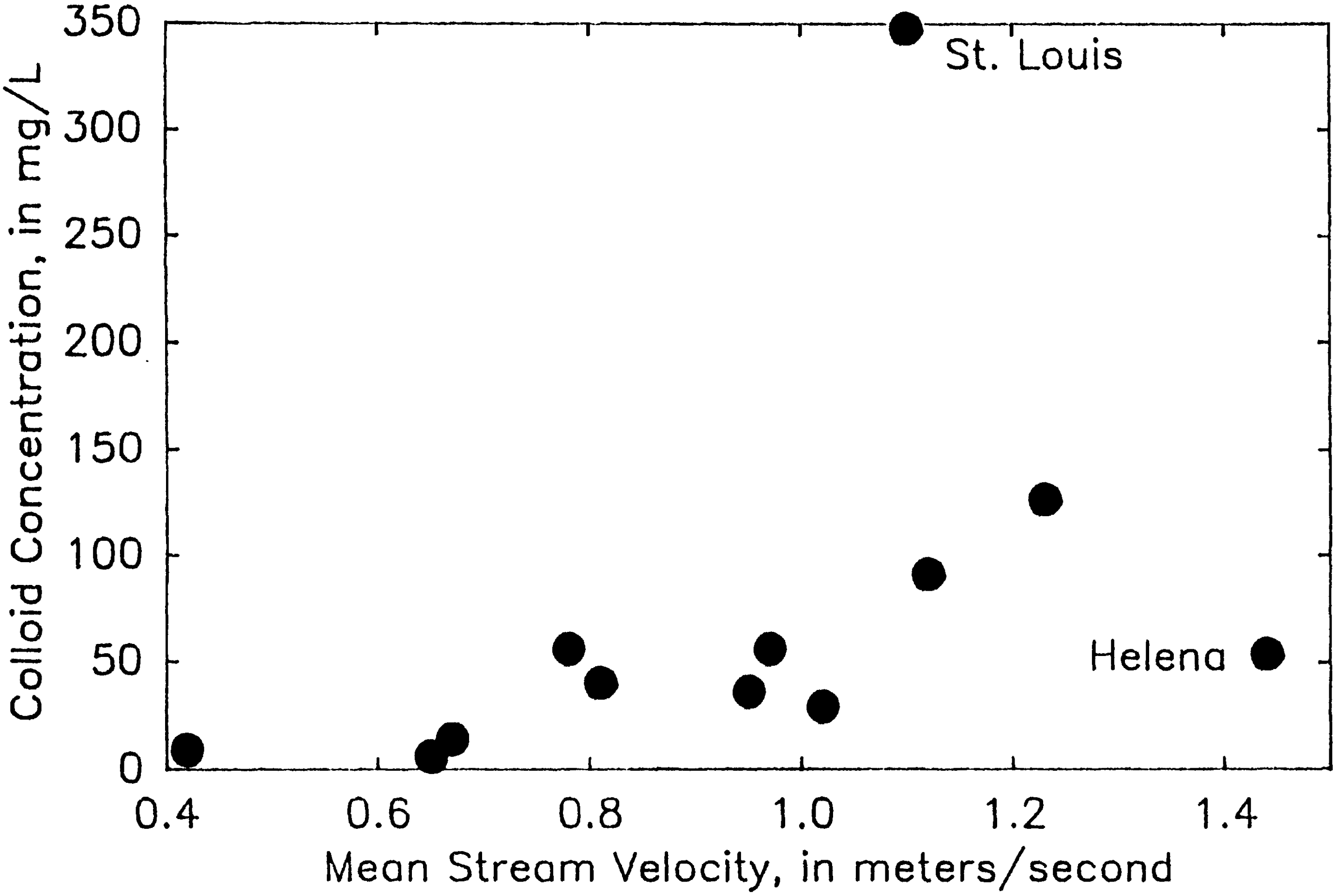

Figure H-7.—Relation of colloid concentration to mean stream velocity, Cruise 1—July 19 through August 7, 1987.

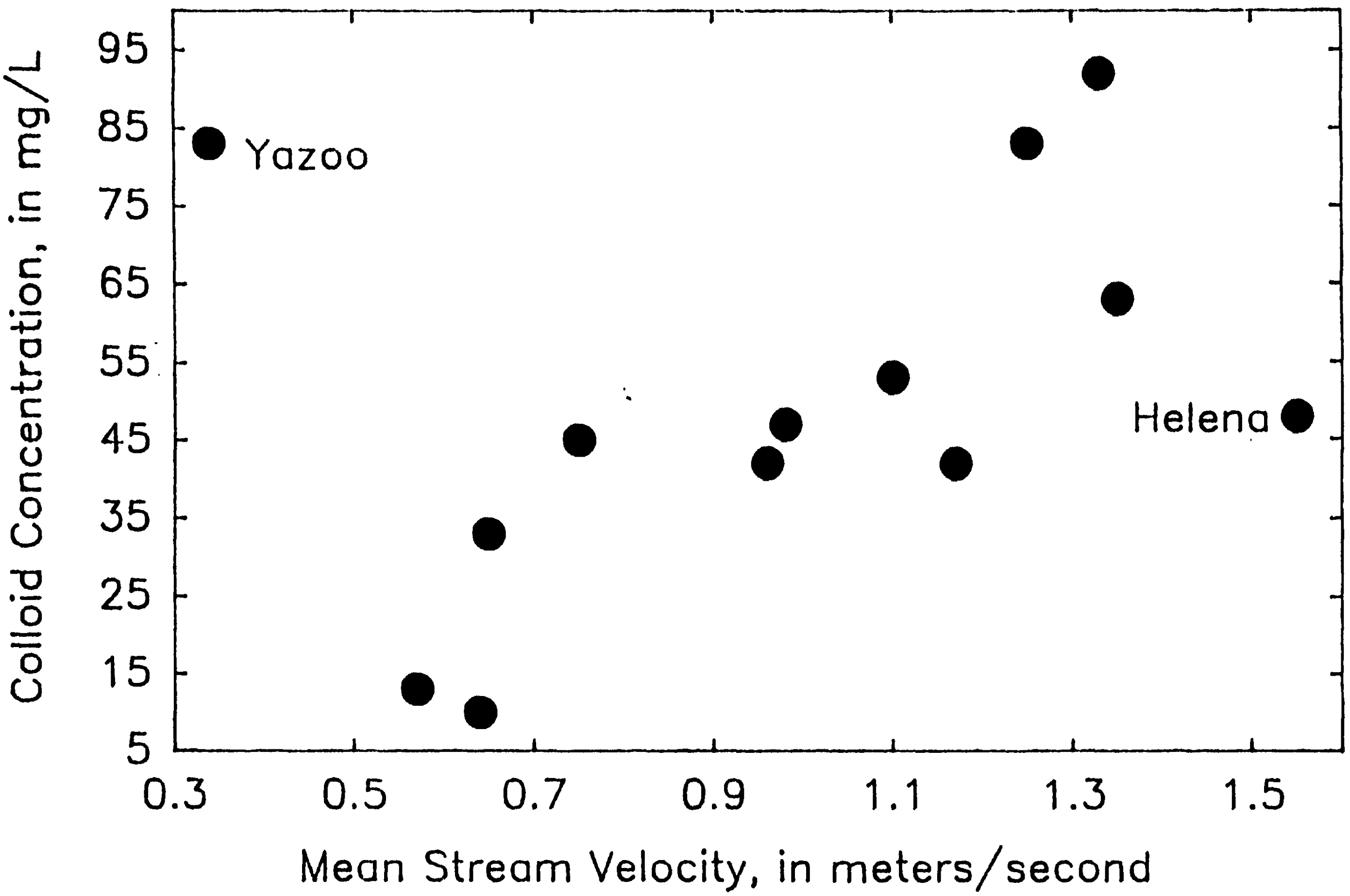

Figure H-8. – Relation of colloid concentration to mean stream velocity for Cruise 2 – November 29 through December 21, 1987.

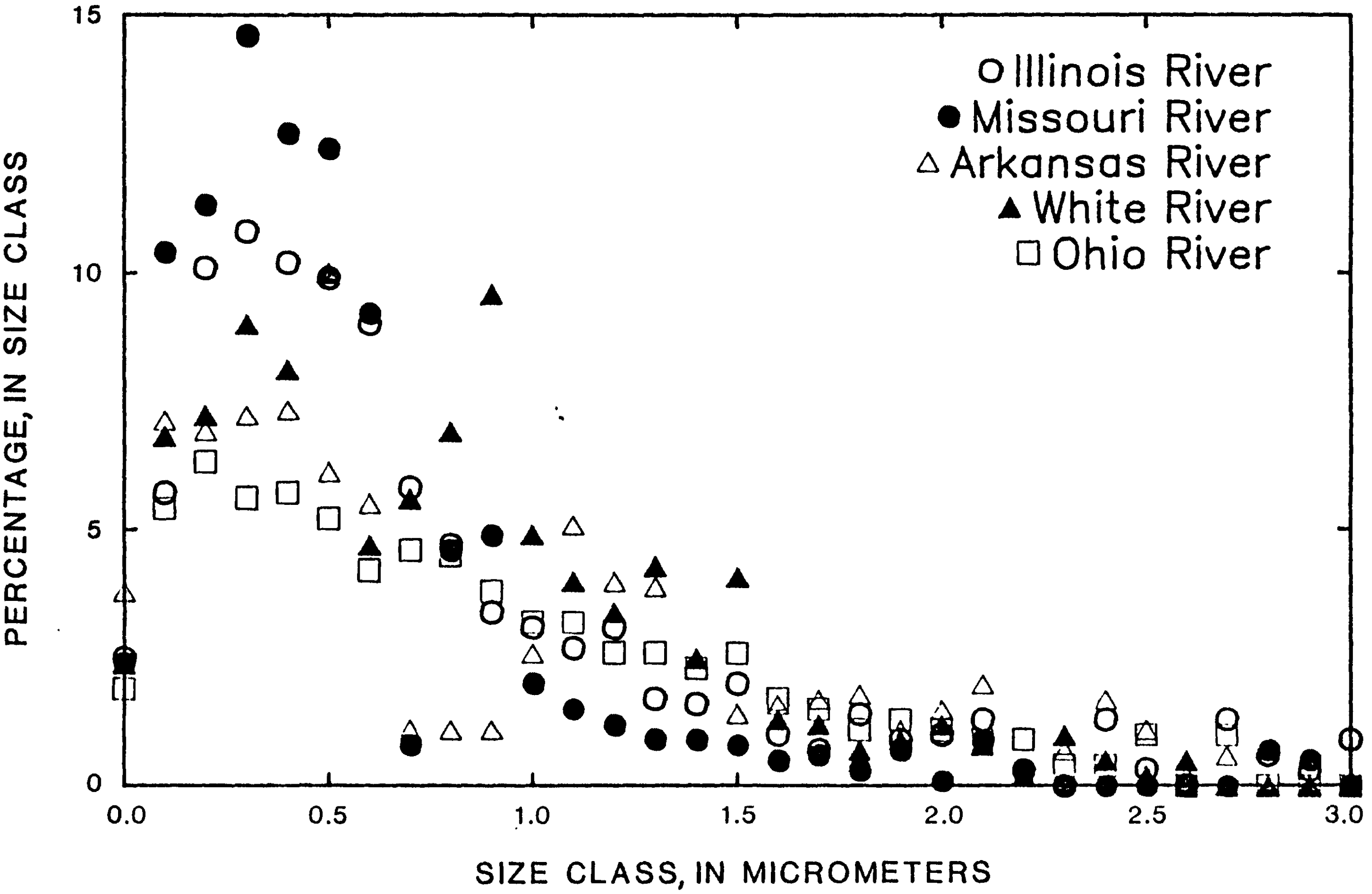

Figure H-9.—Particle size distribution for the Illinois, the Missouri, the Arkansas, the White, and the Ohio Rivers.

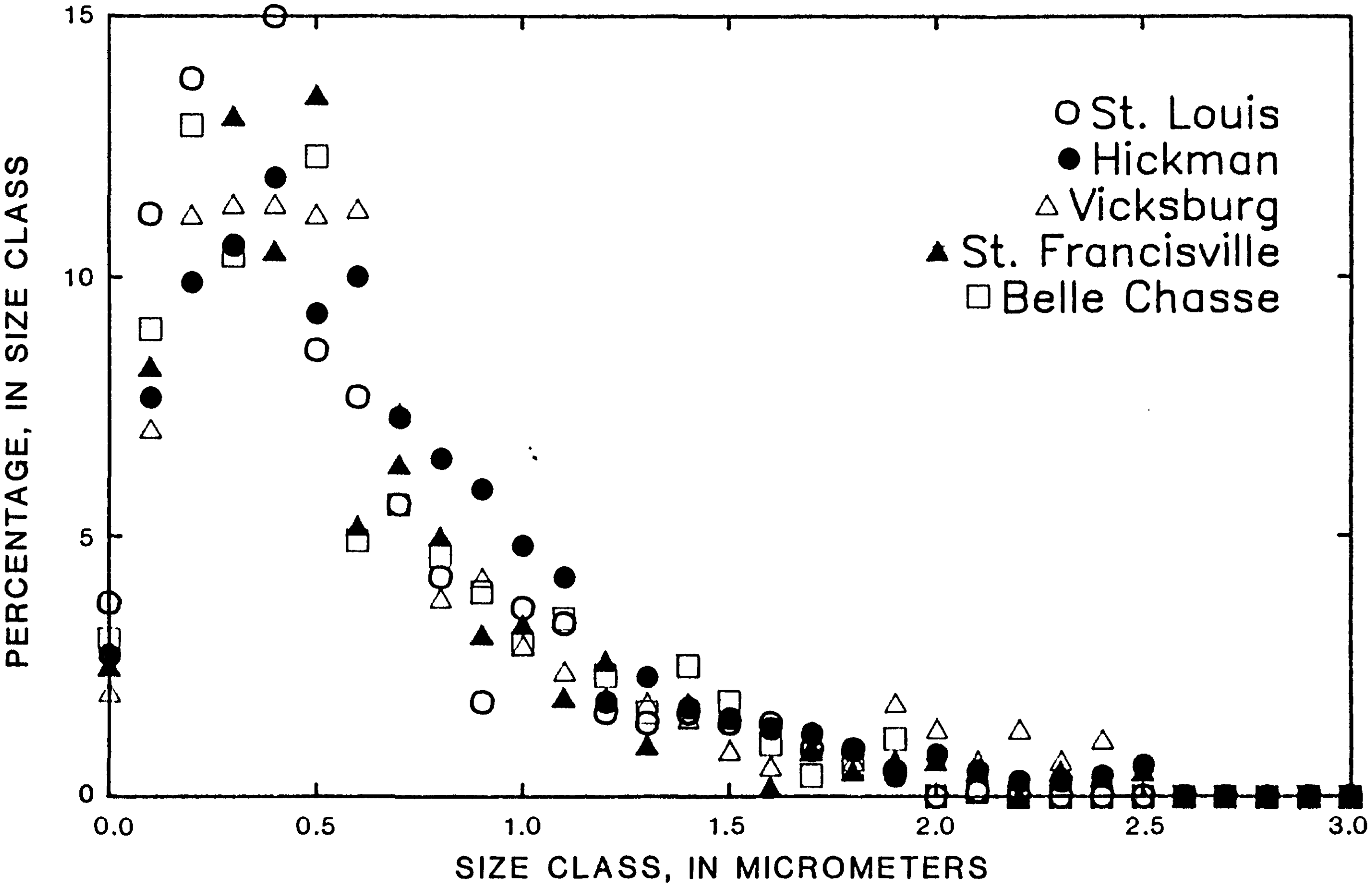

Figure H-10.—Particle size distribution for the Mississippi River at the St. Louis, Hickman, Vicksburg, St. Francisville, and Belle Chasse sites.

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USE OF A SIMPLIFIED TRANSPORT MODEL FOR PESTICIDES IN THE UNSATURATED ZONE

By A.T. Rutledge[1] and J.O. Helgesen[2]

ABSTRACT

A steady-state mathematical model calculates pesticide residence time and fraction of pesticide remaining as functions of depth in the unsaturated zone. The use of the model in an example problem is demonstrated, and results of the use of the model on a simplified hypothetical situation are used to determine sensitivity of ground-water contamination potential to selected variables. The model can simulate the presence of numerous lithologic layers in the unsaturated zone, continuous water-content variation with depth, pesticide retardation, pesticide-decay rates that differ between layers, and root uptake of pesticide. The model output includes time and fraction of pesticide remaining as functions of depth, if the pesticide is introduced at the land surface. If the fraction of pesticide remaining at the water table represents contamination potential, then the model indicates the variables to which the ground-water contamination potential is most sensitive. For conditions that represent the subhumid to semiarid region of the Midwestern United States, these variables are, in order of importance, deep percolation rate, organic-carbon content in the bottom part of the unsaturated zone, half-life of pesticides, and depth to the water table.

INTRODUCTION

The occurrence of pesticides in the High Plains aquifer of south- central Kansas has been evaluated (Stullken and others, 1987) as part of the Toxic Waste--Ground-Water Contamination Program of the U.S. Geological Survey (Helsel and Ragone, 1984). Although use of the herbicide atrazine on row crops grown in the area is common, atrazine generally is not detected in the underlying ground water. As a result, research is being directed toward the intervening unsaturated zone as the principal medium through which the movement and fate of the pesticide are determined. Some of the more important processes in this regard include rate of downward water flux, soil properties, sorptive properties of the chemical, and persistence of the chemical in the environment. A combination of slow movement and degradation of the chemical, for example, could account for the absence of a pesticide in ground water beneath an area where that chemical is known to have been applied.

As a preliminary effort to simulate the transport and decay of pesticides in the unsaturated zone as they move from the land surface to the water table, a simple mathematical model was developed and applied. The model could help direct future efforts to develop an improved understanding of the processes of pesticide transport. Use of the model also could help identify the important factors that affect the presence and distribution of pesticides in ground water.

This paper (1) describes the mathematical model for transport of pesticides in the unsaturated zone, (2) demonstrates use of the model with example input and output data, and (3) presents results of analyses of sensitivity to selected variables. To test sensitivity, large ranges in values of model input variables are used, so that results reflect conditions throughout the subhumid to semiarid agricultural areas of the Midwestern United States. Although some model results are presented for several different pesticides, atrazine is the compound used for the sensitivity analyses.

DESCRIPTION OF MODEL

The model was developed by assuming the following conditions:

(1) The water content above the water table is described by an equilibrium water-saturation curve (water content as a function of negative pressure head).

(2) Water flux is steady state, is downward, and is calculated as the rate at which water is applied to the surface minus the

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

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

evapotranspiration that occurs above the point of interest.

(3) All water in the unsaturated zone participates in the transport process. Water initially present in the profile is completely displaced downward by water entering from above.

(4) Pesticides are applied at a constant rate.

(5) Pesticides of interest are only in the aqueous phase or are adsorbed to the solid phase; they are not in a nonaqueous liquid phase or gaseous phase.

(6) Adsorption is described by a linear and reversible equilibrium relation.

(7) Pesticide decay is an irreversible first-order reaction.

(8) Pesticides occur at concentrations small enough that the capacities of materials in the unsaturated zone to allow for adsorption and decay of the pesticide are not exhausted.

(9) Root uptake of pesticide is assumed to be proportional to the root uptake of water.

(10) Pesticide flux is steady state, and dispersion of the pesticide is neglected.

This simple mathematical model is useful provided the user is aware of the above assumptions. These assumptions may limit the applicability of the model results. Limitations become less significant if model results are used in a comparative sense.

The residence time, which is the time required for a pesticide particle to travel from land surface to a depth of interest, can be expressed as:

$$ti = \int_0^{zi} \frac{1}{q} [WC + \rho b(Kd)]dz\,, \qquad (1)$$

where

ti = residence time, in days;

zi = depth of interest, in feet;

q = water flux, in feet per day;

WC = water content, fraction;

ρb = dry bulk density, in grams per milliliter;

Kd = partition coefficient, in milliliters per gram; and

z = depth below land surface, in feet.

Water flux (q) at the land surface (z = 0) is set equal to the rate at which water enters the ground, and at the bottom of the root zone is set equal to the rate of deep percolation. For all depths within the root zone, the water flux is linearly interpolated between these values. The water flux below the root zone is considered equal to the rate of deep percolation.

The model determines the water content (WC) at a given point as a function of an equilibrium water characteristic curve of the layer in which the point is located. Within a given layer, the characteristic curve is a continuous relation between water content and the elevation of the point above the water table. The model calculates the characteristic curve for each layer as a function of the layer's wilting point, air-entry level, field capacity, and porosity. Because water characteristic curves may differ significantly from one layer to another, there can be discontinuities in the relation between elevation and water content if the simulated system consists of multiple layers. The use of equilibrium water characteristic curves is only a rough approximation; equilibrium curves are based on the assumption of a hydrostatic pressure distribution in the unsaturated zone, yet hydrostatic conditions will not exist if there is vertical flow.

For a given system configuration, the variables of bulk density (ρb) and partition coefficient (Kd) are constant within any given layer but may differ from one layer to another. Bulk density is related to porosity, and partition coefficient is related to the organic-carbon partition coefficient of the pesticide and the organic-carbon composition of the layer.

The fraction of the original pesticide that remains after the decay that occurs during its transport through the layer (or to a particular point within the layer) can be calculated by solving the equation for irreversible first-order reactions (Tchobanoglous and Schroeder, 1985, p. 242) allowing for the known half-life of the pesticide:

$$RM = e^{-0.693\left(\frac{tl}{Thalf}\right)} \qquad (2)$$

where

RM = fraction of pesticide remaining;

tl = time of travel in the layer of interest, in days; and

Thalf = half-life of the pesticide in the layer, in days.

The values assigned to half-life for each layer in the system are based on empirically obtained figures from field and laboratory experiments, such as those of Armstrong and others (1967). Equation 2 is solved for each layer, allowing for the residence time in each. The amount of the original pesticide applied to the land surface that remains after transport through more than one layer is the product of the values of RM for each layer.

Root uptake of pesticide is assumed to be proportional to the root uptake of water (evapotranspiration). To obtain the fraction remaining after decay and root uptake, the amount of pesticide remaining after decay is multiplied by the ratio of the amount of water flux at the depth of interest to the amount of water entering the ground at the land surface.

EXAMPLE SIMULATION

An example of the use of the model to demonstrate the transport of five chemicals through a four-layer unsaturated zone is shown in figure H-11. The data input file for atrazine also is given in figure H-11. The data input file was the same for the other four chemicals, except for the organic-carbon partition coefficient (KOC) and the pesticide half-life.

The results shown in figure H-11 demonstrate large ranges in transport velocity and decay rates among the various chemicals. Chloride, which is a conservative tracer (KOC = 0), has the shortest residence time in the unsaturated zone (2.4 years), whereas trifluralin penetrates less than 2 feet after 15 years. Of the three pesticides that reach the water table (at 30 feet below land surface), the largest fraction that remains is that of atrazine. Although the residence time of 2,4-D amine is considerably less than that of atrazine, 2,4-D amine is less of a threat to the quality of ground water because of its more rapid rate of decay.

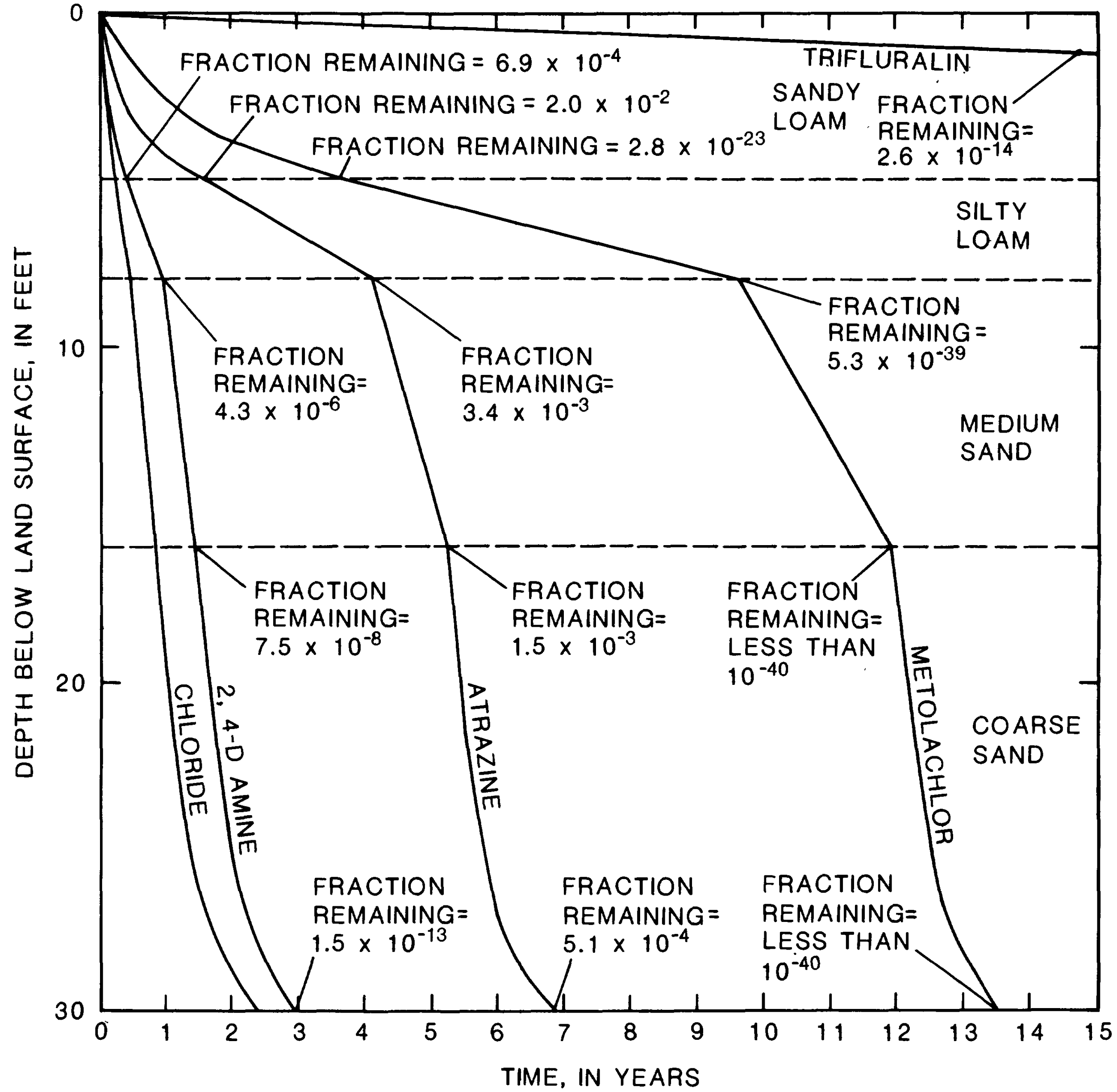
The potential for a given pesticide to contaminate ground water is dependent on the pesticide having a sufficiently small KOC and a sufficiently large half-life. The question as to the levels required for these two variables to pose a threat to ground-water quality depends on local conditions, such as the amount of pesticide applied, amount and type of irrigation, quantities of rainfall, the depth to the water table, and the organic-carbon content of materials in the unsaturated zone.

Several changes in contaminant velocity can be inferred from figure H-11. Velocity varies considerably from land surface to the bottom of the root zone because of variations in water flux. Abrupt changes in velocity occur between layers because of changes in water content. A gradual decline in velocity close to the water table occurs because of an increase in water content in the capillary fringe.

SENSITIVITY TO MODEL VARIABLES

Use of the model to test the sensitivity of transport of atrazine in the unsaturated zone to selected variables is illustrated by using a very simplified hypothetical situation. The unsaturated zone is divided into two layers. The top layer, which is 3 feet thick, corresponds to the soil and root zone; the bottom layer represents the remainder of the unsaturated zone (down to the water table). Reasonable, although arbitrary, values for each required model input variable were selected for the sensitivity analysis. The assigned values resulted, in part, from numerous references, including: U.S. Soil Conservation Service (1981), Cohen and others (1984), Gutentag and others (1984), Dugan and Peckenpaugh (1985), Luckey and others (1986), Nilson and others (1986), and Jury and others (1986). The "intermediate" values (table H-10) do not necessarily reflect average or typical conditions but are believed to be representative of regionally prevalent values. The two layers were assigned different values of organic-carbon content and atrazine half-life. The top layer (soil) is characterized by considerably larger organic-carbon content than the bottom layer (parent material). Half-life is less in the top layer than in the bottom layer, typically as a result of greater aeration and microbial action in the top zone. Other variables are considered to be uniform vertically for purposes of this analysis. Available information was assembled to estimate reasonable ranges in values (table H-10) applicable to the Midwestern United States. The ranges do not describe absolute minima and maxima but are believed to include fairly extreme values.

The sensitivity of this model to a variable is a measure of the amount of influence the changing of that variable has on residence time and fraction remaining. The sensitivity of the model is



Rate at which water enters the ground (inches/year)	60
Rate of deep percolation below roots (inches/year)	10
Thickness of root zone (feet)	4
Depth to water table (feet)	30
Organic-carbon partition coefficient (KOC)	160
Number of layers	4

Depth to bottom (feet)	Air-entry level (feet)	Wilting point (fraction)	Field capacity (fraction)	Porosity (fraction)	Organic carbon (%)	Half-life (days)
5	2.5	0.04	0.16	0.45	0.20	182
8	3.0	.06	.20	.50	.30	365
16	.7	.02	.12	.35	.03	365
30	.2	.02	.10	.30	.00	365

Figure H-11. – Depth of penetration of several chemicals and fraction of chemical remaining as a function of time since application at land surface, and data input file for atrazine.

Table H-10.—*Intermediate values and ranges of extreme values of selected model input variables used in sensitivity analyses*

Model input variable	Intermediate values	Range of values		
Deep percolation (inches per year)	10.0	0.01	-	20.0
Organic-carbon content, top layer (percent)	.8	0.1	-	5.0
Organic-carbon content, bottom layer (percent)	0	0.0	-	0.5
Half-life of pesticide in top layer (days)	182.5	10.0	-	365.0
Half-life of pesticide in bottom layer (days)	365.0	60.0	-	1,825.0
Distance from land surface to water table (feet)	100.0	5.0	-	300.0
Wilting point (feet)	.12	.02	-	.3
Thickness of root zone (feet)	3.0	1.0	-	6.0
Organic-carbon partition coefficient (milliliters per gram)	160.0	50.0	-	250.0
Field capacity (feet)	.20	.10	-	.35
Porosity	.40	.15	-	.60
Air-entry level (feet)	1.0	.1	-	8.0

evaluated in terms of the actual ranges of values of input variables that can be expected in the region of interest. The sensitivity to a given variable was tested by assigning intermediate values to all other variables (table H-10), then comparing the model results when the two extreme values for the variable in question were used. The analysis thus assumes that there is no interdependence among variables.

Changes in residence time caused by varying each input variable over its expected range (table H-10) are shown in figure H-12. The vertical scale is inverted so that small residence time, which relates to large potential for ground-water contamination, is on top. Residence time is most sensitive to deep percolation rate, depth to the water table, organic-carbon content of the bottom layer, and wilting point. Residence time is independent of pesticide half-life. Given that the values for all other variables are kept equal to their intermediate values, the variables that permit the shortest residence time are, in order of importance, depth to water table, wilting point, and deep percolation rate.

Ranges in the fraction of pesticide remaining in water that reaches the water table according to the sensitivity analyses are shown in figure H-13. If the fraction of pesticide remaining at the water table represents contamination potential, then the variables to which ground-water contamination potential is most sensitive are deep percolation (recharge), organic-carbon content of the bottom layer, and pesticide half-life. Given that the values for all other variables are kept equal to their intermediate values, the variables that can allow the greatest potential for ground-water contamination are, in order of importance, depth to the water table, pesticide half-life in the bottom layer, deep percolation rate, and wilting point.

The results of sensitivity analyses are biased by the use of "intermediate" values and the independent variation of model input variables. Results may depend on the values selected as "intermediate."

The results of sensitivity analyses do not demonstrate susceptibility to ground-water contamination under extreme conditions that may exist at some localities. The coexistence of several conditions that favor ground-water contamination may cause contamination to be certain.

CONCLUSIONS

Model results indicate that the variables to which pesticide transport in the unsaturated zone is most sensitive are deep percolation, organic-carbon content in the bottom part of the unsaturated zone, half-life of pesticides, and depth to the water table. Any assessment of nonpoint ground-water contamination by pesticides that originate at the land surface requires quantification of these variables.

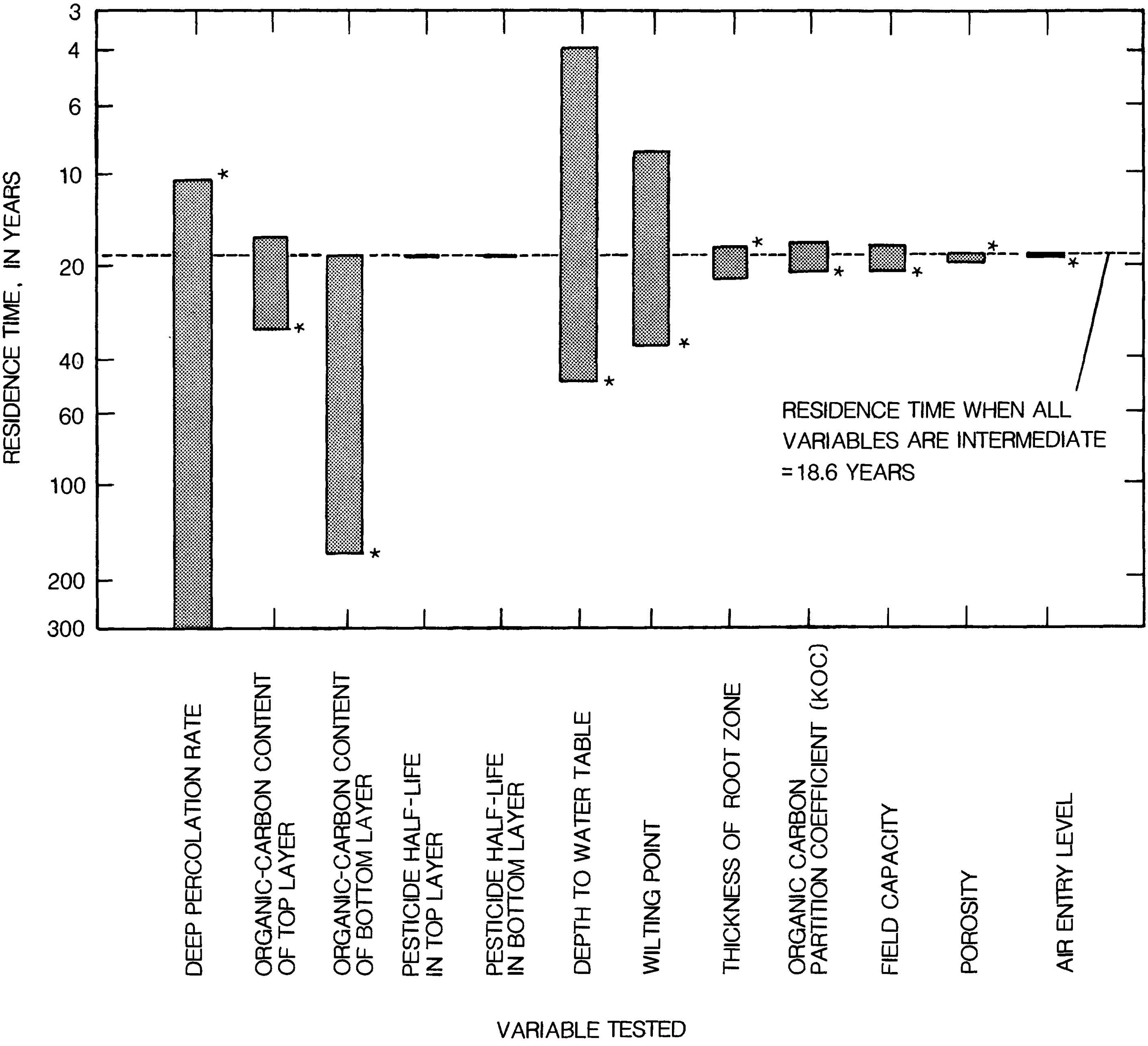


Figure H-12.—Simulated ranges in residence time of atrazine in unsaturated zone. (In each case, the value of the "variable tested" was changed throughout its range of values (table H-10), while other variables were maintained at their intermediate values (table H-10). Asterisk indicates the extreme of range in residence time that is induced by the maximum value of the variable tested.)

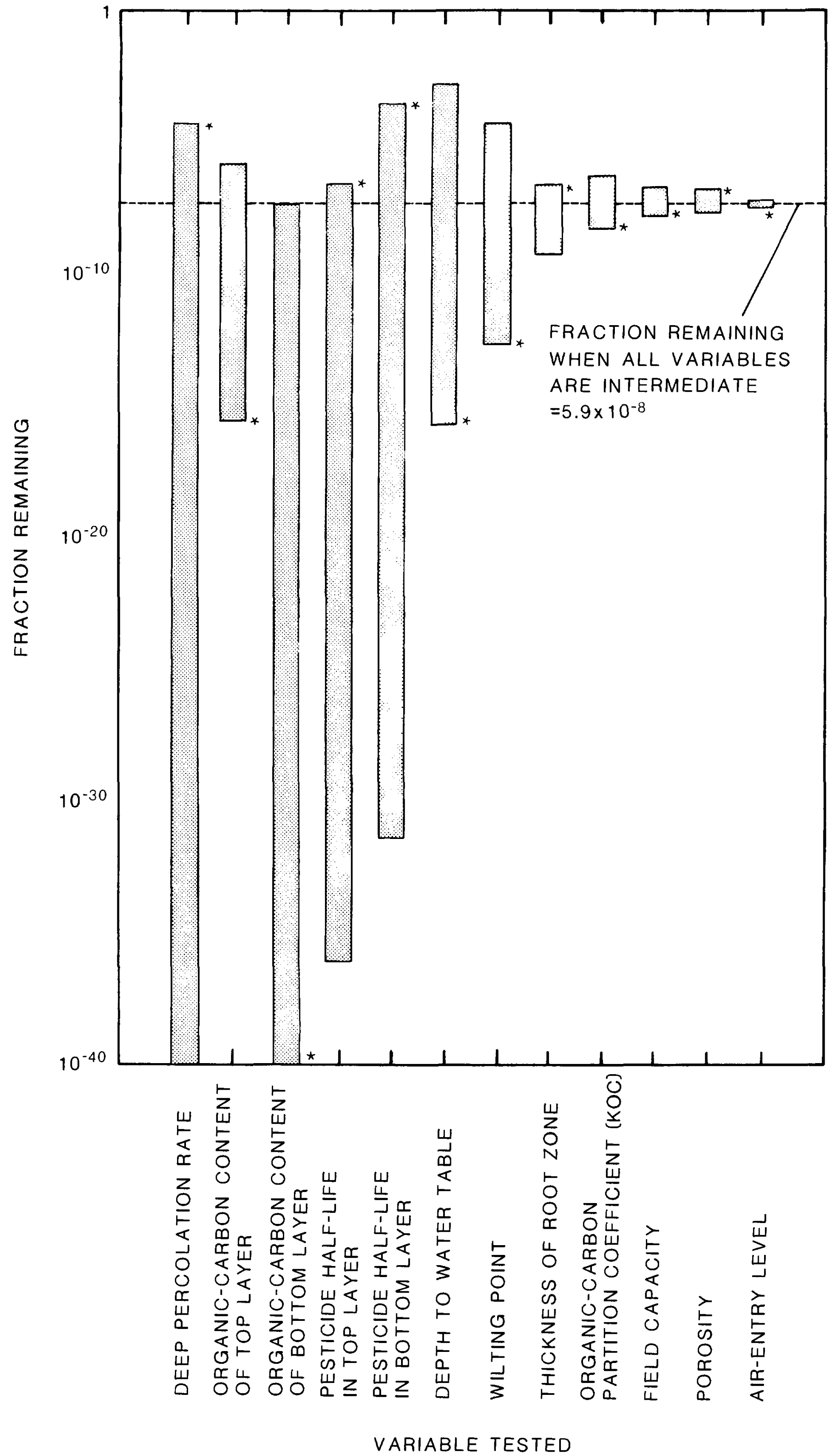


Figure H-13.—Simulated ranges in fraction of atrazine remaining in water that reaches water table. (In each case, the value of the "variable tested" was changed throughout its range of values, while other variables were maintained at their intermediate values (table H-10). Asterisk indicates the extreme of the range in fraction remaining that is induced by the maximum value of the variable tested.)

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METHOD FOR SIMULATING WATER-TABLE ALTITUDES FROM STREAM AND DRAINAGE-BASIN LOCATIONS BY USE OF A GEOGRAPHIC INFORMATION SYSTEM

By William A. Battaglin[1], Randy L. Ulery[1], and Eric F. Vowinkel[1]

ABSTRACT

A method was developed that uses a Geographic Information System to simulate water levels in an unstressed water table for a 7.5-minute quadrangle. The Dupuit-Forchheimer equation was solved for water-table altitude at 1,698 nodes on a grid over the study area. Input data consists of locations and altitudes of streams, locations of drainage divides, and estimates of aquifer hydraulic conductivity and recharge rate. The Geographic Information System calculated altitudes of streams at discrete intervals between points of known altitude, distances between each node and the nearest drainage divide, and distances between each node and the nearest stream. Results were contoured and displayed with Geographic Information System software.

Measured water-table altitudes at 22 wells are compared with simulated water-table altitudes at those points. The median of the absolute value of the residuals for this comparison is 6.2 feet; the first and third quartiles are 2.1 and 8.0 feet, respectively. The median percentage error at the 22 locations is 7.6 percent.

INTRODUCTION

An objective of the U.S. Geological Survey Toxic Waste—Ground-Water Contamination Program is to develop methods and information that aid in evaluating the relation of shallow ground-water quality to hydrogeology and land use on a regional scale. This paper outlines a method that uses a Geographic Information System (GIS) to simulate an unstressed water table with sufficient detail and accuracy for determining altitude and gradient of the water table, flow direction, and thickness of the unsaturated zone at any point. This information can be used to define zones of contribution to wells, variables in mass-balance equations, and the susceptibility of certain areas to ground-water contamination from human activities. All input data used for this method are from available sources, such as the U.S. Geological Survey's 7.5-minute-quadrangle maps and technical reports; data are stored, manipulated, and contoured by the GIS. Assumptions and limitations of this method and accuracy of the results are discussed.

Description of Study Area

The study area is included entirely within the U.S. Geological Survey's 7.5-minute Hightstown quadrangle in Mercer and Middlesex Counties (fig. H-14). This area lies almost entirely within the New Jersey Coastal Plain. Part of the study area is northwest of the Coastal Plain and is underlain by Triassic and Jurassic age rocks of the Newark Supergroup (fig. H-14). Most of the study area lies within the outcrop area of the Potomac Group and Raritan and Magothy Formations. The unconsolidated sediments of these geologic units commonly are grouped as a multilayered hydrogeologic unit referred to as the upper, middle, and lower aquifers of the Potomac-Raritan-Magothy (PRM) aquifer system. Sediments of the Potomac-Raritan-Magothy aquifer system are of Cretaceous age (Zapecza, 1984, p. 6-18). The system crops out in a narrow band, 3 to 6 miles wide, that trends northeast-southwest (fig. H-14). The remainder of the study area lies to the southeast of the PRM outcrop and is underlain by younger Cretaceous aged sediments of the Merchantville Formation, the Woodbury Clay, and the Englishtown Formation. The study area is characterized by broad lowlands that range in altitude from 55 to 130 feet above sea level. The Millstone River is the primary drainage in the study area (fig. H-14).

METHODS OF STUDY

The Dupuit-Forchheimer Equation

The altitude of the water table was approximated by solving a form of the Dupuit-Forchheimer equation at 1,698 nodes within a

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

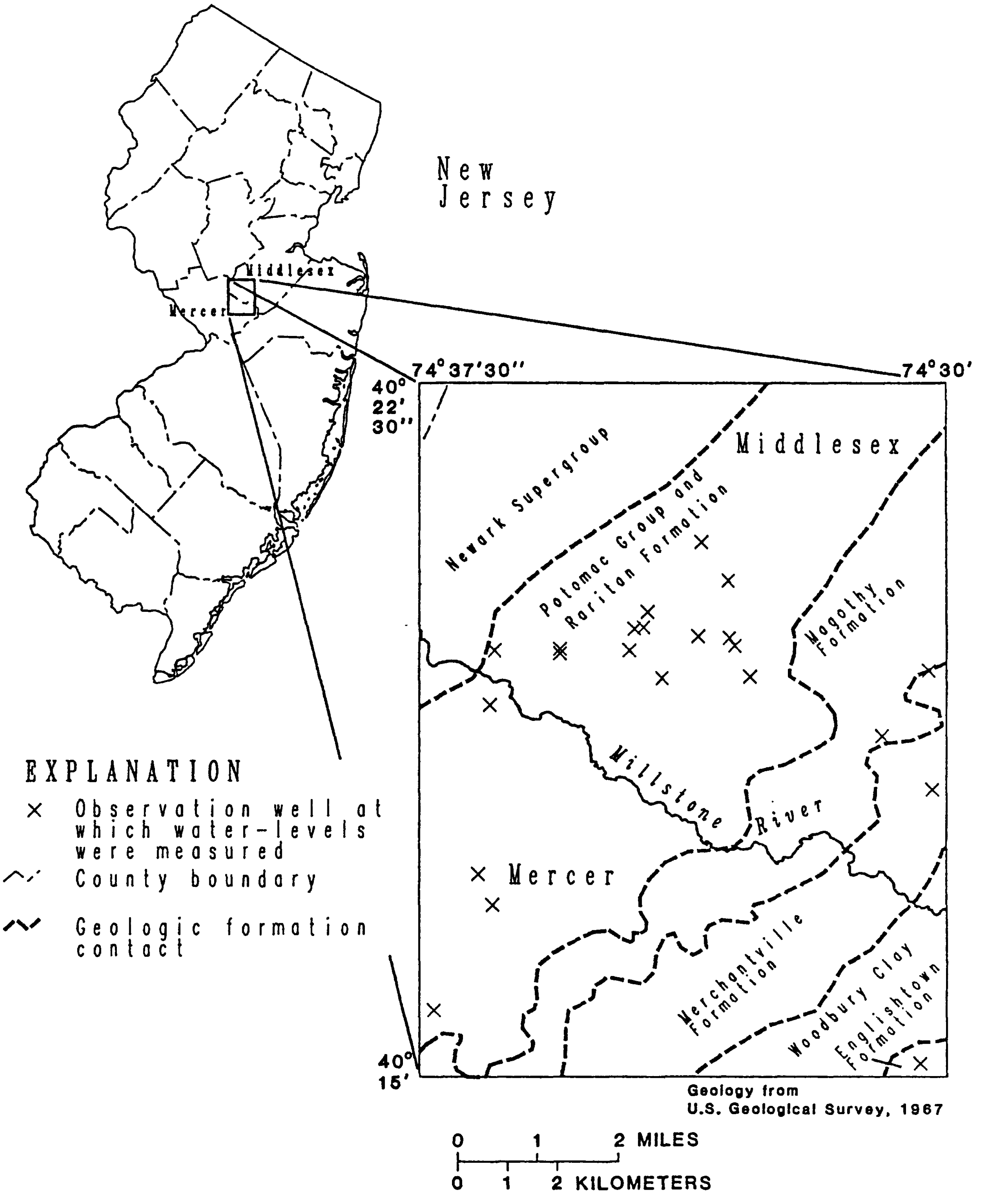

Figure H-14.—Location of observation wells and geology in the study area.

grid over the study area. The form of the equation solved is as follows:

$$h = [h_a^2 + \frac{W}{K}(a^2 - x^2)]^{0.5}, \qquad (1)$$

where h is the altitude of the water table at some point on its surface (fig. H-15), x is the distance from that point to the water-table divide along a flow path, a is the distance along a flow path through that point from the divide to a stream, h_a is the altitude of the stream at the end of the flow path, K is hydraulic conductivity, and W is recharge to the water-table aquifer (Todd, 1980, p. 112-115).

This solution is based on the assumption that flow is horizontal and uniform throughout a vertical section; in addition, the velocity of flow is proportional to the tangent of the hydraulic gradient. These assumptions do not reduce the accuracy of the solution for situations where the water table is nearly flat and the sine and tangent of the gradient are nearly equal (Todd, 1980, p. 113-114).

Data-Base Development

ARC/INFO[2], a proprietary GIS, was used to store and analyze all data used to develop this method. Two classes of spatial data – locational (x,y coordinates), and attribute or feature characteristic (z-coordinate) – are organized by using both a relational and topological model. In this system, information is organized about lines (ARCS), points, or areas (POLYGONS), by using relational data-base tables that link individual locations with the attributes of the feature and store the information in hierarchical computer files called coverages. These coverages can be analyzed individually or in conjunction with other coverages. Triangulated Irregular Network (TIN) data structures are used to simulate surfaces. A TIN is a series of triangles created by connecting each data point in a coverage with its nearest neighbors. Any attribute that is associated with the data points can be used as the z-coordinate for the surface. Values for that attribute can then be estimated at unknown sites within the coverage by use of

Table H-11.—*Type and sources of Geographic Information System coverages needed to generate water-table altitudes*

Model input	Coverage type	Sources
Stream locations	ARC	U.S. Geological Survey 7.5-minute quadrangles
Stream altitudes	Point	U.S. Geological Survey 7.5-minute quadrangles
	ARC	Field collected data
Drainage basin divides	ARC	U.S. Geological Survey 7.5-minute quadrangles
Topography	ARC	U.S. Geological Survey 7.5-minute quadrangles
	Point	altitude of land-surface at observation wells
Point grid	Point	Generated by ARC/INFO
Hydraulic conductivity	POLYGON	Technical reports or field collected data
Recharge rate to water-table aquifer	POLYGON	Technical reports or field collected data

Model output	Coverage type
Water-table altitudes	TIN, ARCS, Points, or POLYGONS
Depth-to-water	TIN, ARCS, Points, or POLYGONS
Distance from well to nearest basin divide	Item in point grid coverage
Distance from well to nearest stream	Item in point grid coverage
Simulated flow path length	Item in point grid coverage

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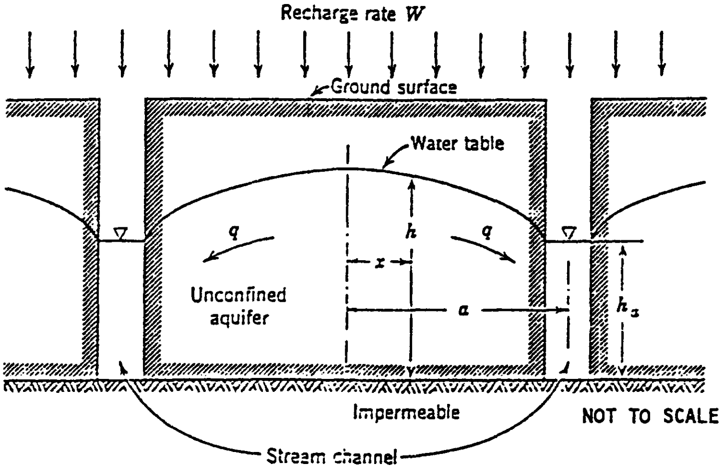
[2] Use of brand or trade names in this paper is for identification purposes only and does not constitute endoresement by the U.S. Geological Survey.



EXPLANATION

h	The altitude of the water table at some point on its surface
h_a	The altitude of the stream at the end of a flow path
a	The distance of a flow path from water-table divide to stream
x	The distance from a point on the water-table surface to the water-table divide along a flow path
W	Ground-water recharge rate
q	Ground-water flow per unit thickness

Figure H-15.—Section view of variables needed to solve the Dupuit-Forchheimer equation. (Modified from Todd, 1980, fig. 4.3.)

interpolation techniques. ARC/INFO commands and feature types are indicated by upper case. Data requirements for this method are summarized in table H-11.

Stream locations were digitized from the Hightstown 7.5-minute quadrangle. The stream coverage used to determine the distances a and x, and the altitude h_a, for equation 1 was generated by removing small tributaries, such as first-order streams (Shreve, 1967) or ephemeral streams that do not have defined basin-divide delineations. Streams remaining in the coverage were processed with the GENERALIZE, DENSIFYARC, and ARCEDIT commands or subsystems so that all streams were composed of 100-meter ARCS. Gradients were determined from points of known stream altitude. An altitude was assigned to each stream ARC between points of known altitude using the ALLOCATE command in the NETWORK subsystem of ARC/INFO.

Drainage basins were digitized from U.S. Geological Survey 7.5-minute quadrangles. The original drainage-basins coverage defined topographic divides between adjacent streams. Some ARCS that represented the divides between streams that were removed from the streams coverage or that represented the divisions between separately gaged parts of a basin were eliminated from the drainage-basins coverage. In some places, drainage-basin divides were approximated by the boundary of the study area.

Topography for the study area was acquired by digitizing lines of equal altitude and benchmarks from the Hightstown quadrangle. These coverages were APPENDED to the stream-altitude coverage and to a point coverage containing the altitude of the land surface at the locations of the observation wells. The appended coverage was used to make a TIN representing altitude of the land surface.

A regularly spaced grid (cells are approximately 280 meters on each side) with 1,698 nodes was created with the GENERATE command. The points representing the grid nodes were assigned to subbasin polygons (fig. H-16), representing either the left or the right side of each stream basin, by creating a POLYGON coverage with the UNION command from the stream and basin coverages and using the IDENTITY command to determine the points that fall within each polygon. Stored with each node were values for the shortest distance from the node to the basin divide, the shortest distance from the node to the stream, the altitude of the stream, a recharge rate, and hydraulic conductivity.

A hydraulic conductivity of 104 ft/d (feet per day) was used for the entire study area. This value was the average of the median conductivities for the upper aquifer of the PRM aquifer system (92 ft/d), and the middle aquifer of the PRM aquifer system (116 ft/d) (A.A. Pucci, U.S. Geological Survey, written commun., 1988). A value of 20 in/yr (inches per year) was used as the long-term, average ground-water recharge to the study area, and is equal to that used by Martin, in press, for average ground-water recharge to the New Jersey Coastal Plain.

Assumptions and Limitations of the Analysis

Two assumptions were made in using the GIS to acquire values for x and a from equation 1. First, it was assumed that ground-water divides coincide with topographic divides. This assumption generally is valid for the New Jersey Coastal Plain (O.S. Zapecza, U.S. Geological Survey, oral commun., 1988). Second, x was assumed to be equal to the shortest distance between a node in the grid and the basin divide, and a was assumed to be equal to the shortest distance between the basin divide and the stream passing through a node in the grid. Both distances are measured to the bounding stream or basin divide that forms the subbasin polygon containing the grid node (fig. H-16). Hence, x and a approximate, but do not equal distances along an actual flow path.

Model Output and Accuracy

The GIS was used to generate TIN surfaces representing the water-table altitude and the depth to water. From these surfaces, attribute data, such as water-table altitude, depth to water, flow direction, hydraulic gradient, and the length of a flow path can be calculated for any point within the study area (table H-11).

A simulated water table is shown in figure H-17. In the study area, the altitude of the simulated water table ranges from 53 to 115 feet above sea level. Measured water-table altitudes at 22 wells (fig. H-14) are compared with simulated water-table altitudes at those locations. The median of the absolute value of the residuals

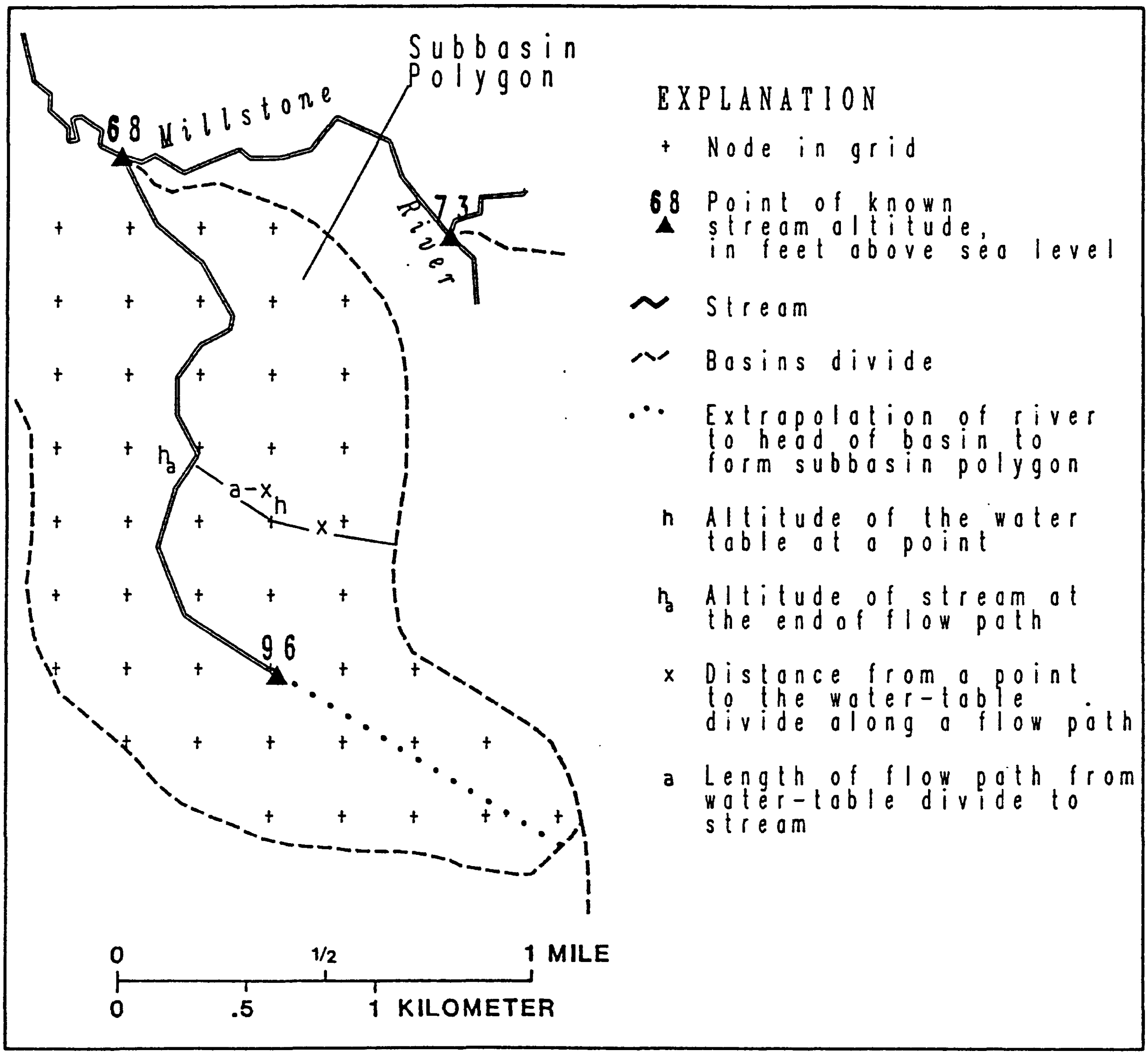


Figure H-16 – Variables in the Dupuit-Forchheimer equation, grid spacing, and subbasin polygon.

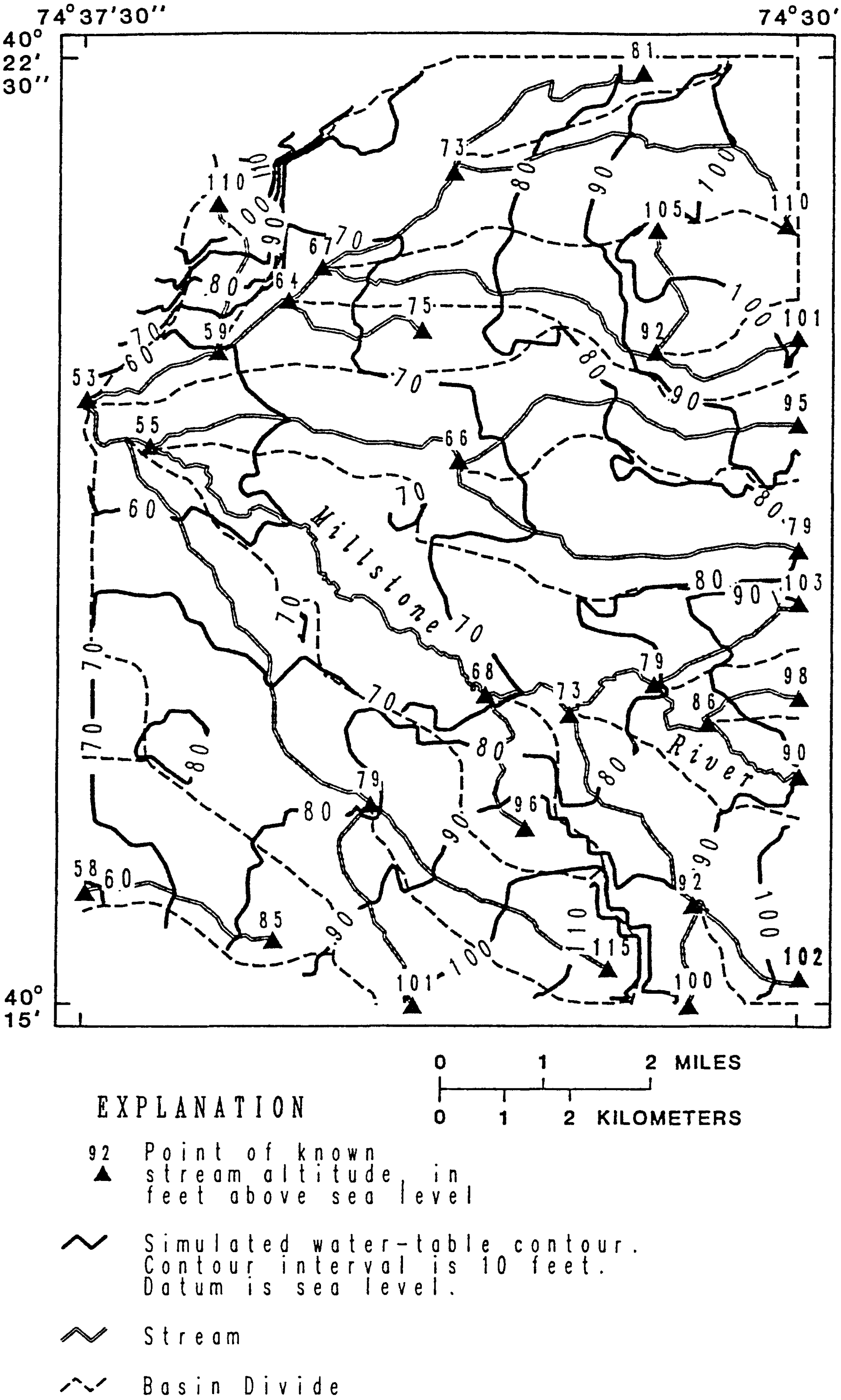


Figure H-17.—Configuration of simulated water table.

(difference between measured and simulated water-table altitudes) for this comparison is 6.2 feet; the first and third quartiles are 2.1 and 8.0 feet, respectively (25 percent of the observations are less than the first quartile and 75 percent of the observations are less than the third quartile). The percent error ([| measured water-table altitude - simulated water-table altitude | / measured water-table altitude] x 100) was calculated at these 22 points. The median percentage error is 7.6 percent; the first and third quartiles are 3.0 and 13.6 percent, respectively. Simulated water-table altitude and depth-to-water values were determined with the TINSPOT command, which interpolates an attribute value from a TIN surface at any point. Simulated flow direction and hydraulic gradient were determined with the IDENTITY command on a coverage of simulated water-table POLYGONS (TIN converted to a polygon coverage).

The accuracy of this method is limited by the accuracy of the input data. Although stream-altitude data may be available in map form, specific field data, such as stream-surface and stream-tributary start-of-flow altitudes are needed to improve model accuracy.

Sensitivity of Method to Hydraulic Characteristics and Grid Spacing

A sensitivity analysis was performed to determine the effects of changes in hydraulic conductivity or recharge rate on model results. It was initially thought that the ratio of recharge rate to hydraulic conductivity (W/K) from equation 1 could be zoned by hydrogeologic unit by providing a unique conductivity value to nodes in the grid that fell within the different hydrogeologic units. However, this resulted in excessively high simulated water-table altitudes in areas where conductivity was expected to be low (for example, outcrops of clays or consolidated rock). It was apparent that the recharge rate to the water-table aquifer is a function of the hydraulic properties of the unit.

Because accurate recharge rates to lower permeability units, such as clays, were not available, a sensitivity analysis was performed on the ratio W/K to determine the variation in the water-table altitude solution with changes in its value. For this analysis, the ratio was altered by two orders of magnitude above and below the initial estimate. Increasing the ratio by a factor of 10 or 100 produced simulated water-table altitudes that were above the land surface over much of the study area. Decreasing the ratio by a factor of 10 caused a lowering of the simulated water table. Decreasing the ratio by a factor of 100 produced results that were nearly identical to those when the ratio was decreased by a factor of 10. Because the simulated water-table altitudes at nodes in the grid ultimately were tied to fixed-altitude values at the streams (h_a from eq. 1), decreasing the ratio had less effect on the simulated surface than did increasing the ratio. These results indicate that the initial estimate of the ratio (0.0000439) was likely to be within an order of magnitude of its actual value at all points in the study area.

Grid spacing also will affect the results. In general, decreasing grid spacing will increase resolution of the water table so that contoured results will be smoother and some detail will be gained. However, size of the study area, scale of the input data, level of accuracy needed in the result, and machine constraints should be considered when selecting a grid spacing.

SUMMARY AND CONCLUSIONS

A method that uses a GIS to simulate water levels in an unstressed water table was developed. The method used the Dupuit-Forchheimer equation to determine water-table altitude at 1,698 nodes on a grid superimposed over the study area. The simulated water-table surface was used to estimate altitude and gradient of the water table, flow direction, and thickness of the unsaturated zone at each node in the study area. The simulation is based on input data derived from available sources, such as U.S. Geological Survey 7.5-minute topographic quadrangle maps and technical reports. Improved accuracy is expected if actual field data, such as stream surface altitudes and water-table altitudes from wells are collected and used.

The results of this method were compared with measured water-table altitudes at 22 wells in the study area. The median of the absolute value of residuals between simulated and measured water-table altitudes is 6.2 feet; the first and third quartiles are 2.1 and 8.0 feet, respectively. The median percentage error at these 22 points is 7.6 percent; the first and third quartiles are 3.0 and 13.6 percent respectively.

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(p.541 follows)

TOTAL ADENYLATE AND ADENYLATE ENERGY-CHARGE MEASUREMENTS FROM BACTERIAL COMMUNITIES IN GROUND WATER

By Myron H. Brooks[1] and Richard L. Smith[1]

ABSTRACT

Adenine nucleotides are essential biochemicals that have been used to estimate microbial biomass and metabolic state in many different ecological settings. These compounds were extracted from free-living bacteria along a longitudinal transect of a plume of sewage contaminated ground water in an attempt to characterize the active bacterial biomass associated with the contaminant plume. Extracts were derivatized with chloroacetaldehyde and analyzed by high-performance liquid chromatography using fluorescence detection. Total adenine nucleotide concentration, an index of active biomass, decreased from 111 picomoles per liter at a distance of 80 feet from the sewage source to 26 picomoles per liter at a distance of 9,590 feet from the sewage source. Adenylate energy charge, an index of metabolic state, was at or near a value of 0.60 for all locations sampled within the plume of contaminated ground water, and was independent of total adenine nucleotide concentrations. Measured adenylate energy charges were comparable to those reported for laboratory cultures in stationary growth phase and indicate that microbial communities in the contaminant plume exist at a metabolic state characterized by external stress such as nutrient limitation.

INTRODUCTION

Adenosine triphosphate (ATP), adenosine diphosphate (ADP) and adenosine monophosphate (AMP) function as energy currency compounds in all living organisms (Stanier and others, 1976). Energy derived from the hydrolysis of ATP drives the many biosynthetic reactions necessary for the maintenance of life, from bacteria to higher plants and animals. ATP and the related adenylates ADP and AMP are essential biochemicals whose presence in an environment indicate that metabolic activity is occurring. As such, extraction and quantification of these compounds from bacterial populations in a particular environment offer a potential tool for studying the influences and effects of micro-organisms on geochemical processes. This paper focuses on the use of adenylate measurements to estimate the amounts and metabolic state of bacteria living in ground water. A brief description of the biochemistry of ATP and intracellular adenylates, a short summary of applications of this type of measurement, and a discussion of analytical techniques available for these measurements is presented. Following this background material, the methods employed and results obtained from extraction and quantification of ATP, ADP, and AMP from bacterial communities living in a sewage-contaminated aquifer on Cape Cod, Mass., are discussed.

BIOCHEMISTRY OF ADENYLATE COMPOUNDS

ATP occupies a central role in the complex web of reactions that constitute cell metabolism. Various energy-producing reactions (catabolism) are harnessed by organisms to synthesize ATP, which in turn is then used to provide energy to thermodynamically unfavorable biosynthetic reactions (anabolism). Thus, ATP serves as a link between energy producing and energy requiring reactions within the cell. The equilibrium between ATP, ADP, AMP and inorganic phosphate in the intracellular environment is extremely dynamic; the time required for replacement of one-half of the terminal phosphate groups of ATP in an actively respiring bacterial cell is a matter of seconds (Lehninger, 1982). Despite this rapid turnover rate, evidence suggests that the relative concentrations of each adenylate are quite stable and this stability is a fundamental property of cell metabolism (Chapman and others, 1971). In general, the more metabolically active a cell is, the greater the ratio of ATP to total adenylates will be. Therefore, the relative amounts of ATP, ADP, and AMP within a cell can be used as indicators of the metabolic state of the cell. Extraction from and quantification of these three compounds from a

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

microbial community offers the potential of not only estimating the living biomass of the community, but also gaging the metabolic state of the organisms in the community.

The measurement of ATP in extracts of environmental samples was first reported for ocean-dwelling micro-organisms in 1966 (Holm-Hansen and Booth, 1966). These authors estimated living biomass from ATP concentrations by using ATP content:cell-carbon (ATP:C) ratios measured in laboratory cultured microorganisms. Since that first application, hundreds of papers have reported the use of ATP or total adenine nucleotide content (TANC) measurements for biomass estimates in numerous ecological settings (Karl, 1980) (TANC = [ATP] + [ADP] + [AMP]; brackets denote molar concentrations). In converting ATP to cell carbon, most investigators have applied a single conversion factor (the most commonly used being ATP:C = 1:250). This approach has been criticized, but in many cases, biomass estimates obtained in this manner have agreed very closely with independent biomass measures obtained from the same community (Sorokin and Lyutsarev, 1978; Sinclair and others, 1979), and significant correlations between ATP content and other indices of metabolic activity have been found (see Karl, 1980). Of interest to workers involved with ground-water contamination is the report of a correlation between ATP content and biodegradation of toluene in subsurface material (Wilson and others, 1986). Application of a single ATP:C conversion factor to an environmental adenylate measurement may or may not result in an accurate biomass estimate. The ratio of ATP to cell carbon varies both between bacterial species and also within species as a function of growth conditions, nutrient limitation, and so forth (Karl, 1980, p. 752-752). An ATP or TANC measurement from a particular environment represents an average of all the species and metabolic states found in the microbial community. This fact needs to be considered when biomass estimates based solely upon ATP or TANC are performed.

If all three intracellular adenylates are quantified, the adenylate energy charge (EC_A) can be calculated. This unitless number has been proposed as a measure of the metabolic state of an assemblage of organisms (Atkinson and Walton, 1967). The EC_A is equal to [ATP] + 1/2 [ADP] / [ATP] + [ADP] + [AMP], and provides a linear measure of the chemical potential energy stored in in the adenylate pool at any moment. Theoretically, the EC_A can range from 0 (AMP only) to 1 (ATP only). In carefully controlled laboratory experiments EC_A values of approximately 0.5 to 0.95 have been measured. EC_A values of about 0.5 are normally associated with senescent cells, values of approximately 0.6 are associated with cells in stationary growth phase, and values greater than 0.85 usually are associated with cultures undergoing exponential growth (Atlas and Bartha, 1981). Use of EC_A values for prediction of community metabolic state has met with mixed success. Recent papers by Riemann and Wium-Andersen (1981), Jewson and Dokulil (1982), and Kaplan and Bott (1985) have suggested that the EC_A is of limited value for monitoring physiological status of microbial communities in lakes and streams, whereas papers by Christensen and Devol (1980), Romano and Daumas (1981), and Brookes and others (1983) report successful application of the EC_A in investigations of microbial communities in marine sediments and water, and soil.

ANALYTICAL TECHNIQUES FOR ADENYLATE MEASUREMENTS

Analytical techniques for the measurement of ATP or TANC are of two basic types. The first technique involves the use of luciferin-luciferase, a complex carboxylic acid and an enzyme isolated from firefly lanterns. Reaction of these compounds with ATP results in a hydrolysis to AMP, and part of the energy released by the hydrolysis reaction is manifested as light. The amount of light released is directly proportional to the ATP concentration, which allows for quantification by comparison to standards of known ATP concentration. This technique is extremely sensitive; analytical detection limits are commonly in the low picomolar range. A modification of this technique whereby ADP and AMP are enzymatically converted to ATP and then quantified has been used to extend the luciferin-luciferase assay to the measurement of TANC and EC_A (Karl and Holm-Hansen, 1978). The second analytical technique for quantification of adenylates involves high-performance liquid chromatography (HPLC). Although less sensitive than the enzymatic assay, this technique offers rapid quantification of all three adenine nucleotides. An improvement in sensitivity has been obtained by forming the 1-N^6 etheno derivative of each adenylate and using fluorescence detection (Preston, 1983). This procedure has lowered analytical detection limits into the low nanomolar range, providing adequate sensitivity for low-biomass environments like ground water.

EXPERIMENTAL

Total adenylate concentrations and adenylate energy charge values were determined for free-living bacteria in a sewage-contaminated sand and gravel aquifer located on Cape Cod, Mass. Bacteria were concentrated from water samples (10-20 liters) by filtration through 0.2 μm (micrometer) pore size membrane filters and intracelluar adenylates were extracted with 0.150 molar, ice-cold phosphoric acid. A mixed internal standard (1 nmol (nanomole) each of ATP, ADP, and AMP) was added to selected extracts. Extracts were neutralized to approximately pH 3.5 with NaOH and stored frozen. Extracts were freeze-dried and then derivatized in 2 mL (milliliters) of 0.5 molar chloroacetaldehyde. The resulting solution, containing the 1-N^6 etheno derivatives of ATP, ADP, and AMP was then freeze-dried again to partially remove excess chloroacetaldehyde prior to chromatography. Derivatized extracts were reconstituted in high-purity water, separated by HPLC, and quantified using fluorescence detection. Operating conditions included a C-18 analytical column, 8 percent methanol/92 percent phosphate buffer (0.15 molar, pH 6) mobile phase, 1 percent per minute linear gradient for 10 minutes, 290 nm (nanometer) excitation wavelength, and 440 nm emission wavelength. Individual compounds were identified on the basis of comparison with retention times of authentic standards. This entire sample concentration and analysis procedure is a modification of the method reported by Walker and others (1986).

RESULTS AND DISCUSSION

A longitudinal transect of the contaminant plume was sampled in July 1988, and results from this sampling are presented in table H-12. TANC and EC_A values in the table are means and standard deviations of replicate samples and analyses. TANC values are 10 to 1,000 times lower than those normally encountered in surface-water environments, yet they still indicate an active biomass within the aquifer. Because of uncertainties associated with conversion of TANC concentrations to cell carbon values, this type of calculation was specifically avoided. The TANC values display a steady decrease with distance from the sewage infiltration beds, an indication that bacterial abundance within the contaminant plume is a function of availability of nutrients from the sewage input. This relation is consistent with the correlations among numbers of free-living bacteria in the aquifer water and distance from the sewage infiltration beds reported by Harvey and others (1984). Adenylate energy-charge values measured throughout the plume were relatively uniform and appeared to

Table H-12. — *Total adenine nucleotide content and adenylate energy-charge values for a longitudinal transect of contaminant plume at Otis Air Force Base*

[TANC = total adenine nucleotide content; EC_A = adenylate energy charge; TANC and EC_A values presented as mean ± standard deviation]

Distance from infiltration beds (feet)	Depth below land surface (feet)	TANC (picomolar)	EC_A
80	49	112 ± 14	0.60 ± 0.03
330	66	100 ± 11	.58 ± .01
570	57	83 ± 24	.53 ± .03
950	46	60 ± 9.9	.56 ± .01
2,790	54	20 ± 4.7	.58 ± .04
4,960	64	46 ± 13	.59 ± .03
6,230	69	22 ± 1.2	.59 ± .06
9,590	64	26 ± 5.5	.57 ± .04

be independent of total adenylate concentrations. Energy-charge values were closely clustered around 0.6; a result that suggests that all of the microbial communities that were sampled were under some type of metabolic stress similar to that encountered by laboratory cultures in stationary growth phase. This result is not surprising; slow growth and stress brought on by lack of nutrients is the rule rather than the exception in most ecological settings (Atlas and Bartha, 1981).

CONCLUSIONS

The feasibility of measuring intracellular adenylate concentrations from bacteria living in ground water has been demonstrated. A method involving concentration by filtration, extraction with cold phosphoric acid, derivatization with chloroacetaldehyde, and separation and quantification of ATP, ADP, AMP by HPLC with fluorescence detection was employed at a sewage-contaminated aquifer on Cape Cod, Mass. Total adenine nucleotide contents closely matched previously reported measures of biomass in the contaminant plume. Adenylate energy charge values indicated that microbial communities in the plume were experiencing metabolic stress.

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PARTITIONING, DISTRIBUTION, AND RECOVERY DNA (DEOXYRIBONUCLEIC ACID) FROM WATER AND SEDIMENT IN A CONTAMINATED AQUIFER IN CAPE COD, MASSACHUSETTS

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

ABSTRACT

Recently, a method was developed for fluorometrically estimating deoxyribonucleic acid (DNA) concentrations in a contaminated, nutrient-poor sandy aquifer. This method was found to require alkaline extraction and phosphate buffering for efficient recovery (up to 90 percent) of DNA from sediment. Sediment fines (containing greater than 90 percent of bacterial numbers) were aseptically separated from larger grained abiotic particles by wet sieving, followed by alkaline lysis/extraction and DNA recovery. Partitioning of DNA (nonadherent microbial DNA compared to particle-associated bacterial DNA compared to particle-associated extracellular DNA) was estimated using measurements of well water and aquifer sediment samples. Extracellular DNA was estimated by using differences in sediment total DNA and prelysis DNAase-treated sediment samples. There was a decrease in DNA recovery, DNA per cell, and total DNA per gram of sediment coincident with decreased contaminant and nutrient concentrations over the length of the contaminant plume. Differences in recovery were found to be primarily due to pH, choice of buffer system, and sediment mineralogy. DNA per cell and DNA partitioning differences were found to be dependent upon location, nutrient conditions, and bacterial abundance.

INTRODUCTION

Increasing attention has focused on the measurement and study of deoxyribonucleic acid (DNA) in the environment. A number of recent surface-water and surface-soil studies have involved measurement of DNA (bacterial and extracellular) or have involved the behavior of extracellular DNA in particle-laden systems (DeFlaun and others, 1986, Lorenz and Wackernagel, 1987, Ogram and others, 1987, Paul and others, 1987). However, little is known about DNA in the subsurface. The lack of knowledge concerning subsurface DNA has resulted, in part, from a lack of suitable methodology to measure this highly surface-active macromolecule at very low levels in the presence of mineral surfaces. Also contributing to the problem of DNA measurement in subsurface material has been the difficulty in obtaining representative and uncontaminated samples.

Information on the distribution and measurement of extracellular and bacterially associated DNA in aquifer samples is germane to studies involving contaminated aquifers for several reasons:

(1) There is much concern over the use of genetically engineered micro-organisms and environmental release of recombinant DNA in aquifer biorestoration experiments because the fate and behavior of extracellular DNA in the subsurface is unknown. This concern arises, in part, from findings that bacteria in aquatic environments release intact DNA and that dissolved and adsorbed DNA can result in genetic transformations of other bacteria (Lorenz and Wackernagel, 1987).

(2) It is possible that extracellular DNA in nutrient-poor ground water may serve as potential sources of nitrogen, phosphorus, and nucleic acid precursors for indigenous bacteria involved in the degradation of organic contaminants (Litchfield and Seyfried, 1979).

(3) Quantification of intracellular bacterial DNA may be useful in the development of an improved method for estimating adherent bacterial biomass in contaminated aquifer sediments.

A study was done to develop a DNA assay that provides efficient recovery from sandy aquifer sediment. There is much to be learned about the distribution, adsorption behavior, and fate of DNA in aquifers. The sequential acidic-extraction techniques currently used for quantifying bacterially associated DNA in heterogenous

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

sediments yield low results (typically less than 2 percent) and are labor-intensive (Aardema and others, 1983, Lorenz and others, 1981, Torsvik and Goksoyr, 1978). This paper describes a basic extraction procedure for estimating levels of bacterially associated and extracellular DNA in well and aquifer core samples. Also presented are data on the levels, solid/solution partitioning, and pH-dependent adsorption behavior of extracellular DNA and on spatial variations in average bacterial DNA content in aquifer sediments collected along vertical and longitudinal transects through a plume of organically contaminated ground water at the U.S. Geological Survey ground water contamination study site at Cape Cod, Mass (fig. H-18).

MATERIALS AND METHODS

Water samples for DNA assays were obtained from a network of screened (250-μm (micrometer) slot width) polyvinyl-chloride-pipe observation wells (50.0 mm (millimeter) diameter) located along the longitudinal axis of the contaminant plume. Samples were collected with a stainless steel submersible pump connected to Teflon[2] tubing and collected in sterile plastic bottles after specific conductance and pH of the well water had stabilized. Samples of aquifer sediments were collected by using a piston-type coring device in conjunction with a hollow-stem auger drill. The cores were collected immediately adjacent to the well screens so that DNA in aquifer sediments could be directly compared to DNA in sediment-free ground water. In contrast to previous studies at the Cape Cod site, no drilling muds were used to obtain the core material, thereby minimizing contamination.

Development of an accurate method for estimating DNA and DNA partitioning (adsorbed:dissolved and extracellular:intracellular) in aquifer sediment required consideration of a number of factors. The pH-dependent adsorption behavior of DNA was examined in the presence of unaltered and alkaline-treated core material obtained from different locations in the contaminant plume, inasmuch as DNA recovery from core material depended, in part, on sediment minerology and solution chemistry. The variability in DNA recovery efficiency, in amounts of extracellular dissolved and adsorbed DNA, and in the number of copies of DNA (genomes) per bacterium were also observed. This was done because these characteristics differ from sample to sample and can affect the interpretation of DNA-recovery data. Efficiency of bacterial lysis was examined for each sample to assess whether or not compositional differences in aquifer sediments can affect the efficiency of the lytic treatment and, consequently, the efficiency of the extraction procedure for bacterially associated DNA.

Modifications were made to a previously published method (DeFlaun and others, 1986) for fluorometric determination of DNA in estuarine and open ocean systems. Because more than 90 percent of the bacteria in the aquifer sediments are attached to silt-sized sediment particles (less than 60 μm diameter)(Harvey and others, 1984), a wet-sieving procedure was used to separate bacteria-containing, silt-sized particles from the larger sand grains that are largely devoid of attached micro-organisms (Harvey and George, 1987). Particles less than 100 μm in diameter were collected in filter-sterilized water and handled volumetrically as a suspension. Enhanced recovery of DNA from sediments was accomplished by three additional modifications of the DNA quantification procedure: (1) addition of phosphate buffer (0.1 M (molar) final concentration), which at high concentrations competes for DNA-binding sites on the particle surfaces; (2) addition of ethylene diamine tetraacetic acid (EDTA) (200 mM (millimolar) final concentration) in a TRIS buffer (20 mM final concentration, pH 6.5) to chelate divalent cations that would otherwise promote readsorption of DNA; and (3) pH adjustment to slightly alkaline conditions 7.5 to 8.5, where readsorption of extracted DNA was observed to be minimal. Lysozyme/triton used with sonication proved to be the most efficient lytic agents, yielding 100 percent lysis of free-living bacteria and 75 to 90 percent lysis of adherent bacteria. A protocol for this technique is given in figure H-19.

RESULTS AND DISCUSSION

The modified DNA-measurement procedure yielded substantially higher recovery of DNA from aquifer sediments than procedures using the method developed for surface-water

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

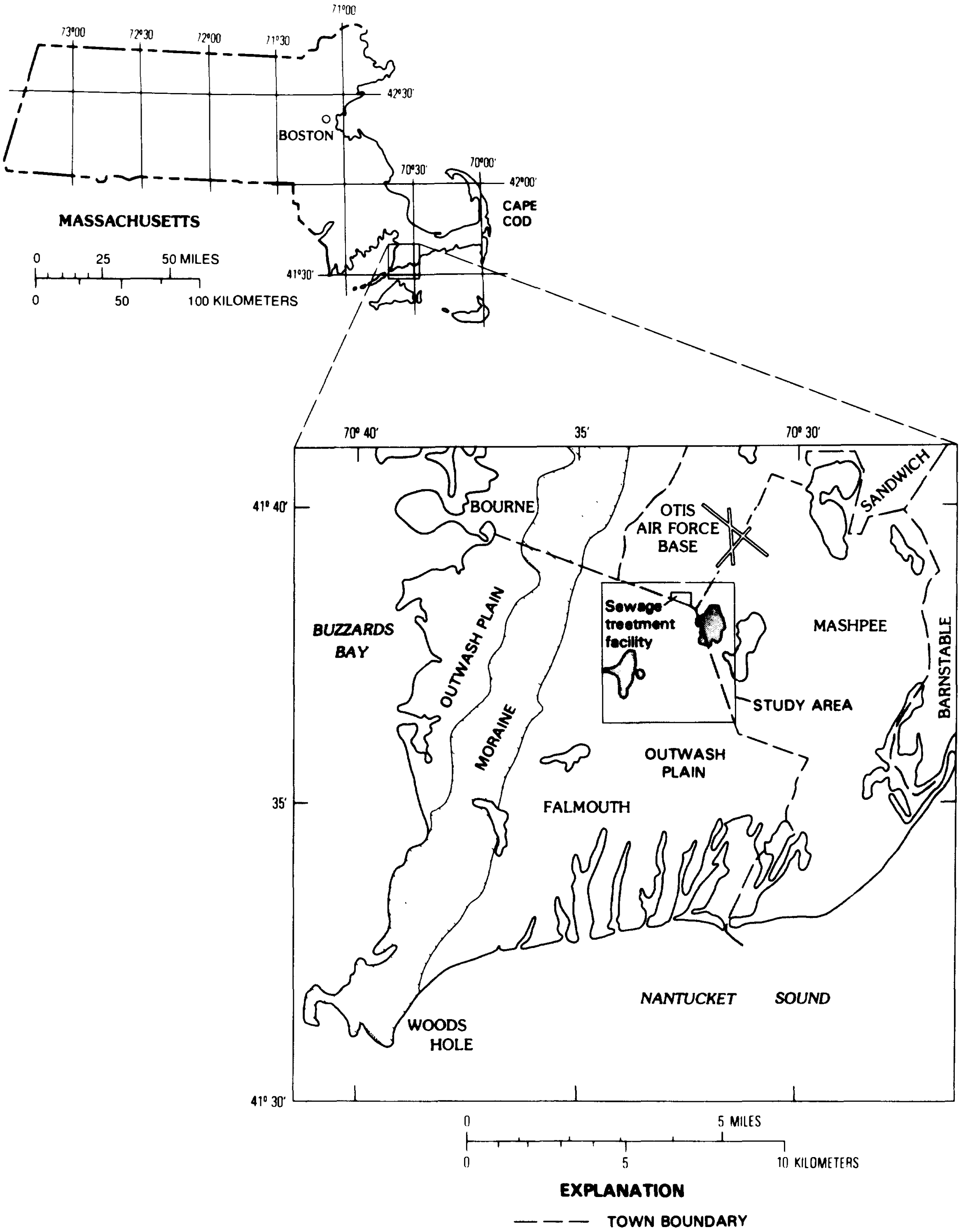

Figure H-18.—Study area.

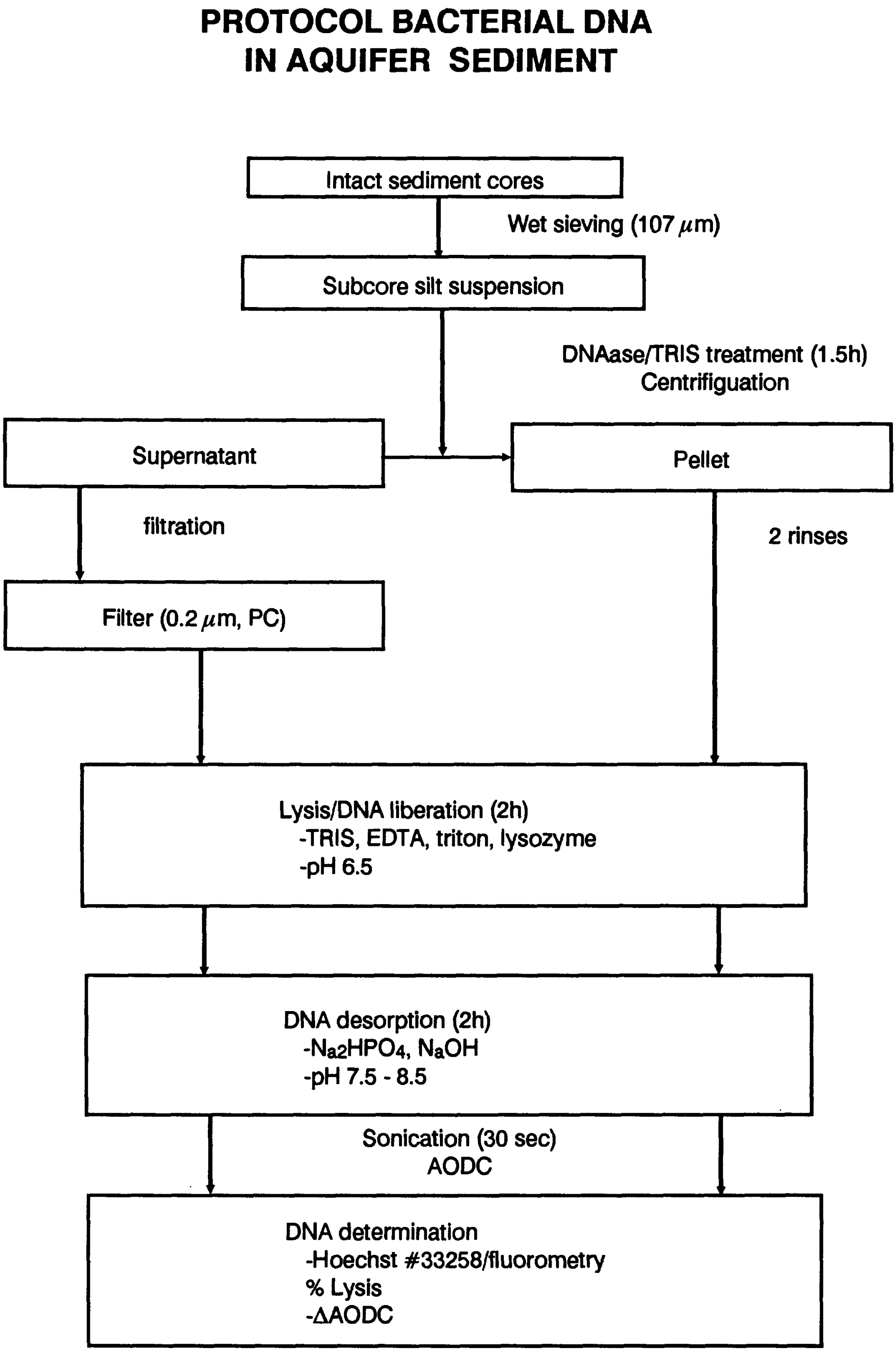

Figure H-19.—Protocol for measuring bacterial DNA in aquifer sediment.

environments (DeFlaun and others, 1986). The method reported here allows estimation of DNA concentrations from 50 to 2,000 ng/mL (nanograms per milliliter). However, there were a number of problems that may cause variability in DNA recovery, such as (1) extremely low levels of DNA, (2) strong sorption of DNA to aquifer sediment, (3) sediment heterogeneity over the length of the contaminant plume, (4) variability in amounts of extracellular and adsorbed DNA, and (5) variations in lytic-agent efficiency.

Most important in the recovery of DNA from aquifer sediments was the efficiency at which sorption or readsorption of extracted DNA could be minimized. Desorption of DNA from mineral surfaces was found to be highly pH dependent. Unlike many organic acids, maximal adsorption of DNA onto mineral surfaces occurred both at high and low pH and optimal recovery of DNA occurred under slightly alkaline conditions (pH 7.5-8.5). In general, the pH-dependent absorptive behavior of DNA was quite sensitive to changes in the geochemical makeup of the sediments. Therefore, the optimal pH for DNA recovery and the magnitude of fractional recovery depended, in part, upon the sediment mineralogy, which varied among core samples collected from different locations in the aquifer. Other factors also are likely to be involved, such as solution chemistry and the ratio of extractable DNA to the number of DNA-binding sites on the sediment-particle surfaces. Desorption of DNA from sediment could be enhanced by addition of EDTA, which chelates divalent cations, and by additions of phosphate and TRIS buffers, both of which may compete for DNA-binding sites. In contrast to several other DNA measurement techniques, sodium chloride (0.154M)/sodium citrate (0.154M) (SSC) was not used in this study, because readsorption of liberated DNA was found to be further minimized by keeping the ionic strength as low as possible (Lorenz and Wackernagel, 1987); the effect of ionic strength-induced compression of the electrical double layer (EDL) on DNA recovery from sediments was not a part of this study.

The data in table H-13 are a summary of results of sampling along the October 1987 transect. Although bacterial-lysis efficiency generally was good (from 90 to 100 percent), recovery of

Table H-13.—*Adsorbed, bacterially associated, and total DNA for aquifer sediments of differing silt content collected from five locations along a plume of organically contaminated ground water in Cape Cod, Massachusetts*

[NA, not applicable; W, water sample; C, core sample]

Location		Distance[1]	[Cell][2]	[DNA]t[3]	[Silt][4]	[DNA/g silt][5]	[DNA]b[6]	[DNA/cell][7]	[DNA]e[8]
318-36	W	0.05	4.51	0.096	NA	NA	0.096	2.130	NA
"	C	.05	12.23	.475	0.0435	100.42	.209	1.191	0.266
314-51	W	0.08	2.24	.049	NA	NA	.049	2.196	NA
"	C	0.08	20.60	.258	.6190	74.49	.176	0.746	.083
347-M1	W	.45	.96	.029	NA	NA	.029	3.075	NA
"	C	.45	NA	NA	NA	NA	NA	NA	NA
S230-49	W	.19	2.16	.037	NA	NA	.037	1.719	NA
"	C	.19	26.02	.534	.144	40.74	.252	.753	.282
350-13	W	3.03	.35	.016	NA	NA	.016	4.708	NA
350-68	W	3.03	.48	.0056	NA	NA	.0056	1.181	NA
"	C	3.03	393.430	.0565	.6980	28.07	.0563	.166	0.0002

[1] (From source, in km)
[2] (x10^9 cell/Ml)
[3] (μg DNA/Ml)
[4] (g silt in 30g core)
[5] (x 10^8 DNA/g silt)
[6] (μg DNA/Ml)
[7] (x 10^{-15}g DNA/cell)
[8] (μg DNA/ml)

[DNA]t-total DNA [DNA]b-bacterial DNA [DNA]e-exogenous DNA sediment-associated DNA varied from 28 percent (for the sample with the highest silt content collected at a point 3 km (kilometers) from the source of ground-water contamination) to 90 percent (for the sample with the lowest silt content collected closest (0.1 km) to the contaminant source). The extracellular/intracellular partitioning of sediment-associated DNA did not appear to follow a pattern with distance downgradient from the outfall and varied from 1 to 50 percent. The amount of DNA associated with particle surfaces (both adsorbed and intracellular) accounted for 65 to 99 percent of the DNA in the aquifer. In general, DNA sorbed to particle surfaces represents an important part of the DNA pool. Although the turnover rate of adsorbed DNA in the contaminant plume is not known, it is likely to be much longer than that reported for extracellular DNA in surface waters, probably because of increased resistance of adsorbed DNA to nuclease attack, although it is not known whether levels of nucleases in contaminated aquifers are comparable to those of surface waters.

The data also indicate that the average bacterial-DNA content decreased with increasing distance from the outfall for both the free-living and adherent populations. A similar spatial trend also has been observed for growth rates of free-living bacteria (Harvey and George, 1987). Therefore, it would appear that the comparatively fast-growing populations in relatively high-nutrient ground water may have a substantially higher DNA content.

Measurement of recovered bacterial DNA may be used to estimate biomass of adherent bacterial populations in aquifer sediments, although variability in DNA content per cell clearly must be taken into account. The present method of estimating bacterial biomass in aquifer core material by using epifluorescence/direct-counting procedures can be problematic because of statistical difficulties that arise during enumeration of low numbers of bacteria in the presence of more numerous abiotic particles and because of bacteria-sized autofluorescing mineral bodies that cause high background counts. Because measurement of bacterial DNA in aquifer sediments involves an extraction procedure, particle interference is not a problem in the DNA measurement once the DNA has been separated from the sediment. However, recovery of DNA from aquifer sediment decreased substantially with increasing silt content of the core material. Therefore, the usefulness of the DNA measurement technique to estimate bacterial biomass in clay lenses and very fine grained aquifer sediments is questionable. More research needs to be done to improve the characterization of DNA in subsurface environments.

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(p. 555 follows)

SCALES OF LENGTH AND CONNECTIVITY FROM GROUND PENETRATING RADAR

By Gary R. Olhoeft[1], Jeffrey E. Lucius[1], and Regina M. Bochicchio[2]

ABSTRACT

Ground penetrating radar cross sections of the Bemidji, Minnesota, research site show details of the subsurface stratigraphy with resolution on the order of 20 centimeters. Computer processing of the radar images has been applied to correct for the geometric distortions of the data acquisition process. A "rubber sheeting" technique is used to correct for variations in vehicle movement and topography. A normalization correction is applied for geometric spreading, reflection, and other losses. Migration is used to correct for differing electromagnetic velocities of propagation above and below the water table. The result is an undistorted, geometrically correct cross section. Analysis of these cross sections shows variation in the horizontal connectivity of subsurface structures with distance and scale throughout the site.

In this context, "scale length" means a length in the radar data over which a stratified structure appears to be connected (or continuous). Data for the entire site are not yet processed, so these observations are preliminary. However, no horizontal scale lengths greater than 100 meters have been seen. The unsaturated zone has horizontal scale lengths in the 50 to 100 meter range. The saturated zone has horizontal scale lengths in the 20 to 50 meter and shorter range. The geometry and logistics of the radar operation produce high sensitivity to both vertical and horizontal change but has high sensitivity to only horizontal scale lengths. To determine vertical scale lengths, the radar must periodically follow the infiltration of a rainfall wetting front as was performed at the research site on Cape Cod, Massachusetts.

John Cherry noted at the Second Toxic Waste Technical Symposium on Cape Cod that the structures that appear to control hydrological flow are of horizontal scale lengths on the order of meters to tens of meters. He stated that they could only be adequately observed at the Canadian Forces Base Borden research site by trenching. We suggest that these hydrologically controlling structures are what the ground penetrating radar is seeing. If so, the high resolution and rapid operation of ground penetrating radar may prove to be one of the most efficient ways to acquire scale-dependent information for hydrological modeling. To confirm this hypothesis, the details of these horizontal scale lengths are being investigated and calibrated by trenching along ground penetrating radar profiles.

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

[2] Water Resources Center, Desert Research Institute, Las Vegas, Nev.

(p. 557 follows)

CHAPTER I – CREOSOTE WASTE IN GROUND WATER NEAR PENSACOLA, FLORIDA

(p.559 follows)

BIODEGRADATION PATHWAYS FOR BENZOTHIOPHENE IN METHANOGENIC MICROCOSMS

By Edward M. Godsy[1] and Dunja Grbić-Galić[2]

ABSTRACT

Microbial transformation of benzothiophene, the major two-ring sulfur heterocyclic compound in creosote, has been studied under methanogenic conditions. Microcosms seeded with low-biomass methanogenic aquifer material from an abandoned wood-preserving site in Pensacola, in northeastern Florida, were fed benzothiophene at a concentration of 10 milligrams per liter as the sole carbon and energy source in an anaerobic mineral medium. High-performance liquid chromotography and gas chromotography/mass spectrometry were used to separate and identify intermediate compounds that appeared before the onset of methanogenesis. The first transformation step consisted of oxidation and cleavage of the S-heterocyclic ring. After cleavage of this ring, the substituent side chains and the remaining homocyclic ring were subjected to various reactions including oxidation, decarboxylation, desulfurylation, and O-methylation. These reactions were followed by reduction of the homocyclic ring, cleavage of this ring, β-oxidation, and mineralization to methane, carbon dioxide, and hydrogen sulfide. The major degradation pathway intersects segments of both the benzoic acid and phenol anaerobic-degradation pathways. A minor pathway starting with the oxidation of the homocyclic ring with subsequent ring reduction, ring cleavage, degradation of the remaining S-heterocyclic ring, and mineralization was also observed.

INTRODUCTION

The ultimate fate of organic compounds in subsurface environments is controlled by various transport and transformation processes. Potentially the most important, but currently the least understood, process affecting ground-water quality is biotransformation of organic compounds by indigenous microorganisms. Ground water contaminated by waste products from coal gasification, coal-tar production, and creosote wood-preserving operations commonly contains elevated concentrations of phenolic compounds; nitrogen-, sulfur-, and oxygen-containing heterocyclic (NSO) compounds; and single- and double-ring aromatic compounds. Many of these compounds have been found to be biodegradable under anaerobic conditions (Berry and others, 1987a), but very little information is available on the biotransformation of this class of compounds under methanogenic conditions. Recent investigations on the fate and movement of creosote-derived compounds in an anoxic freshwater aquifer contaminated by waste from 80 years of wood treatment have revealed that a small but active methanogenic population is actively transforming many of the NSO compounds to methane (CH_4) and carbon dioxide (CO_2) (Godsy and others, 1987).

Benzothiophene is the major two-ring S-heterocyclic compound in wastes from the previously mentioned operations and is the subject of this paper. A thorough search of the literature has revealed no reports on methanogenic fermentation of S-heterocyclic compounds; however, one report (Maka and others, 1987) has described the transformation of benzothiophene and dibenzothiophene under anaerobic conditions. The purpose of this paper is to present evidence for the biotransformation of benzothiophene under methanogenic conditions similar to those existing in the aquifer at the research site, and examine possible pathways for biotransformation on the basis of intermediate compounds that appear in the growth medium before and just after the onset of methanogenesis.

MATERIALS AND METHODS

The research site is located within the city limits of Pensacola, Fla., at an abandoned wood-preserving plant (Mattraw and Franks, 1986). Aquifer material was collected using the continuous-flight auger method described by Schalf and others (1981). This method causes soil

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

[2] Stanford University, Stanford, Calif..

cuttings during boring to be carried upward along the auger flights without the use of drilling fluids. Aquifer samples were collected from a depth of 5 to 6 meters at a site 30 meters downgradient from the contamination source and were immediately placed in sterile 4-liter glass bottles. The bottles were gently flushed with oxygen (O_2)-free argon (Ar) gas during filling to maintain anoxic conditions, sealed with butyl-rubber stoppers, and shipped by overnight mail to the laboratory. The bottles were stored in an anaerobic glove box at 22 °C (degrees Celsius).

Approximately 20 grams of the aquifer material was placed aseptically into a 25 x 142-mm (millimeter) anaerobic isolation roll-streak tube filled with 20 mL (milliliters) of prereduced, anaerobically sterilized mineral-salts solution. All operations were performed in an anaerobic glove box containing an atmosphere of 90 percent Ar – 10 percent H_2. The tube was then sealed with a butyl rubber stopper with a recessed top. The recessed top allowed for removal of the liquid by syringe techniques. The mineral-salts solution was composed of the following: KH_2PO_4, 0.75 g/L (grams per liter); K_2HPO_4, 0.89 g/L; $MgCl_2 \cdot 6\ H_2O$, 0.36 g/L; NH_4Cl, 0.9 g/L; trace-metal solution (Zeikus, 1977), 9.0 mL/L (milliliters per liter); vitamin solution (Wolin and others, 1963), 5.0 mL/L. The pH was adjusted to 7.0, and the medium was boiled, cooled, and dispensed under a stream of O_2-free Ar gas. The medium was then sterilized at 121 °C (1.05 kg/cm^2 (kilograms per square centimeter)) for 15 minutes. Just prior to use, 0.2 mL (milliliter) of a 5 percent solution of Na_2S was added as a reducing agent.

The roll-streak isolation tubes were placed horizontally on a wrist-action shaker for 30 minutes at 200 reciprocations per minute. Samples were then removed for acridine orange direct counts (AODC) using the method described by Wilson and others (1983). Numbers of methanogenic bacteria were determined using a five-tube most-probable-number (MPN) method based on the presence of CH_4 in the head space above the growth medium after incubation for 21 days as described by Godsy (1980).

Microcosms used for the study were prepared in 500-mL serum bottles that contained approximately 400 grams of aquifer material and 250 mL of the previously mentioned mineral-salts solution with benzothiophene at a concentration of 10 mg/L (milligrams per liter), using amorphous FeS as the reducing agent (Brock and O'Dea, 1977) in lieu of Na_2S. Two controls were prepared: (1) an identical microcosm minus the benzothiophene; and (2) an autoclaved microcosm.

Samples were collected daily in 16 x 100-mm test tubes with Teflon[3]-lined screw caps and frozen until analyses for degradation intermediates by gas chromatography/mass spectrometry (GC/MS) and substrate utilization by high-performance liquid chromatography (HPLC). A Hewlett-Packard HP 5970A mass selective detector interfaced to a HP 5890A gas chromatograph with data system was used. Chromatography was performed by splitless injection on a fused-silica capillary column and the oven temperature was programmed from 70 °C at 7 °C per minute, to 250 °C, the maximum temperature limit of the column. A 60-m x 0.25-mm DB-5 column, obtained from J & W Scientific, Inc., Rancho Cordova, Calif., having a 0.25-μm (micrometer) bonded liquid phase was used.

Samples for substrate utilization were analyzed by HPLC at 3-day intervals using a dual pump gradient system with a variable wavelength UV detector. Chromatography was performed by injecting 100 μL (microliters) of centrifuged microcosm sample onto a reverse phase C_{18} column and eluted starting at 100 percent water programming linearly to 100 percent acetonitrile in 15 minutes, at a constant flow rate of 2.0 mL per minute. The effluent was monitored at a wavelength of 280 nm (nanometers).

RESULTS

AODC were performed on five separate aliquots of aquifer material; the mean value ± one standard deviation was $5.5 \pm 0.4 \times 10^5$ organisms per gram dry weight of sediment. The MPN of methanogenic bacteria was 140 organisms per gram dry weight of sediment. No significant difference in the starting and ending bacterial densities could be detected.

The substrate disappearance curve for benzothiophene is shown in figure I–1. Benzothiophene degradation started after a 12-day lag period and continued for approximately 25-days,

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

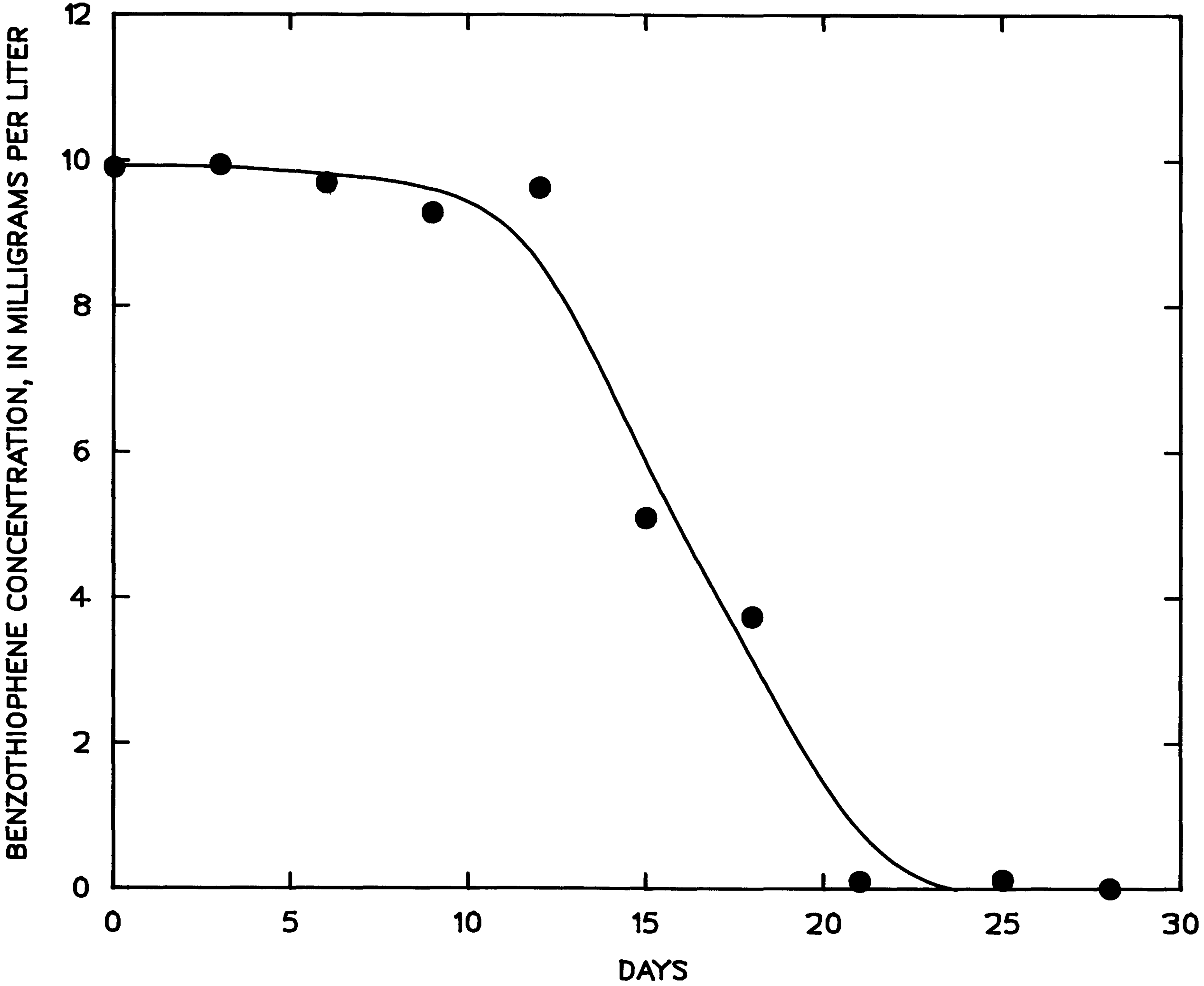


Figure I-1.—Benzothiophene utilization in methanogenic laboratory microcosms.

at which time the concentration was below detection limits. The evolution of gases was not quantified for these microcosms.

The compounds that were detected in the growth liquor of the microcosms, but not found in the controls, are shown in figure I–2. Intermediates were detected throughout the duration of the experiment, with the majority of compounds appearing just before and after the onset of methanogenesis around day 12. It is suggested, based on the report by Vogel and Grbič-Galič (1986) of the incorporation of water into the ring structure of benzene and toluene, that the first transformation step consisted of oxidation, followed by cleavage of the S-heterocyclic ring. After the cleavage of this ring, the substituent side chains and the remaining homocyclic ring were subjected to various reactions including oxidation, decarboxylation, desulfurylation, and O-methylation with the ultimate conversion to benzoic acid and phenol. These reactions are most likely followed by the previously described pathways (Berry and others, 1987a) consisting of the reduction of the homocyclic ring, cleavage of this ring, β-oxidation, and mineralization to CH_4, CO_2, and H_2S. A minor pathway starting with the oxidation of the homocyclic ring with subsequent ring reduction, ring cleavage, degradation of the remaining S-heterocyclic ring, and mineralization also is proposed on the basis of some breakdown products that were identified (thiophene-2-ol and diethyl-disulfide).

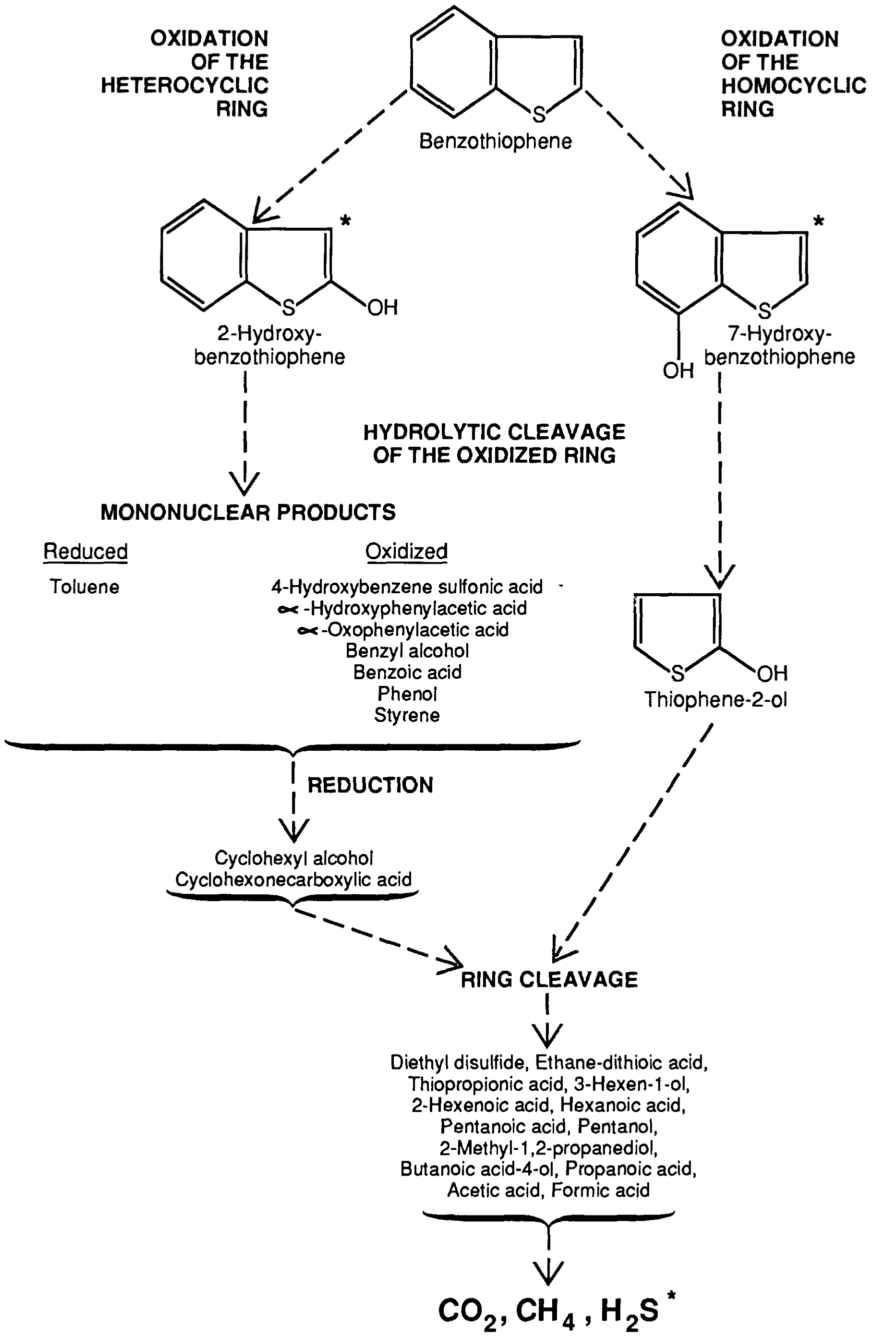
DISCUSSION AND CONCLUSIONS

Environmental contamination by heterocyclic compounds is widespread, but very little information is available on the biotransformation of this class of compounds under methanogenic conditions and even less on the environmental fate of these compounds in contaminated ground water. The existence of microbes in the subsurface has only recently become known. Several reports have clearly demonstrated the presence of active microorganisms in these environments (see, for example, Ghiorse and Balkwill, 1983; Harvey and others, 1984). The AODC counts for the aquifer material at this site are lower than previously reported by one to two orders of magnitude. The number of methanogenic bacteria appears to be low for a site contaminated with organic compounds, but these numbers are virtually the same as those detected by Belyaev and Ivanov (1983) in aquifer sediments associated with gas and oil deposits. However, the microbial population, especially the methanogenic population, appears to be quite active as demonstrated by the relatively rapid use of benzothiophene in the microcosms. According to microbial numbers in the microcosms, the concentration of benzothiophene used in our experiment, together with unidentified organic compounds present in the aquifer material, was sufficient to maintain the initial microbial population, but no growth (increase in number) could be assessed.

Studies on the methanogenic transformation of aromatic compounds in general have demonstrated that two major transformation pathways are used (Berry and others, 1987a): the benzoic acid pathway, and the phenol pathway. Because the ground-water consortium used for this study was a mixed culture, it is not surprising that the proposed major transformation pathway for this compound intersects segments of both pathways. It is not possible to determine at this point if phenol or benzoate are of more importance as key intermediates in the methanogenic transformation of benzothiophene.

As expected, the major pathway for anaerobic transformation of benzothiophene seems to be initiated by the oxidation and then cleavage of the S-heterocyclic ring. This observation is in line with the findings of Berry and others (1987b), who demonstrated that the first step in the methanogenic transformation of indole, the nitrogen analog of benzothiophene, was the oxidation of the N-heterocyclic ring to form oxindole. Similarly, Pereira and others (1988), were able to demonstrate the oxidation of the N-heterocyclic ring of quinoline using $H_2{}^{18}O$ to form ^{18}O-labeled 2(1H)-quinolinone under methanogenic conditions; however, they were not able to demonstrate the methanogenic fermentation of this compound as were Godsy and others (1987) using an experimental design similar to this series of experiments. This probably results from their use of sewage sludge as the inoculum for the microcosms rather than the ground-water consortium as was used by Godsy and others (1987). The substituent side chains attached to the homocyclic ring after the cleavage of the heterocyclic ring are then subjected to various transformation reactions, as exemplified by the myriad of single-ring compounds found. The large number of compounds is, undoubtedly, a result of the activity of a complex ground-water consortium.

The other, as yet unreported minor pathway involves an initial oxidation of the homocyclic



* Proposed intermediate or product

Figure I-2.—Proposed major and minor pathways for the biotransformation of benzothiophene under methanogenic conditions. The compounds listed are those that appeared just before and after the onset of methanogenesis.

ring, cleavage of this ring and then attack on the heterocyclic ring. Recently, Vogel and Grbić-Galić (1986) showed that the oxidation of an unsubstituted aromatic ring was possible when they demonstrated the oxidation of benzene and toluene to CH_4 and CO_2 by a mixed methanogenic culture. The magnitude and importance of the minor transformation pathway for benzothiophene and, possibly, other NSO compounds is presently being assessed.

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CHAPTER J—ACIDIC GROUND-WATER CONTAMINATION FROM COPPER MINING NEAR GLOBE, ARIZONA

(p.567 follows)

MOVEMENT OF INORGANIC CONTAMINANTS IN ACIDIC WATER NEAR GLOBE, ARIZONA

By James H. Eychaner[1]

ABSTRACT

Acidic water has contaminated a ground-water flow path 15 kilometers long to a depth of at least 50 meters in a copper-mining district in Arizona. Aluminum, copper, and iron concentrations exceed 100 milligrams per liter at pH less than 5. The aquifer includes a surficial unconsolidated alluvium as much as 50 meters thick overlying a thicker, carbonate-cemented alluvial conglomerate. Movement of acidic water is retarded by reaction with calcite, but low-pH water may reach a perennial stream within 6 to 15 years. The stream is already contaminated with about 2,000 milligrams per liter of sulfate and 30 milligrams per liter of manganese at a pH greater than 6.

INTRODUCTION

This paper describes contamination of an arid-zone aquifer and stream by acidic water in a copper-mining district in eastern Arizona. An ongoing study is focused on transport and transformation processes in the system rather than identification of specific contaminant sources. General characterization of the contaminants is nearly complete, and detailed studies of processes are beginning. Neaville (1989, this Proceedings) describes a hydraulic simulation of the flow system, Stollenwerk and Eychaner (1989, this Proceedings) describe models of chemical reactions in the ground water, Haschenburger (1989, this Proceedings) addresses manganese deposition in the stream, and Eychaner (1989, this Proceedings) presents potential areas for process-oriented research at the site. Previous results have been presented by Eychaner and Stollenwerk (1985; 1987) and by Eychaner (1988).

GEOHYDROLOGIC SETTING

Copper has been mined since 1903 from granite porphyry adjacent to an aquifer near Globe, Ariz. (fig. J-1). The ore body was formed by hydrothermal leaching of metals into granite (Peterson, 1962). Ore minerals, which were originally deposited as sulfides, are disseminated in the granite mass and locally enriched in abundant small quartz-filled veins. Chalcocite, chalcopyrite, and pyrite predominate in the deeper parts of the ore body. As erosion removed the overlying leached layer, however, the upper zone of the ore body was oxidized, resulting in a zone of oxide ores, largely chrysocolla, malachite, and azurite. Contaminated ground water related to mining has long been recognized in the area, but was first quantified in 1983 (Envirologic Systems, Inc., 1983).

The area includes block-faulted mountains and valleys that range from 670 to 2,400 meters above sea level; mining operations are at about 1,100 meters. Average precipitation ranges from 340 to about 780 mm/yr (millimeters per year) and is about 450 mm/yr near the mines (Sellers and others, 1985). Precipitation occurs as brief summer thunderstorms or as winter storms that may last several days. Snow accumulates in the mountains above 2,000 meters, and most recharge to the aquifer occurs during winter and spring. Average monthly temperatures near the mines range from 6 to 29 °C (degrees Celsius), with extremes of -15 and 45 °C. Ground-water temperatures are 17 to 19 °C.

The aquifer adjacent to the ore body (fig. J-1) is bounded laterally and downgradient by low-permeability rocks (Eychaner and Stollenwerk, 1987). An unconsolidated alluvium in a band 300 to 800 meters wide, as much as 50 meters thick, and about 20 kilometers long forms the upper, central part of the aquifer in a valley along Miami Wash and Pinal Creek (fig. J- 2). Materials range in size from clay to boulders, and fine sand to coarse gravel predominate. Finer and coarser materials generally are present in local lenses or stringers. Uncontaminated parts of the alluvium contain about 0.3 percent calcite by weight. The hydraulic conductivity of the alluvium is on the order of 200 m/d (meters per day). The hydraulic gradient is about 0.008, and most flow is nearly parallel to the land surface. Average ground-water velocity is estimated to be about 5 m/d.

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

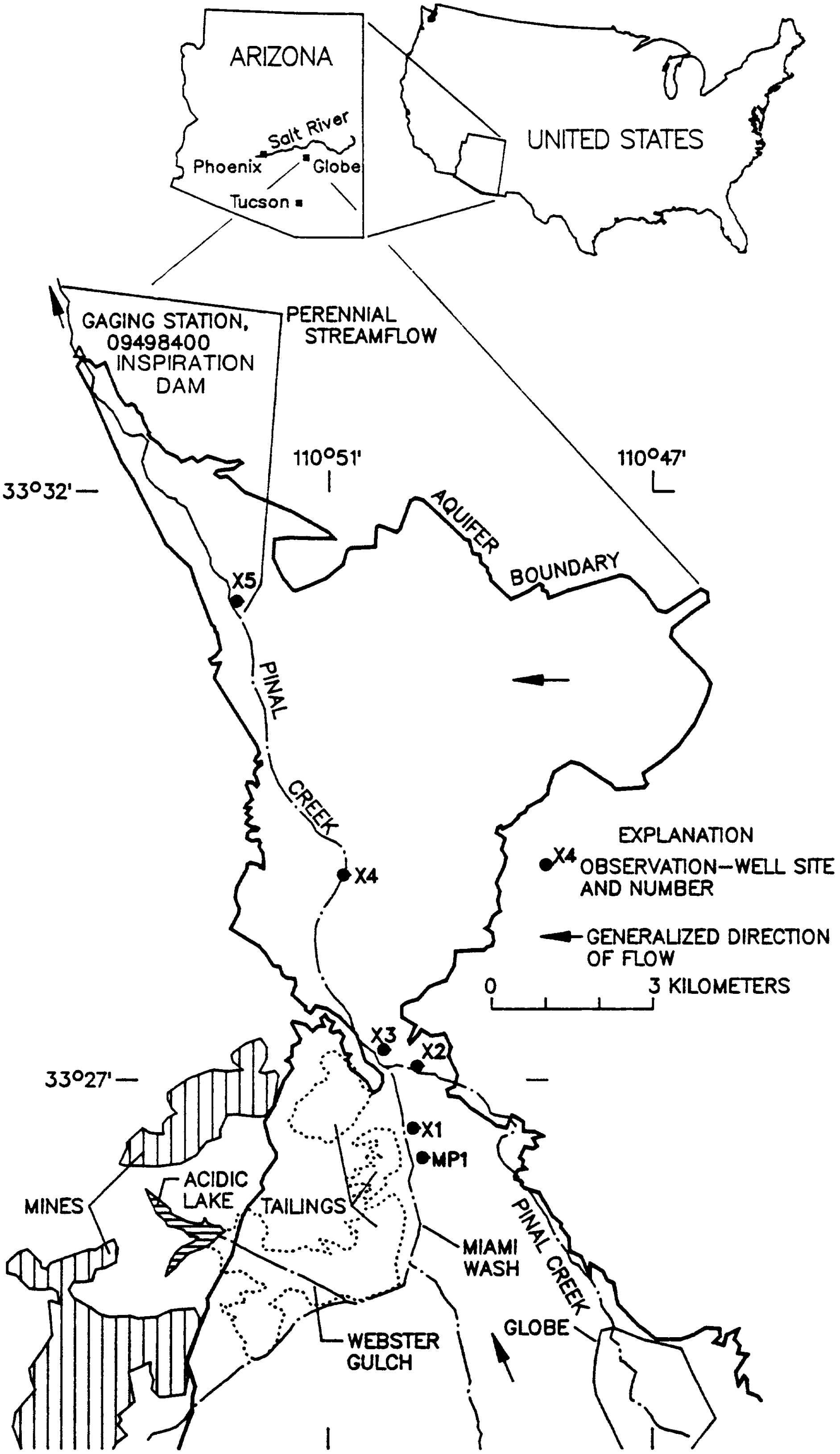

Figure J–1.—Area of study.

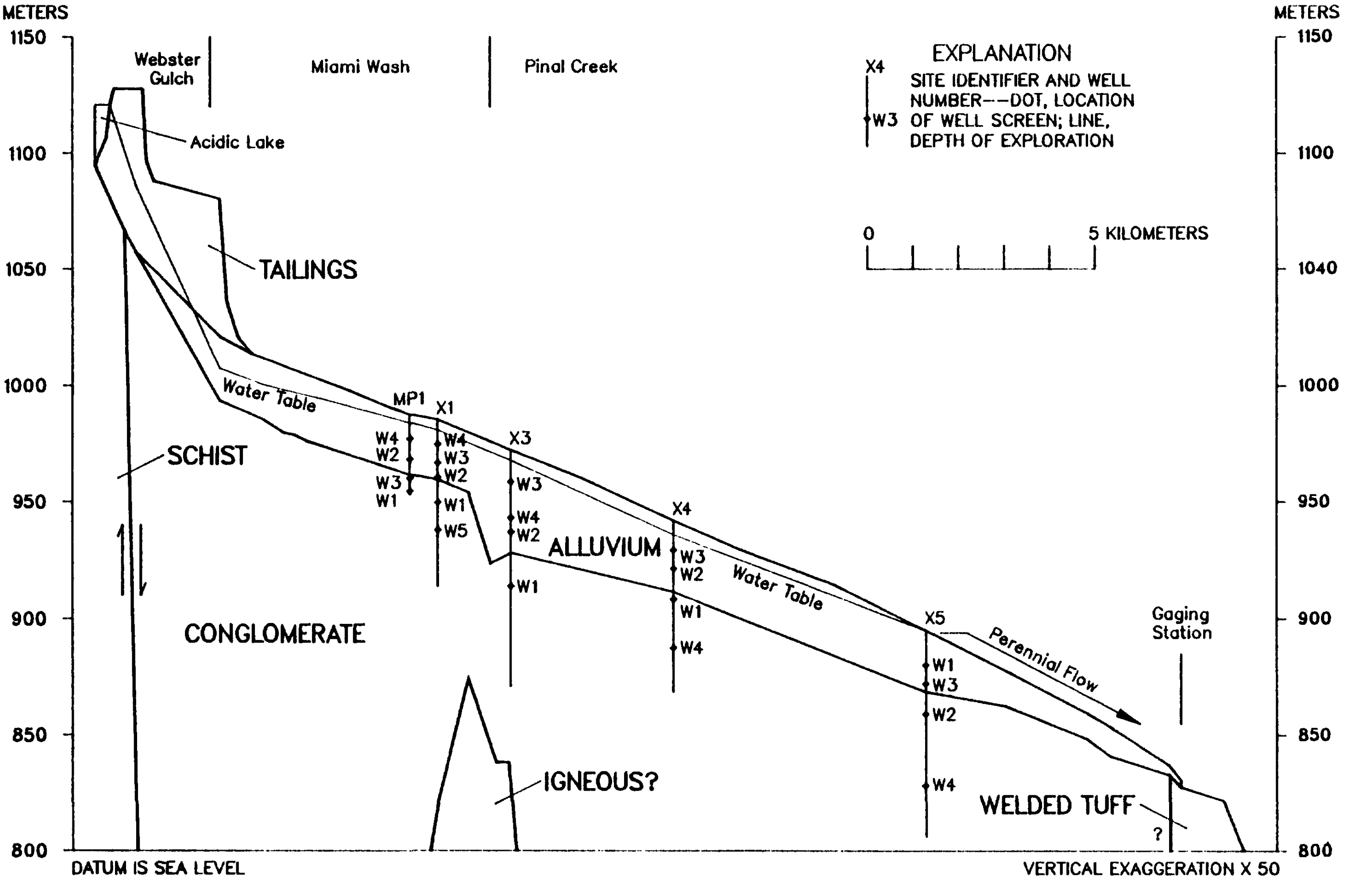

Figure J-2. – Generalized geologic section of the aquifer.

An alluvial conglomerate forms the remainder of the aquifer. It is 100 to 1,200 meters thick and 2 to 9 kilometers wide and lies beneath and adjacent to the unconsolidated alluvium. The conglomerate consists of unsorted angular rubble, well-rounded pebbles and cobbles, and firmly cemented sand and silt (Peterson, 1962, p. 41-44). Its calcite content is about 1.5 percent. Hydraulic conductivity is on the order of 0.1 m/d but may be as much as 3 m/d in discontinuous zones of coarse material. Two major east-trending faults and many minor faults offset the high-conductivity zones and impede flow in the conglomerate.

Water levels and quality have been monitored since 1984 in 23 observation wells in 6 groups near the stream channels (fig. J-1). The wells have screens 0.9 meter long at depths of 10 to 68 meters (fig. J-2). Water levels range from 1 to 10 meters below land surface (fig. J-3). The lowest head in each group is near the contact between the alluvium and conglomerate, and higher heads are observed in both deeper and shallower wells. Seasonal and interannual variations in recharge cause rapid water-level changes even for wells more than 50 meters deep. Water levels generally rose during 1984-85 but have been declining since mid-1986. Streamflow is ephemeral above most of the aquifer, but perennial flow begins near site X5 (fig. J-1). Discharge and water quality have been monitored since 1979 at a gaging station 6 kilometers downstream from site X5. Discharge from the aquifer to the stream was 0.2 to 0.4 m^3/s (cubic meters per second) during 1980-87. Streamflow dissolved-solids concentration has been increasing despite dilution during wet years (fig. J-4).

OCCURRENCE AND MOVEMENT OF CONTAMINANTS

During 1940-86, acidic waste solutions from one mine were discarded in an unlined lake formed behind waste and tailings piles (figs. J-1, J-2). The pH of lake water was about 2.7 in 1986, and volume was about $5.5x10^6$ m^3 (cubic meters). The U.S. Environmental Protection Agency (1987) ordered the lake drained to eliminate it as a major source of contamination. By May 1988 virtually all of the lake water had been spread on inactive tailings piles to evaporate. Other sources of contaminated water in the mined area have been described (Envirologic Systems, Inc., 1983), but the identification of specific sources has been impractical because of the duration of mining, the number of possible sources, and limited access to active mining areas.

The major process retarding acidic water movement is dissolution of calcite from the aquifer, which raises solution pH and causes most metals to precipitate. Stollenwerk and Eychaner (1989, this Proceedings) provide details of the significant reactions. All available calcite has been consumed for at least 15 kilometers along a ground-water flow path below the lake. At a point 6 kilometers from the lake, water at the base of the alluvium has a pH of 3.6 and elevated concentrations of dissolved metals and sulfate (fig. J-5, table J-1). In the lower alluvium, pH increases gradually to 4.5 at a point 15 kilometers from the lake, then increases more rapidly in the space of 2 kilometers to 6.1 at site X5. The distribution of iron (Fe) in the aquifer is closely related to pH, which controls Fe solubility. Neutralized water (table J-1) is similar to that found in the alluvium downstream from X5 and in a fringe around the acidic plume upstream. All the alluvium and about 25 meters of conglomerate below it are contaminated with acidic or neutralized water, but uncontaminated water is present at greater depth and in conglomerate adjacent to the alluvium (fig. J-5). Uncontaminated water contains small solute concentrations characteristic of flow in contact with several silicate minerals (table J-1).

Dissolved-solids concentration of streamflow at the gaging station increased to about 3,400 mg/L (milligrams per liter) in late 1987 despite dilution from high snowmelt runoff during 1983-85 (fig. J-4). The concentration was about 800 mg/L in 1942 and about 2,700 mg/L in 1980 (Envirologic Systems, Inc., 1983, p. 6). Sulfate has a similar trend and is about 60 percent of the dissolved load. The pH of the stream remained above 7.5 in April 1988. Comparison of neutralized contaminated ground water near the head of streamflow with water at the gaging station 6 kilometers downstream (table J-1) shows dilution equivalent to about 14 percent uncontaminated water plus the absorption of oxygen from the atmosphere.

Dissolved manganese (Mn) at the gaging station increased from 0.5 mg/L in 1979 to as much as 35 mg/L in late 1987 (fig. J-4). More than 50 mg/L of Mn has been measured in the

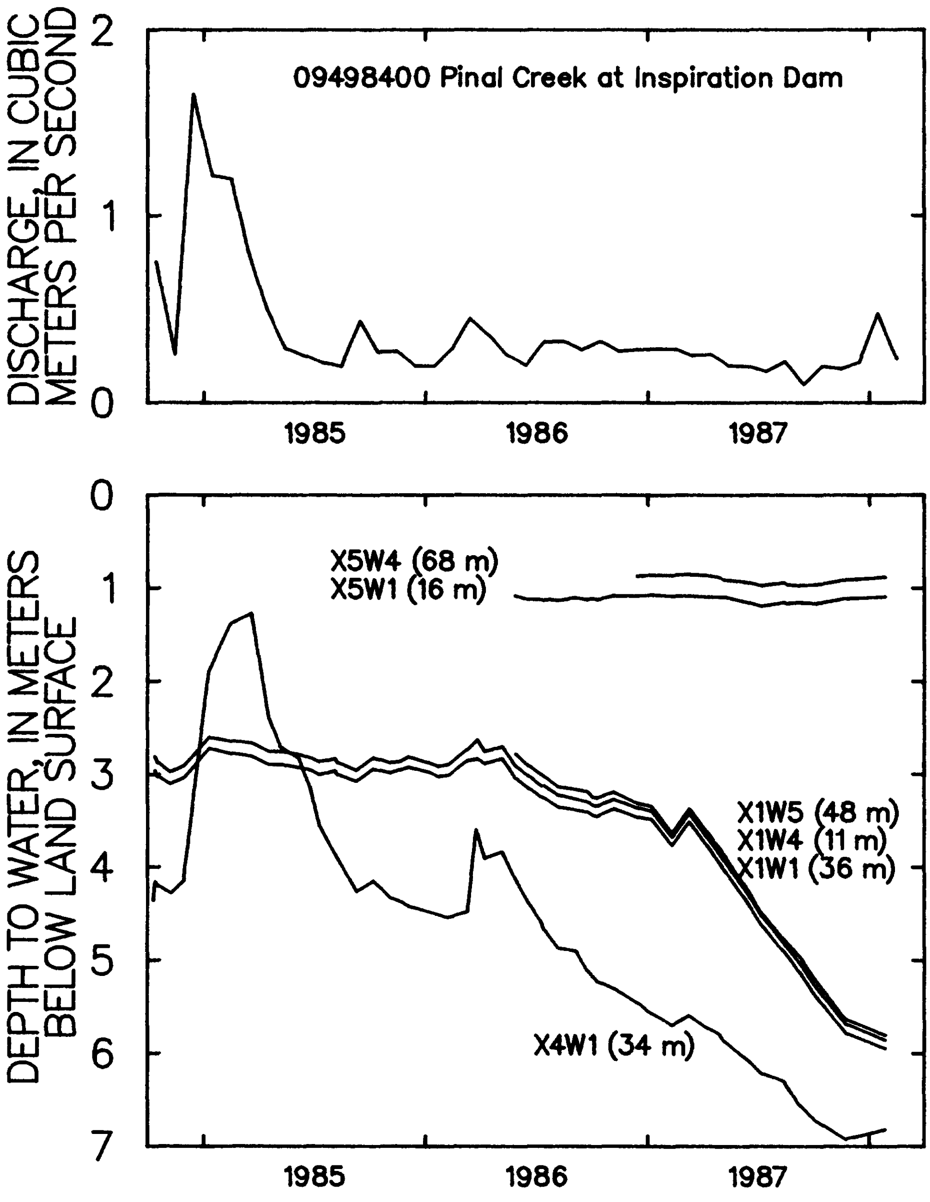

Figure J-3.—Streamflow and ground-water levels.

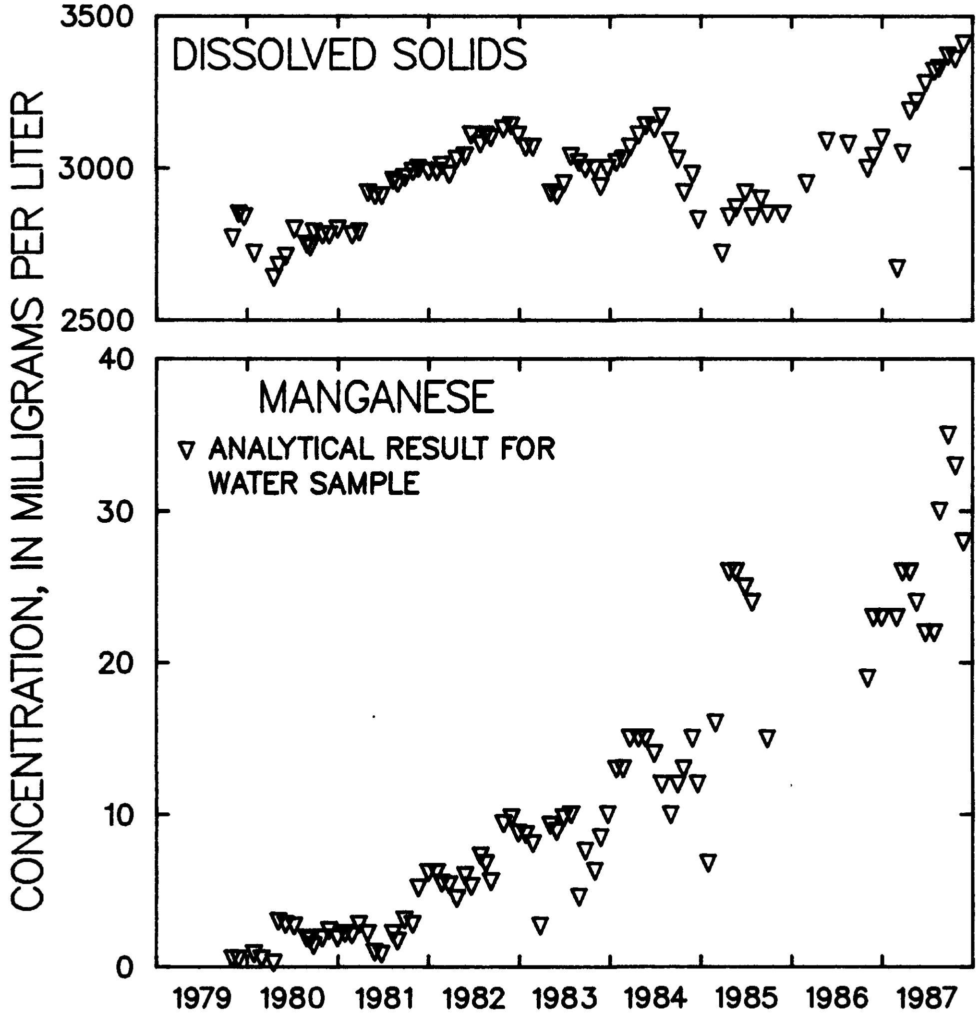

Figure J–4. – Dissolved-solids and manganese concentrations at gaging station 09498400, Pinal Creek at Inspiration Dam, 1979–87.

stream 5 kilometers upstream from the gage, but black Mn oxides precipitate on the streambed and decrease Mn concentration as pH and dissolved oxygen increase. The large variation of Mn concentration at the gage apparently reflects variation in the rate of Mn precipitation. Visible accumulations of Mn were first observed in 1985. Streambed sediments provide only a temporary sink for Mn, however, because flood discharges break up and transport the cemented sediments (Haschenburger, 1989, this Proceedings).

A front of acidic water, at which pH falls below 5, has advanced through the alluvium at a rate of 0.2 to 0.3 km/yr (kilometers per year) during the past several decades. The front, with its associated large increase in Fe and other metals, was about 2 kilometers from the head of streamflow in late 1987 and about 3 kilometers from the location of the highest measured Mn concentration. Assuming the front continues to advance at its historic rate, a breakthrough of Fe and other metals to the stream would be expected within 6 to 15 years. Although these dates describe the breakthrough as if it were an abrupt arrival, the history of increasing streamflow Mn concentration indicates that an initial increase could occur several years earlier. A major contaminant source has been eliminated by draining the acidic lake, but several years will pass before the effects reach the acidic front. About 10^8 m^3 of water at a pH of less than 5 is in transit through the aquifer, and that water may break through to the stream before the effects of upstream cleanup could arrive.

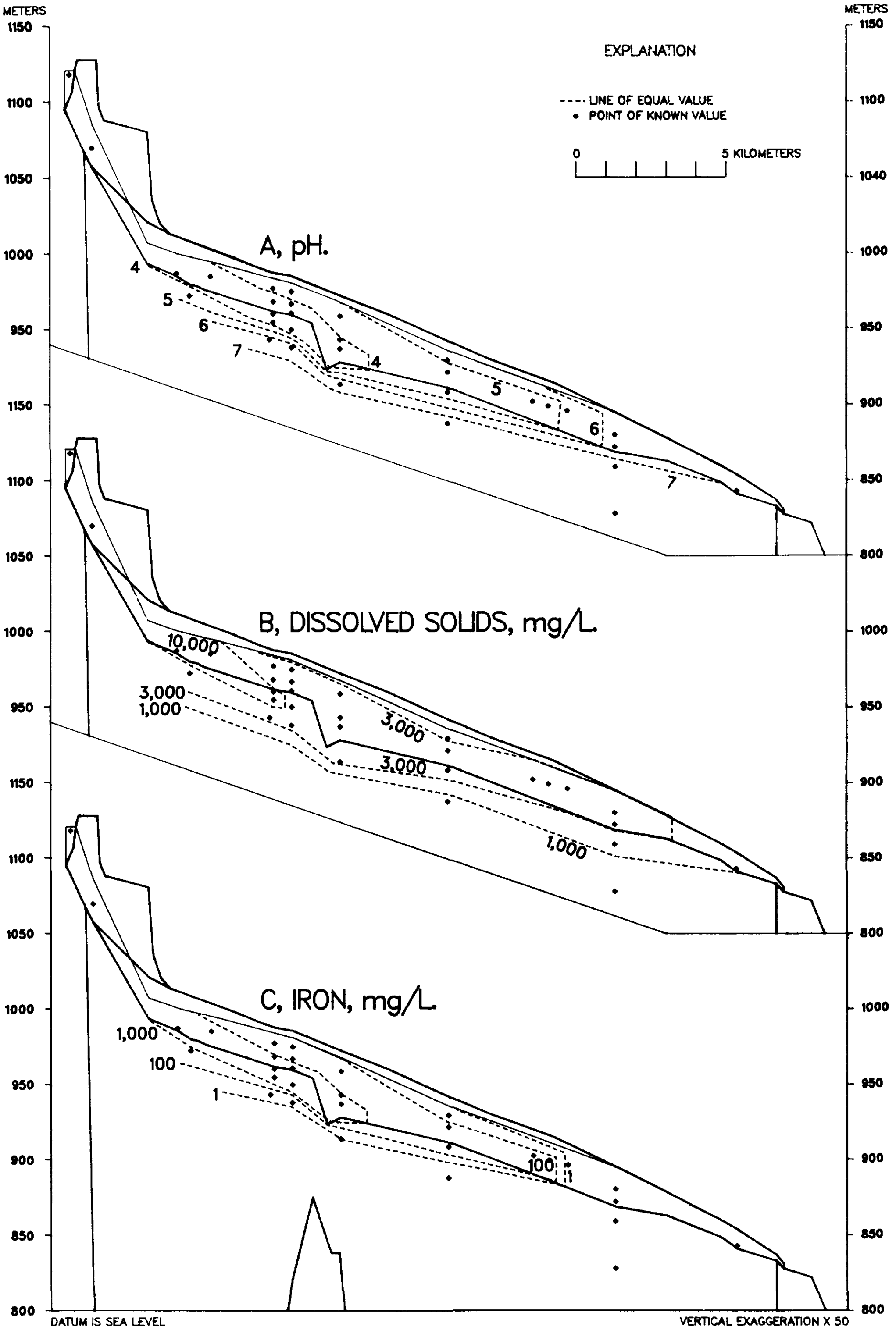

Figure J-5. – Distribution of (A) pH, (B) dissolved solids, and (C) iron in the aquifer.

Table J-1.—*Chemical analyses showing the range of dissolved properties*

[Sample date is for the majority of constituents; at no well were all constituents sampled on a single date. Parentheses indicate estimated value from analysis of water from a similar source; — indicates no entry; < = less than]

Property	Well number			Gaging station 09498400
	X4W4	MP1W1	X5W1	
Sample date	8-20-87	8-18-87	8-19-87	7-30-87
Water type	Uncontaminated	Acidic	Neutralized	Neutralized
Geologic unit	Conglomerate	Conglomerate	Alluvium	—
Depth, meters	56	35	17	—
pH	7.6	3.6	6.1	8.0
Temperature, °C	19	18	18	25
Conductance, μS/cm	420	11,000	3,800	3,200
Redox potential, mV	—	430	—	—
Density, g/mL	1.000	1.014	1.001	—
	Constituent, in milligrams per liter			
Calcium (Ca)	40	440	610	520
Magnesium (Mg)	13	390	150	120
Sodium (Na)	27	210	75	68
Potassium (K)	3.0	9.3	4.0	4.7
Bicarbonate (HCO_3)	230	0	140	200
Alkalinity ($CaCO_3$)	187	0	117	163
Inorganic carbon (C)	45	40	69	—
Sulfate (SO_4)	18	8,800	2,000	1,900
Chloride (Cl)	8.3	340	110	97
Fluoride (F)	.6	.3	.2	.2
Silica (SiO_2)	32	100	70	60
Oxygen (O_2)	5.9	.5	.8	7.7
Organic carbon (C)	1.4	3.8	(1.7)	—
Ammonia (N)	<.01	(1.5)	.38	.16
Ammonia + organic (N)	.7	(2.2)	.9	1.0
Nitrate + nitrite (N)	1.6	(<.1)	<.1	<.1
Orthophosphate (P)	<.01	(.16)	.06	.02
Aluminum (Al)	<.01	250	<.01	<.08
Cobalt (Co)	<.003	13	.01	<.02
Copper (Cu)	.02	150	.08	.004
Iron (Fe)	.013	2,800	.024	.03
Manganese (Mn)	.1	75	45	22
Zinc (Zn)	.048	22	.038	.02
	Constituent, in micrograms per liter			
Arsenic (As)	—	(<5)	—	<1
Barium (Ba)	16	9	29	<100
Berylium (Be)	<.5	190	<2	—
Boron (B)	20	—	70	60
Cadmium (Cd)	<1	600	5	2
Lead (Pb)	<10	210	70	<5
Lithium (Li)	21	630	220	—
Nickel (Ni)	<100	3,100	200	2
Strontium (Sr)	200	1,300	2,300	2,000
Mercury (Hg)	—	.2	—	<.1
Molybdenum (Mo)	<10	<90	30	—
Vanadium (V)	<6	600	<18	—

SUMMARY

Water moving from an area disturbed by copper mining has contaminated an arid-zone aquifer and perennial stream near Globe, Ariz. Ground water in a plume 15 kilometers long and at least 50 meters deep has a pH of less than 5 and concentrations of aluminum, copper, and iron exceeding 100 mg/L. Movement of the acidic water is retarded by reaction with calcite in the aquifer, but the finite supply of calcite upstream from the head of the perennial stream may be exhausted within 6 to 15 years. An additional 10 kilometers of aquifer and the stream are contaminated with about 2,000 mg/L of sulfate and at least 30 mg/L of manganese at a pH greater than 6.

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SIMULATION OF GROUND- AND SURFACE-WATER FLOW IN THE GLOBE AREA, ARIZONA

By Chris C. Neaville[1]

ABSTRACT

Acidic water with elevated concentrations of metals has contaminated a stream and alluvial aquifer in a mining district near Globe, Arizona. The aquifer consists of a narrow layer of unconsolidated alluvium along the drainage system that overlies an extensive conglomerate. The flow system is being simulated by a three-dimensional, finite-difference, ground-water flow model that maintains a streamflow water budget. Results of the simulations are to be used to evaluate rates of movements of the contaminants in subsequent modeling.

INTRODUCTION

Acidic waters containing elevated concentrations of metals drain from areas disturbed by mining activities near Globe, Ariz., and have created a contamination plume about 15 km (kilometers) long in a stream and alluvial aquifer (Eychaner, 1989, this Proceedings). To facilitate understanding and management of the plume, several computer simulations are planned to evaluate rates of movement of contaminants under typical and extreme climatic conditions. The purpose of this paper is to discuss briefly the initial design of a flow model that will be the basis of subsequent transport and reaction models.

HYDROLOGIC SETTING

The hydrology of the study area has been described in detail by Eychaner (1989, this Proceedings). The flow model will simulate a structural basin near Globe, Ariz., that is drained by Pinal Creek and its tributaries (Eychaner, 1989, this Proceedings, fig. J-1). The primary unit of interest for this study is a layer of unconsolidated alluvium as much as 50 meters thick that has been deposited along the drainage system. Most of the contamination has occurred in this layer because of the large ground-water flow velocities. Horizontal hydraulic conductivity of the alluvium is estimated to be 100 to 200 m/d (meters per day) and is greatest at the base. Underlying the alluvium is an extensive conglomerate that ranges in thickness from about 1,200 meters at the south end of Miami Wash to less than 100 meters about 6 km to the north. Hydraulic conductivity of the conglomerate is estimated to be 0.03 to 0.1 m/d.

Ground-water levels near the streams respond rapidly to recharge received primarily from intermittent streamflow in the tributaries in the southern part of the basin. In general, water levels indicate that head decreases with depth in the alluvium and increases from the alluvium to the conglomerate due to upward vertical gradients. In the northern 5 km of the valley, Pinal Creek flows perennially where low hydraulic conductivity rocks truncate the aquifer and force ground-water flow to the surface. Discharge from the aquifer to the stream was 0.2 to 0.3 m^3/s (cubic meters per second) during 1980-86 (Eychaner, 1989, this Proceedings). Stream-aquifer interactions also are significant along the ephemeral reaches upstream. During prolonged runoff in 1985, recharge to the aquifer was 0.13 m^3/s in a 3-km reach of the stream, and 0.1 m^3/s discharged from the aquifer in another 1.6-km reach.

MODEL DESIGN

The flow model being used is the modular, three-dimensional, finite-difference, ground-water flow model (MODFLOW) of McDonald and Harbaugh (1984). Transient flow will be simulated and each stress period will represent a different season. The flow model will include the streamflow-routing package that was developed recently for MODFLOW (D.E. Prudic, U.S. Geological Survey, written commun., 1988). With this package, flow can be simulated in ephemeral stream reaches when the hydraulic head in the aquifer is higher than the streambed. A surface-water budget is maintained throughout the simulation and recharge is limited by the head in the stream. This program option is well suited to the intermittent and interrupted streamflow conditions along the Miami Wash-Pinal Creek drainage system.

Horizontally, the aquifer has been discretized into 47 rows and 27 columns with the narrowest grid spacing aligned with the high-conductivity

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

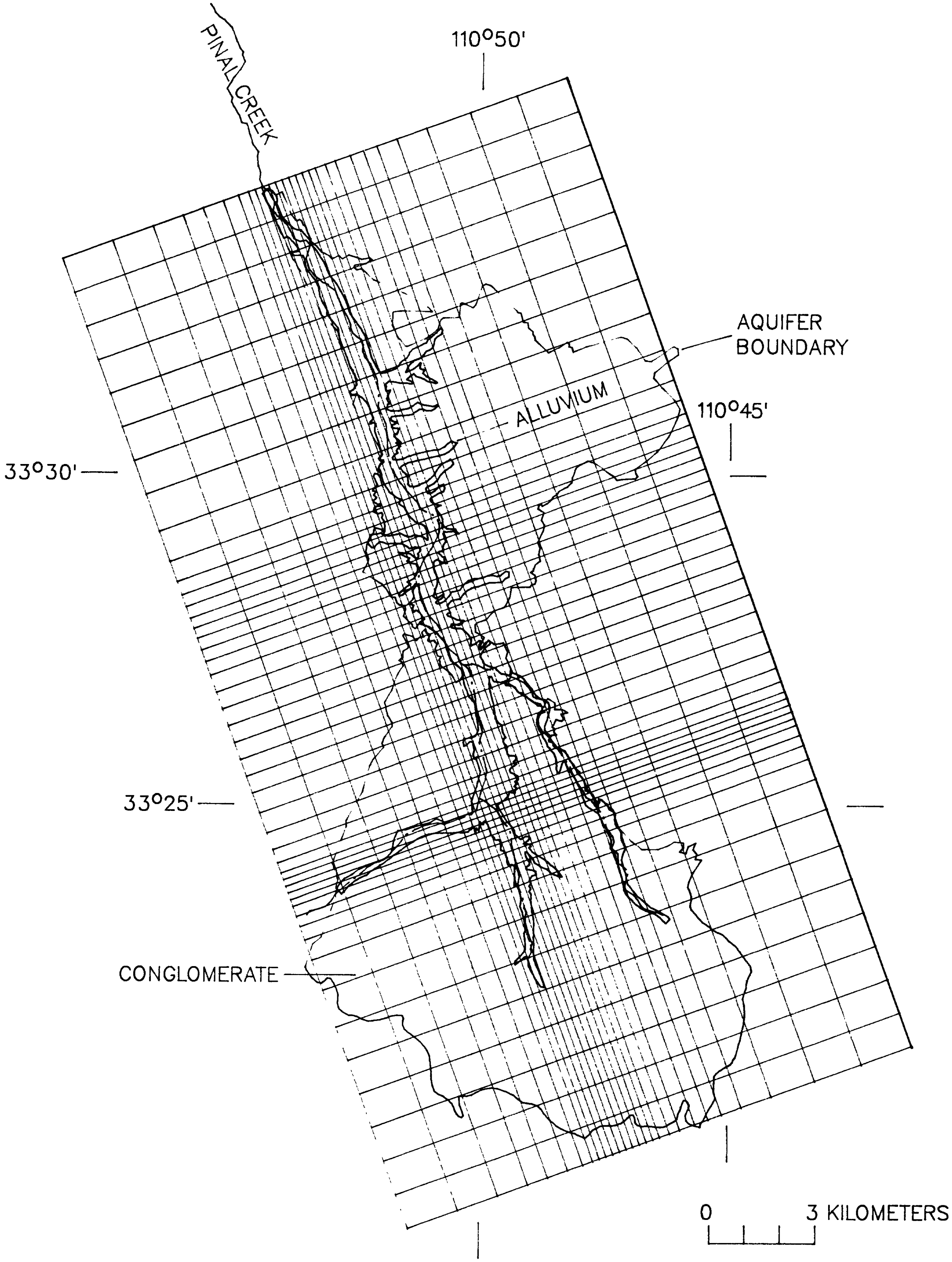

Figure J–6.—Model grid for the proposed flow model near Globe, Arizona.

alluvium (fig. J-6). The aquifer boundary shown in figure J-6 is the same as that shown in figure J-1 in Eychaner (1989, this Proceedings). Orientation of the grid was selected so that the columns are as nearly parallel to the drainage system as possible and all model cells outside the aquifer boundary are no-flow cells. The aquifer has been separated into four layers. The alluvium is represented by the top two layers; the second layer is used to simulate the high-conductivity zone at the base of the alluvium. All model cells outside the boundary of the alluvium represent the conglomerate. Transmissivity values used in the simulations were estimated from aquifer-test results for the conglomerate and specific capacities for the alluvium. At the northern end of the basin, the cross-sectional area, gradient, and outflow of the alluvium are known; this information provides an additional constraint for transmissivity of the system.

Initially, the boundary conditions for the model will be no-flow boundaries along the lateral boundaries of the conglomerate and a head-dependent boundary along the length of Pinal Creek and Miami Wash. Recharge will be simulated by specifying fluxes for the stream segments near the mountain fronts where most of the recharge enters the aquifer. Calibration will be based on measured water levels from 30 wells, outflow at the downstream end, and measured seepage losses along the length of Pinal Creek and Miami Wash. As part of the sensitivity analysis, small fluxes will be specified along the contacts of the aquifer where underflow may be significant. Transmissivity, specific yield, pumpage rates, recharge, and evapotranspiration will also be evaluated during the sensitivity analysis.

SUMMARY

Acidic water with elevated concentrations of metals has contaminated an alluvial aquifer in a mining district near Globe, Ariz. The aquifer consists of a narrow layer of unconsolidated alluvium along the drainage system that overlies an extensive conglomerate. The ground-water flow system is being modeled using MODFLOW, and the results of the flow simulations are to be used to simulate contaminant transport. Stream-aquifer interactions will be simulated with a streamflow-routing package.

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SOLUBILITY OF ALUMINUM AND IRON IN GROUND WATER NEAR GLOBE, ARIZONA

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

ABSTRACT

Identification of a unique set of minerals that can be used to explain the chemical composition of ground water near Globe, Arizona, is needed so that predictions concerning future changes in solution composition can be made. Geochemical modeling of about 200 ground-water samples indicates that pH and Eh are the predominant variables that ultimately affect the concentration of most solutes, especially metals. Comparison of ion-activity products calculated for the ground-water samples with thermodynamic equilibrium constants indicate that aluminum solubility may be controlled by precipitation of a basic aluminum sulfate ($AlOHSO_4$) *and kaolinite* [$Al_2Si_2O_5(OH)_4$] *at pH values less than 4.9. However, the range in ion-activity products for both minerals vary by more than an order of magnitude, indicating that more than one mechanism and/or mineral may control aluminum solubility. At pH values greater than 4.7, microcrystalline gibbsite* [$Al(OH)_3$] *is supersaturated and should precipitate. Solubility of iron is affected by pH and redox conditions in the aquifer. Almost all of the iron in solution is in the ferrous oxidation state. Oxidation to ferric iron is limited by the rate of oxygen addition to the aquifer and pH. Once oxidized, ferric iron rapidly precipitates as amorphous ferric hydroxide* [$Fe(OH)_3$].

INTRODUCTION

A zone of acidic ground water containing large concentrations of dissolved metals and sulfate is moving through a shallow aquifer near Globe, Ariz. (Eychaner, 1989, this Proceedings). Ground water in the most acidic part of the study area has a pH of 3.5 and contains 11.4 mmol/L (millimoles per liter) aluminum (Al), 54.4 mmol/L iron (Fe), 114 mmol/L sulfate (SO_4), and several other constituents (Eychaner and Stollenwerk, 1985). The concentrations of dissolved constituents in the acidic ground water are attenuated along the flow path by dilution with ground water from other sources and through chemical reactions. Differences in the solubility of each element result in a chromatographic effect where zones of different ground-water chemistry exist downgradient from the core of the acidic ground water.

One of the objectives of this study is to predict the future distribution of constituents in this aquifer, including arrival time for the different chemical fronts at the downstream end of the aquifer and rinse-out of constituents after the source of acidic ground water has been removed. A sequential, or multistep modeling procedure is to be used to make these predictions because of the large number of chemical equations that will be needed to describe the complex geochemistry of this system. This procedure involves the use of a geochemical mass transfer model to separately solve for all reactions occurring in an individual cell of the aquifer, followed by transport in a hydraulic model to the next cell where new equilibrium conditions are calculated. This procedure is repeated until the simulation is complete.

This type of modeling procedure has two requirements: First, a hydraulic model of the aquifer is needed; one is currently in development by Neaville (1989, this Proceedings). Second, a geochemical model must be able to accurately describe the existing distribution of constituents in ground water and predict future changes in composition along the flow path. In this paper, Al and Fe are used as examples to elucidate some of the problems associated with the adaptation of a geochemical model to this site.

METHODS

Concentrations reported in this paper are for ground-water samples collected from 23 observation wells (Eychaner and Stollenwerk, 1985, Eychaner, 1989, this Proceedings) in 9 sampling rounds from November, 1984 to August, 1987. All samples were filtered immediately through

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

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

0.45 μm (micrometer) filters. Preliminary studies on sampling methodology indicated an absence of colloids smaller than 0.45 μm (Eychaner and Stollenwerk, 1985). Locations of the wells are shown in Eychaner (1989, this Proceedings, figs. J-1 and J-2).

In the field, pH was measured by glass electrode and dissolved oxygen by probe. Ferrous (Fe(II)) and total Fe were measured in the field during one sampling round using the bipyridine colorimetric procedure (Skougstad and others, 1979). Eh measurements were made in the field for one sampling round using a polished platinum electrode and a silver-silver chloride reference electrode, calibrated with Zobell's solution between measurements. In the laboratory, A1 and total Fe were determined with a Jarrell-Ash Atom Comp 975[3] inductively coupled atomic emission spectrophotometer. Sulfate was determined by the turbidometric procedure (Fishman and Friedman, 1985).

The geochemical model PHREEQE (Parkhurst and others, 1980) was used to determine the speciation of measured elements in ground water and their degree of saturation with respect to selected minerals. The thermodynamic data base in PHREEQE was supplemented with data from WATEQ3 (Ball and others, 1981), Nordstrom (1982), and the Handbook of Thermodynamic Data (Naumov and others, 1971). The list of minerals compiled from these sources was narrowed down to those which might be expected to form in a low temperature environment.

RESULTS

Composition of ground water in the study area is primarily controlled by reactions that are directly or indirectly dependent on pH. The most important reaction for neutralizing H^+ is dissolution of calcite:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-, \qquad (1)$$

followed by:

$$HCO_3^- + H^+ \rightarrow H_2CO_3. \qquad (2)$$

The carbonate content is approximately 0.3 percent for unconsolidated alluvium and 4.5 percent for the Gila Conglomerate, and occurs mostly as coatings on grains and as cement between grains. Concentrations of inorganic carbon (H_2CO_3) ranging from 2.8 to 5 mmol/L as C have been measured in ground water with pH values less than 4.5. Reactions with carbonate minerals are relatively fast.

Reaction with silicate minerals should also consume H^+; two examples are:

$$\underset{\text{(feldspar)}}{3KAlSi_3O_8} + 2H^+ \rightarrow \underset{\text{(k-mica)}}{KAl_3Si_3O_{10}(OH)_2} + 2K^+ + 6SiO_2 \qquad (3)$$

and,

$$\underset{\text{(olivine)}}{(Mg,Fe)_2SiO_4} + 4H^+ \rightarrow 2(Mg,Fe)^{2+} + H_4SiO_4^0. \qquad (4)$$

Petrographic examination of alluvium from the acidic ground-water zone shows extensive alteration of silicate minerals to clay minerals; however, the rates of these reactions are expected to be much slower than 1 and 2. The effect of silicate minerals on pH, Fe, and Al concentrations in the study area is unknown at this time.

Finally, H^+ can be neutralized by reaction with bicarbonate in uncontaminated ground water. The volume of uncontaminated ground water that mixes with acidic ground water in the study area is unknown at this time, but is estimated to be less than 25 percent. The effect of uncontaminated ground water on pH is considered to be minor.

As pH values increase, the concentration of metals and TDS decrease (Eychaner, 1989, fig. J-7 and table J-1). An approach to the geochemical modeling of constituents in this aquifer is to base the model on the changes in pH that result from dissolution of carbonate minerals. For example, after a volume of acidic ground water is transported to the next downgradient cell, all the carbonate minerals in the new cell are reacted and the increase in pH calculated. The geochemical model then calculates new equilibrium conditions for all the other constituents and precipitates or dissolves solid phases as necessary. The feasibility of using pH as the master variable for modeling the solubility of A1 and Fe is discussed below.

Aluminum

The aluminum concentrations measured in ground water are plotted as a function of pH in figure J-7. A relation between increasing pH and decreasing Al is evident (regression coefficient (r^2) = 0.64); however, the variability in Al

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

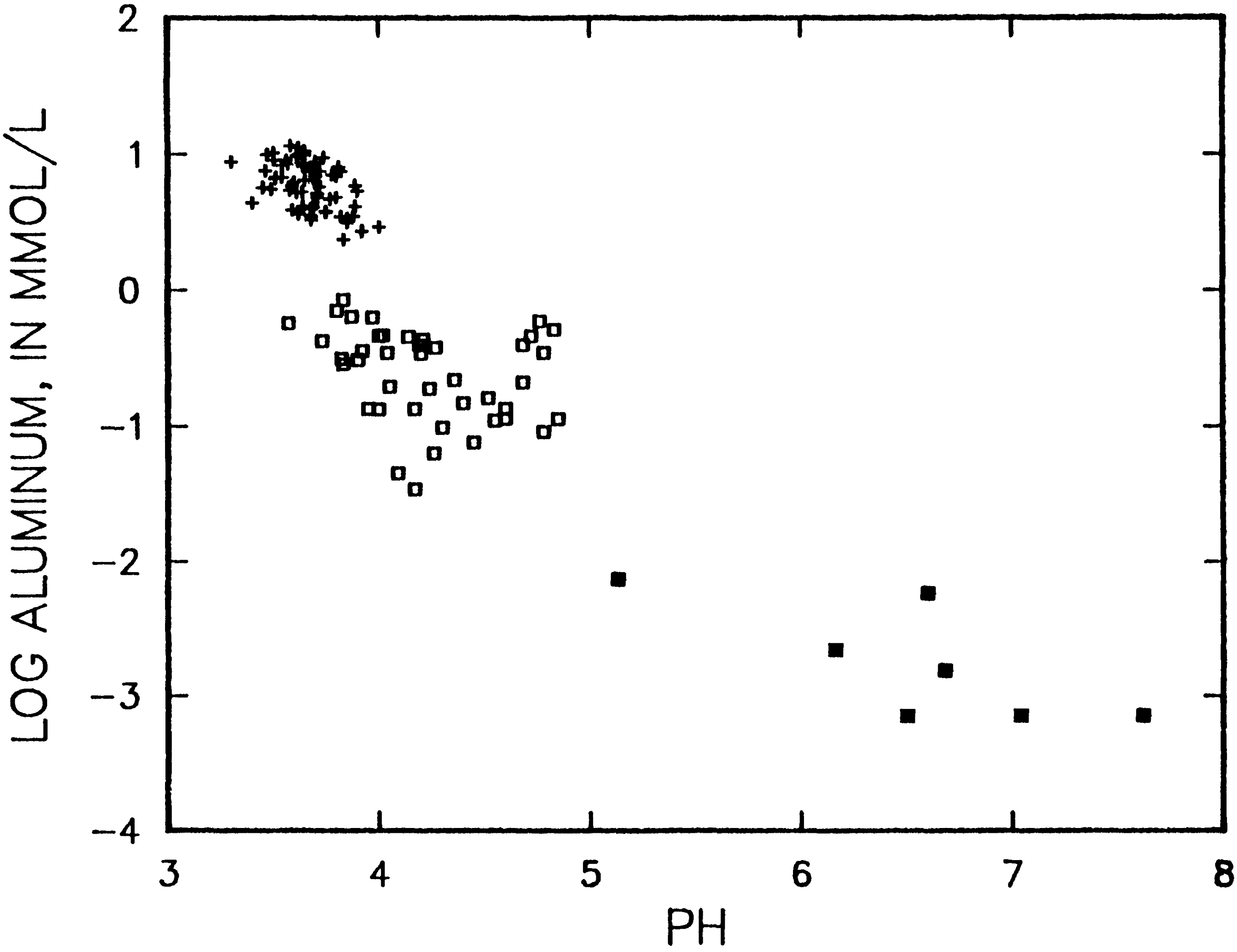

Figure J-7.—Plot of log aluminum concentration versus pH for ground-water samples. Plus symbols represent samples from the core of the acidic plume, open squares from the periphery of the acidic plume, and closed squares from areas where significant neutralizing capacity still remains. These symbols are used in figures J-7 through J-11.

concentration for a given pH can be large. For example, at a pH of 3.5, Al ranged from 5.56 to 10.3 mmol/L. Such variability indicates the lack of a unique relation between Al and pH, and suggests that more than one mechanism and/or mineral is controlling the solubility of Al.

An interesting feature of figure J-7 is the clustering of data into three groups. The plus symbols represent samples from eight wells located in the most acidic part of the plume, where most if not all of the carbonates have been dissolved. Open squares represent samples collected from five wells located around the periphery of the acidic core; geochemical data indicate that some carbonates may still be present. Samples represented by closed squares are from wells outside of the acidic plume where carbonate minerals are still abundant enough to maintain relatively high pH values.

Several minerals that may control the solubility of Al in ground water were evaluated in PHREEQE. Only those that had the closest match between ion-activity product (IAP) and the thermodynamic equilibrium constant (KT) were considered as possible solubility controls. The ratio of IAP to KT is the saturation index. Positive values indicate that the solution is supersaturated with respect to the solid phase and the mineral should precipitate. Negative values indicate undersaturation. Activities of the various ionic species used in these calculations were computed from elemental concentrations by PHREEQE. Theoretically, the mineral with the log IAP/KT closest to zero (but still positive) should precipitate, although in many cases some degree of supersaturation is required to initiate precipitation.

The IAP/KT data indicated that more than one mineral could control the concentration of Al in ground water at a specific pH, and that the minerals differed with changes in pH. At pH values less than 4.9, ground water is supersaturated with respect to a basic Al sulfate mineral ($AlOHSO_4$), alunite [$KAl_3(SO_4)_2(OH)_6$], and for some samples, kaolinite [$Al_2Si_2O_5(OH)_4$]; however, evidence from several studies indicates strong kinetic inhibition to alunite precipitation at low temperatures (Nordstrom, 1982).

The $\log_{10}$ of the ratio of IAP/KT for $AlOHSO_4$ is plotted as a function of pH in figure J-8 for all ground-water samples with pH values less than 4.9. $AlOHSO_4$ was undersaturated in all samples with a pH greater than 4.9 and the data are not plotted. Two distinct groups of data are evident. Ground-water samples from the most acidic part of the plume are supersaturated with respect to $AlOHSO_4$ by 0.8 to 1.5 orders of magnitude, and ground water from the periphery of the acidic core ranges from undersaturation to 1.4 orders of magnitude supersaturation. There is no apparent evidence that pH can be used to predict Al concentrations based on the assumption that Al solubility is controlled only by $AlOHSO_4$.

A plot of the log IAP/KT for kaolinite (fig. J-9) shows that several ground-water samples are also close to saturation with kaolinite between pH 3.7 and 4.4, indicating that kaolinite may partially control the solubility of Al in some of these samples. The data in figures J-8 and J-9 emphasize the difficulty in modeling the geochemistry of Al based only on ground-water analyses. The solid phases that are precipitating from solution need to be identified in alluvium from the aquifer before Al transport can be modeled at pH values less than 5.

A major difficulty in comparing ion-activity products with thermodynamic equilibrium constants concerns the question of kinetic processes. For all but the simplest of geochemical systems, the assumption of local chemical equilibrium along each point of a flow path is often not valid. Furthermore, the degree of nonequilibrium can vary over orders of magnitude. Thus, an intermediate metastable phase may readily precipitate from ground water, but it may take days, weeks, or months of recrystallization before the thermodynamic properties match those of any known mineral that can be used in PHREEQE. Compounding the problem of reaction kinetics is the potential lack of thermodynamic data for some of the mineral phases that may control solubility of Al.

At pH values of 4.7 and greater, the solubility product is exceeded for microcrystalline gibbsite [$Al(OH)_3$]. In figure J-10, Al activity is plotted as a function of pH. At pH values greater than 4.7, the slope of the data corresponds to the solubility of microcrystalline gibbsite and amorphous $Al(OH)_3$. Prediction of the transport of Al should be feasible by assuming equilibrium with either phase. The slope of the Al activity data at pH values less than 4.7 does not correlate with any known Al mineral indicating either precipitation of mixed phases, or dilution.

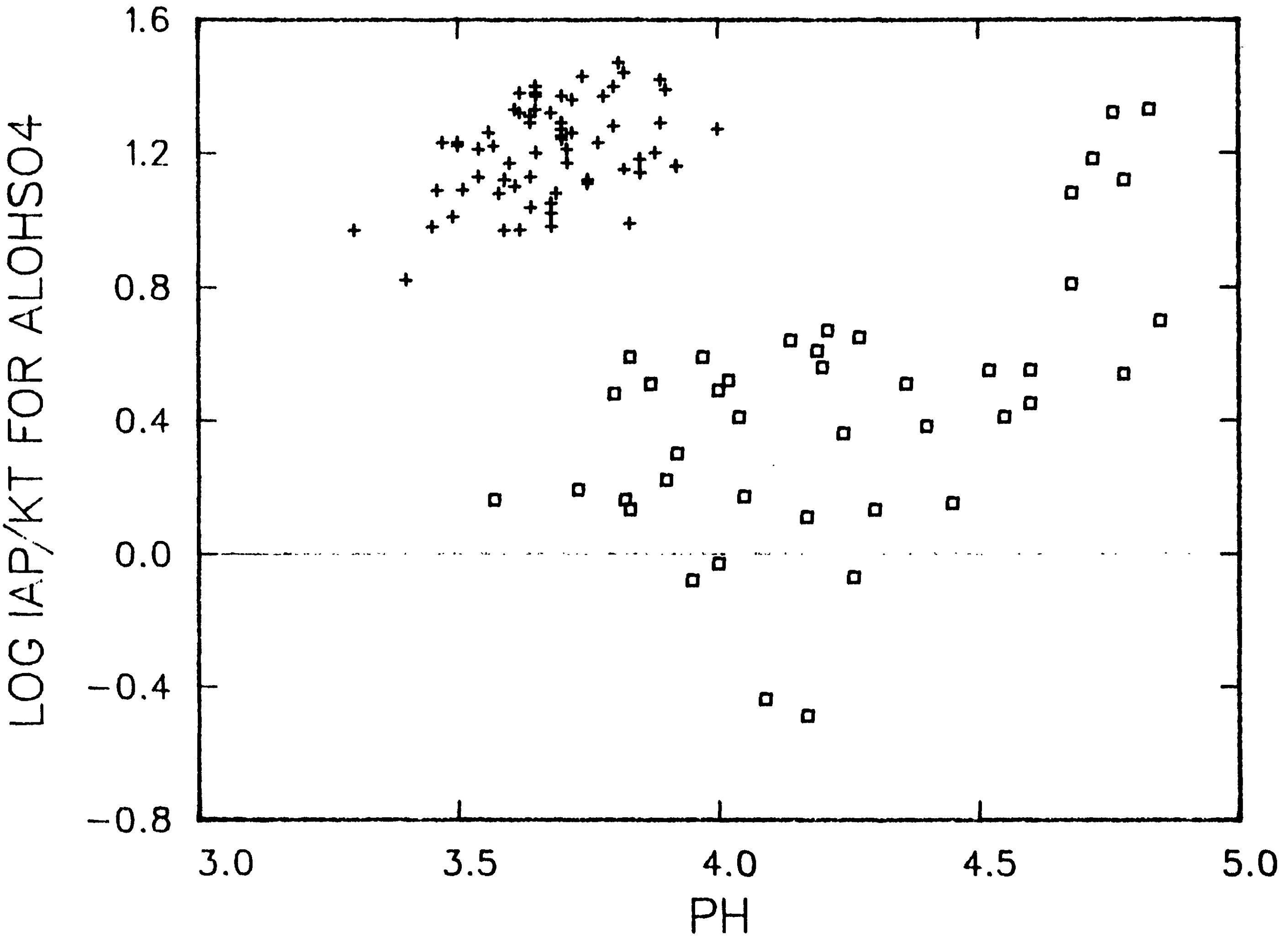

Figure J–8.—Log of the ion activity product divided by the thermodynamic equilibrium constant for AlOHSO4, plotted as a function of pH.

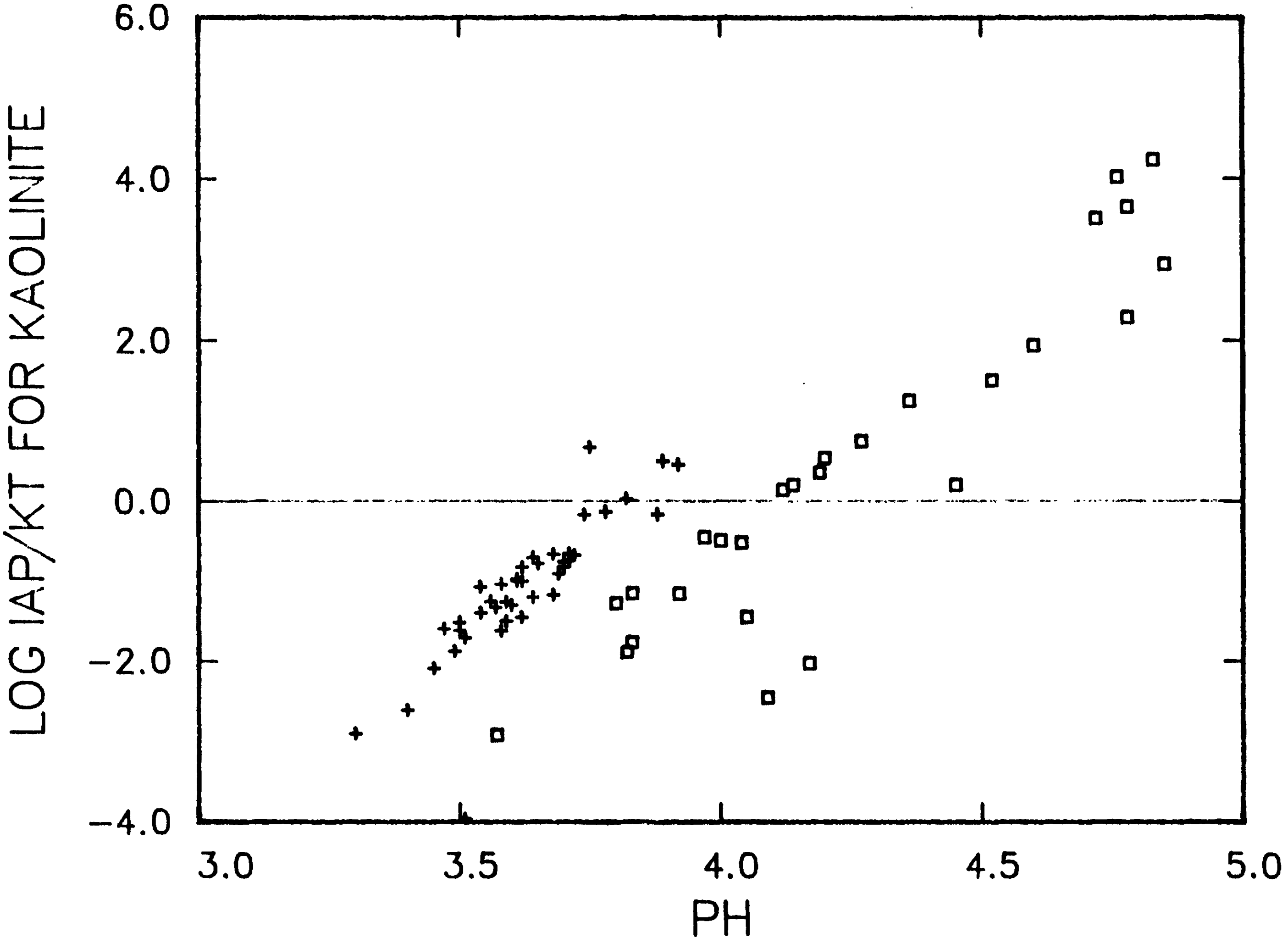

Figure J-9.—Log of the ion activity product divided by the thermodynmic equilibrium constant for kaolinite, plotted as a function of pH.

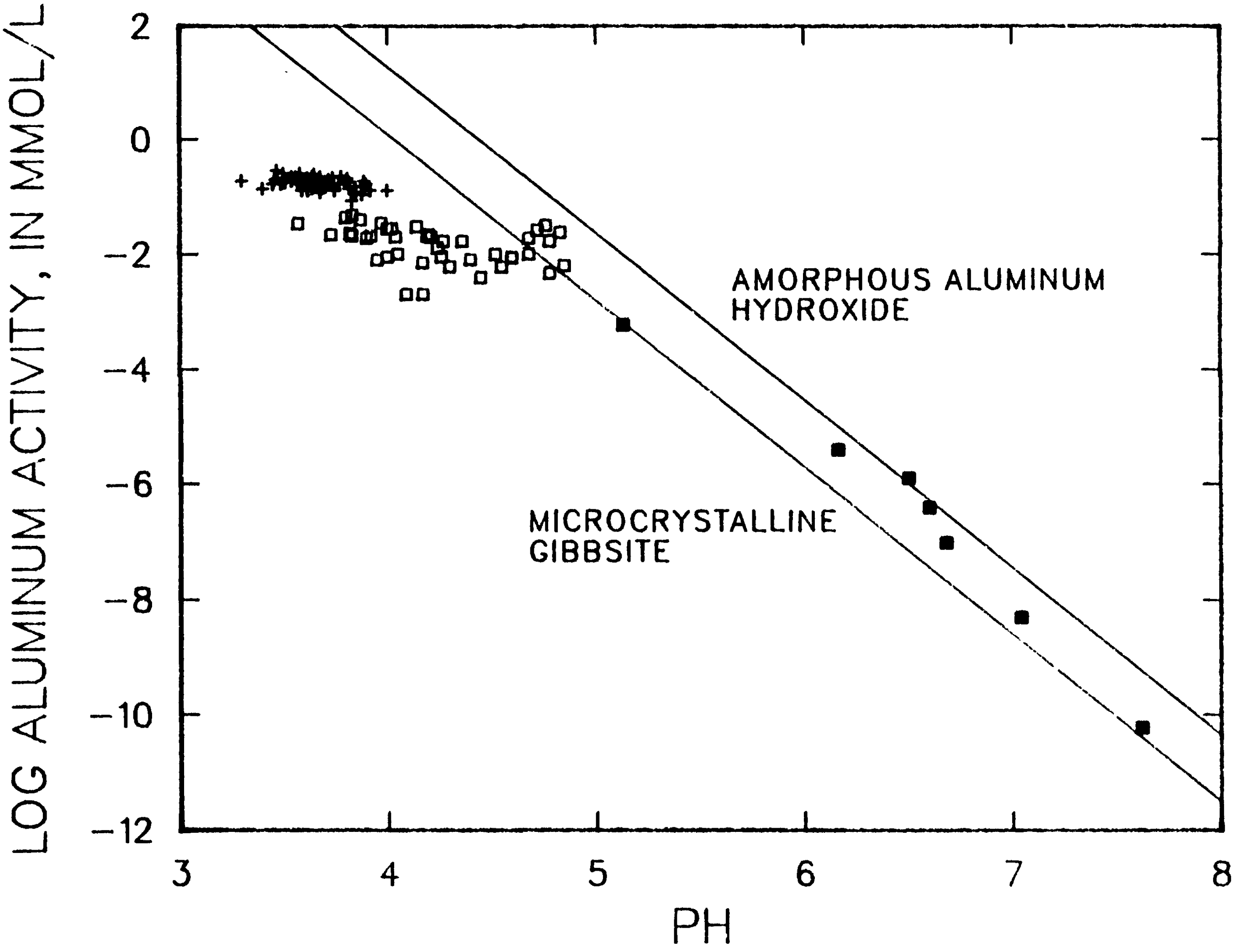

Figure J–10. – Log of the aluminum activity plotted as a function of pH.

Iron

Fe concentrations as great as 54 mmol/L have been measured in ground water from the study area. Virtually all of the Fe in solution is in the ferrous oxidation state. The small amount of ferric iron (Fe(III)) that was present could not be distinguished analytically from Fe(II), and was inferred from speciation calculations by PHREEQE. These calculations indicate that the ratio of Fe(II) to Fe(III) ranged from approximately 500:1 to 2,000:1 for most ground-water samples. The assumption that Fe(III) was present is valid because dissolved oxygen (0.003 to 0.03 mmol/L) was detected in most ground-water samples.

Solubility of Fe is controlled by the redox potential (Eh) of ground water and pH. Similarly to Al, Fe in ground water has a negative correlation with pH (fig. J-11, $r^2 = 0.74$), and the scatter in the data make it difficult to accurately predict Fe concentrations in ground water based only on pH. The data in figure J-11 also fit into the same three groups based on well locations as did Al.

Several minerals were evaluated as potential controls on the solubility of Fe. Of these, only melanterite ($FeSO_4 \cdot 7H_2O$), jarosite [Na,K,H) $Fe_3(SO_4)_2(OH)_6$], and amorphous ferric hydroxide [$Fe(OH)_3$], had thermodynamic equilibrium constants that approximated the ion-activity products calculated by PHREEQE.

Melanterite was undersaturated in all ground-water samples by 1 to 2 orders of magnitude; however, the compound is highly soluble and the uncertainty in its KT is large. Nordstrom and others (1979) report that precipitation of melanterite is usually associated with waters having a greater ionic strength and lower pH than the ground water in this study.

Jarosite was supersaturated in all ground-water samples by 5 to 10 orders of magnitude. This large degree of supersaturation indicates that jarosite minerals are not controlling the solubility of Fe. There may be kinetic factors that need to be overcome before jarosite can precipitate, or, as Nordstrom and others (1979) suggest, precipitation of jarosite might occur only in microenvironments where the water chemistry is different than in the bulk solution. Neither melanterite nor jarosite have been identified by X-ray diffraction in alluvium from the contaminated part of the aquifer.

Amorphous $Fe(OH)_3$ appears to be the dominant compound controlling the solubility of Fe. Alluvium that has come into contact with the acidic plume is coated with iron oxides that are amorphous to X-ray diffraction, and precipitation of amphorphous $Fe(OH)_3$ is consistent with the chemistry of the ground water (slightly oxidizing). However, there is difficulty in matching the KT for amorphous $Fe(OH)_3$ with the IAP for the ground-water samples because of the uncertainty in Eh. The IAP is calculated using:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (5)$$

$$(\log KT = -4.891)$$

and the activity of Fe^{3+} is calculated from:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-. \qquad (6)$$

Thus, an Eh measurement that accurately reflects the true redox potential is necessary for determining the saturation state of ground water with respect to amorphous $Fe(OH)_3$.

Eh can be calculated from the activities of Fe^{2+} and Fe^{3+} using equation 6. This approach requires that the concentration of both Fe(II) and Fe(III) be known so that their activities can then be computed. This method could not be used in this study because the small concentrations of Fe(III) could not be detected in the presence of Fe(II).

Eh can also be measured directly in the field; however, there are problems associated with the correlation between field Eh potentials and the actual redox state of a water (Lindberg and Runnells, 1984). Generally, most Eh measurements do not accurately reflect the true redox state of a water sample. Exceptions usually involve the Fe^{2+}-Fe^{3+} redox couple (Stumm and Morgan, 1970; Nordstrom and others, 1979). Even with this couple, concentrations of both Fe^{2+} and Fe^{3+} should be at least 10^{-5}M (molar) in order to provide an exchange current at the electrode-solution interface great enough to establish a Nernstian Eh.

The Eh of ground-water samples was measured in November 1985. Only those values for ground-water samples that had Fe concentrations greater than 10^{-5}M were considered. Field Eh values (table J-2) ranged from 0.38 to 0.47 V (volts). These values were used in PHREEQE to calculate the activity of Fe^{3+} (table J-2). The activity of Fe^{3+} in all samples was less than 10^{-7}M; thus, Fe^{3+} may not have generated sufficient exchange current to yield an accurate Eh.

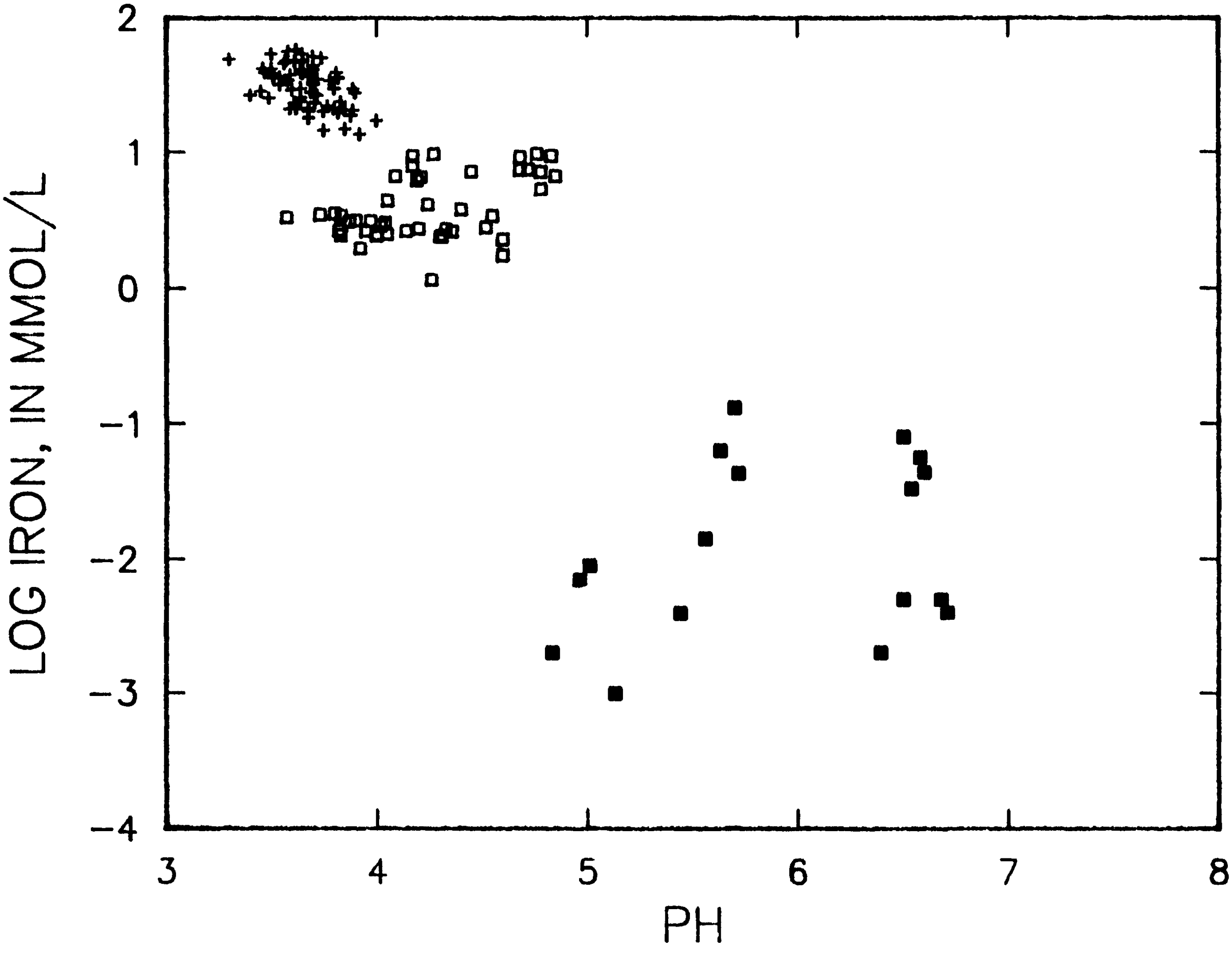

Figure J–11. – Plot of log iron concentration versus pH for ground-water samples.

Table J-2.—*Comparison of Eh values measured in the field with those calculated by assuming equilibrium with amorphous* $Fe(OH)_3$

Sample	Field Eh (volts)	(Fe^{3+}) (mols per liter[1])	Calculated E (volts[2])
MP1W2	0.43	$10^{-7.0}$	0.57
MP1W2	.45	$10^{-7.2}$	.60
X1W1	.44	$10^{-7.1}$	.57
X1W2	.46	$10^{-7.2}$	.59
X1W3	.45	$10^{-7.3}$	.57
X1W4	.47	$10^{-9.1}$	.57
X3W2	.41	$10^{-7.2}$	.57
X3W3	.43	$10^{-9.4}$	.50
X4W1	.38	$10^{-9.0}$	.44
X4W2	.43	$10^{-9.1}$	.55

[1] Calculated activity of Fe^{3+} in solution.

[2] Assumes equilbrium between (Fe^{3+}) and amorphous $Fe(OH)^3$.

Eh can be calculated using equation 6 if equilibrium between dissolved Fe and amorphous $Fe(OH)_3$ is assumed. These calculations were made by maintaining pH and total dissolved Fe at the values measured in the water samples and allowing Eh to vary until equilibrium with amorphous $Fe(OH)_3$ was attained (IAP/KT = 0). The Eh values calculated by this method (table J-2) are within 30 percent of those measured in the field. Although the assumption of equilibrium with amorphous $Fe(OH)_3$ may not be completely accurate, it may be a good enough approximation for modeling transport of Fe.

CONCLUSIONS

Geochemical processes occurring in the aquifer near Globe, Ariz., are complex. Decreasing concentrations of aluminum and iron correlate with increasing pH; however, the correlation is not adequate to allow an accurate prediction of the concentration of either element based only on pH.

Aluminum in solution appears to be controlled by microcrystalline gibbsite at pH values greater than approximately 4.7 to 4.9. At pH values less than 4.9, an unidentified aluminum mineral, or an assemblage of aluminum minerals may control solubility.

Physical evidence from alluvium, and chemical data from ground water indicate that the solubility of iron at all pH values is controlled by amorphous ferric hydroxide. This assumption makes possible calculation of the Eh values necessary for geochemical modeling of the system.

Additional statistical work is needed to identify other parameters that may correlate with aluminum and iron, and the solid phases forming in the aquifer need to be better characterized. The significance of kinetics in the various reactions also need to be evaluated. Finally, the effect of dilution on concentration must be quantified.

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MANGANESE IN CHANNEL SEDIMENTS OF PINAL CREEK, ARIZONA

By Judith K. Haschenburger[1]

ABSTRACT

Elevated concentrations of dissolved manganese in the lower perennial reach of Pinal Creek are linked to ground-water transport from the Globe-Miami mining district, Arizona. This study investigates the manganese that has precipitated onto stream sediments as oxides. Representative channel measurements and sediment samples were collected within 200-meter-long sampling segments in five geomorphically distinct subreaches. Samples were collected from the perennial-flow channel and from that part of the flood plain that is sufficiently inundated for manganese-oxide deposition. Sampling was designed in anticipation of finding higher manganese concentration in areas of fine-grained sediments than in areas of coarser sediments. Manganese mass in sediments within 60 millimeters of the surface of the 12.9-kilometer length of channel that contains perennial flow is estimated to be a minimum of 37 megagrams. This estimate is the sum by subreaches of volumetric channel dimensions, sediment bulk density, and sample manganese concentration in excess of background concentration. A zone of increased manganese concentration in channel margins immediately adjacent to the flowing stream is estimated to contain an additional 10 megagrams. The mass of manganese in stream sediments has been increased by 135 percent because of upstream mining activity. Some manganese oxides have been removed from temporary storage by sediment-transport processes.

INTRODUCTION

Mining in the Globe-Miami district, Ariz., has increased metal availability to the ground-water system in the Pinal Creek basin. Dissolved metals from a leaking acidic water reservoir have entered the underlying shallow alluvial aquifer. Elevated concentrations of dissolved manganese (Mn) in the lower perennial reach of Pinal Creek are the result of transport through the ground-water system (Eychaner and Stollenwerk, 1985). The Mn has precipitated onto sediments as oxide coatings in this channel reach. This paper describes a study that estimates the mass of Mn contained in the sediments as the result of Mn oxide deposition related to mining in the Pinal Creek basin.

DESCRIPTION OF STUDY AREA

The lower perennial segment of Pinal Creek is 12.9 km (kilometers) in length and constitutes the study reach (fig. J-12). This reach displays a compound channel pattern, consisting of a low-flow meandering channel and a high-flow braided channel (Graf, 1988). Braided channel characteristics are especially evident upstream from a streamflow-gaging station (fig. J-12). Downstream from the gaging station, however, the channel lies within a narrow canyon, and its morphology is largely controlled by bedrock outcrops and large boulders near the channel borders.

Longitudinal sorting of channel-bed material has created areas where sediments are mainly fine-grained and areas where the sediments are mainly coarse-grained. The fine-grained sediments consist of sand-sized particles, whereas the coarse-grained sediments include particles that range from sand to large cobbles and small boulders.

METHODOLOGY

The study reach was divided into five subreaches that define segments with similar channel bed morphologies and valley widths. Within each subreach, a 200-meter-long sampling segment was identified to represent channel, sediment, and Mn concentration characteristics. Measurement at 20-meter intervals provided cross-sectional width of the base-flow channel and the adjacent flood plain. The width measurements included the part of the flood plain sufficiently inundated during higher discharges for development of Mn oxides. Changes in vegetation density, bed material size, and slope determined the upper extent of this flood-plain area.

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[1] Department of Geography, Arizona State University, Tempe, Ariz.

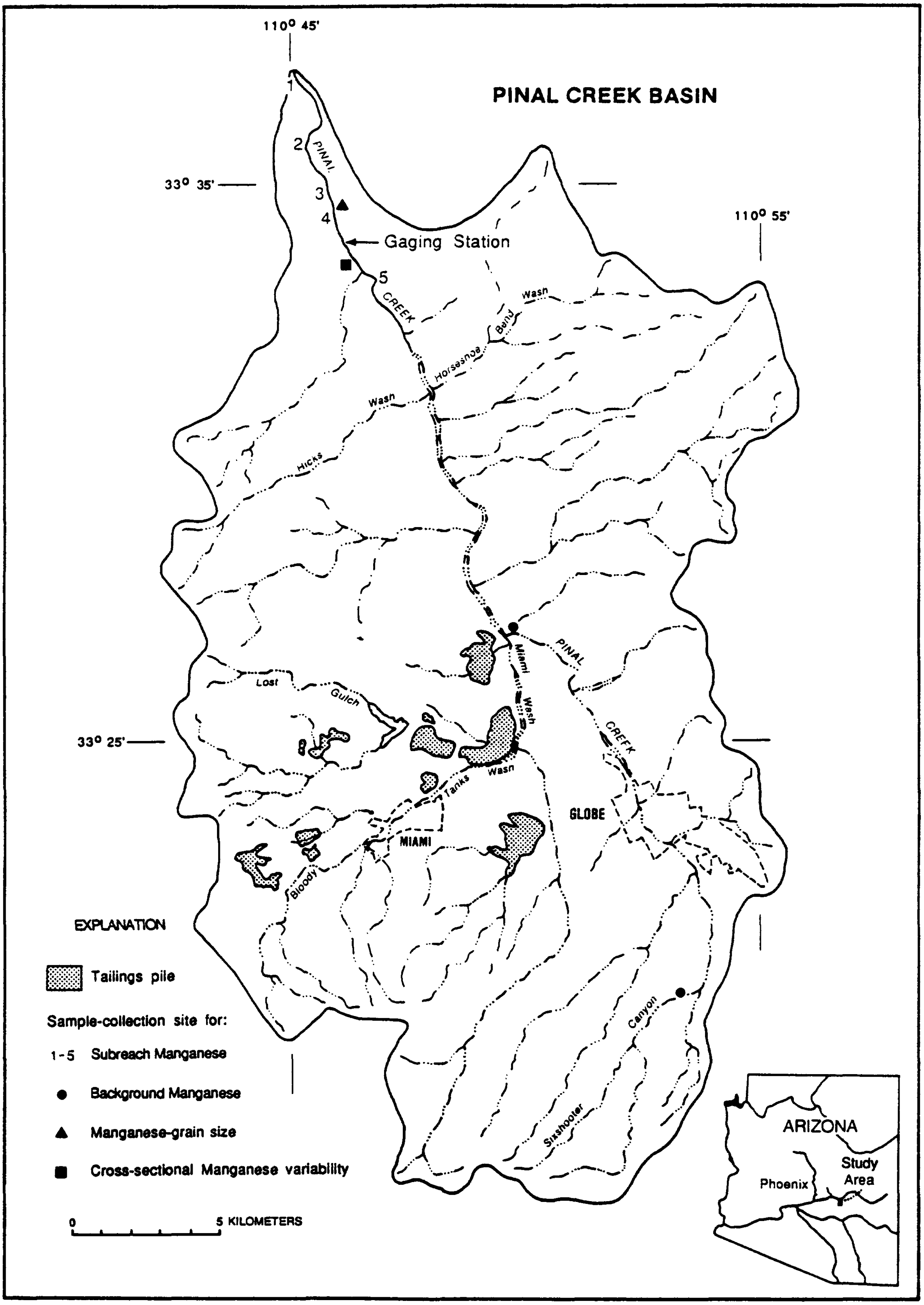

Figure J-12.—Pinal Creek basin. Symbols of sample collection sites for subreach manganese and manganese grain size represent two channel cross sections, where one cross section is located in fine- and coarse-grained sediment.

Ten channel cross sections, two in each subreach, were selected to depict Mn concentrations for mass calculations (fig. J-12). In each subreach, one channel cross section was identified in the midportion of channel-bed sediments composed of fine bed material and one cross section was selected in the midportion of bed sediments consisting of coarse bed material located downstream from the fine-grained sediments. Cross sections composed of fine-grained particles would be expected to have higher bulk Mn concentrations than cross sections composed of coarse-grained particles, because metal concentration is inversely related to particle size (Salomons and Forstner, 1984). Thus, characterization of Mn concentration should be improved by considering both types of channel-bed sediments.

Along each cross section, two samples were collected from the base-flow channel between channel margins and the midchannel area, and two from the associated flood plain in the midsection on each channel side. The 100-mm (millimeter) diameter cylindrical sampler used to collect sediments penetrated the channel bed to a depth of 60 mm. Preliminary sediment sampling at three different channel bed depths indicated that a standard 60 mm sampling depth would include the majority of subsurface sediment affected by Mn oxide precipitation.

Five additional channel cross sections were sampled for supplemental concentration data (fig. J-12). Background Mn concentrations were sampled in one cross section 500 meters upstream from the Pinal Creek-Miami Wash confluence and another about 5 km upstream from the Globe urban area and the major mines. In subreach 3, sediment samples were extracted from one cross section consisting of fine-grained sediment and one cross section composed of coarse-grained sediment to evaluate the relation between Mn concentration and particle size. Finally, cross-sectional Mn variability was sampled in subreach 5 by collecting two samples each from the base-flow channel, channel margins, and flood plain; one sample was collected from the high-flow channel.

Sediment samples were air dried and weighed. Cross-sectional samples were combined into bulk samples as spacing of samples was approximately equal. These combined samples were sieved to construct particle-size-distribution curves (Folk, 1974). Sediment splits were pulverized to pass through a 100-mesh screen (0.15 mm). Aqua regia (3:1 hydrochloric-nitric acid) was added to 1-gram samples, which were heated for 1 hour. Atomic-absorption spectroscopy was used to determine Mn concentration in the extracts.

RESULTS

Sediments in Pinal Creek consist primarily of sands and fine gravels with small amounts of clays and silts (fig. J-13). Average particle diameter was 3.3 mm in the fine-grained sediment and 5.3 mm in the coarse-grained sediment. These diameters are the mean of the D16, D50, and D84 sizes, which more accurately represents bimodal, heterogeneous particle-size distributions than the D50 diameter (Folk, 1974).

The randomization test of matched pairs statistic (Siegel, 1956) determined that the particle diameters of the cross sections composed of fine-grained sediment and cross sections composed of coarse-grained sediment were statistically different at the 90-percent confidence level. Underrepresentation of particles larger than 100 mm in diameter in the samples of coarse-grained sediment has most likely reduced the diameter difference between these two groups.

An average background Mn concentration of 1.2 mg/g (milligrams per gram) exists in stream sediment. Mn-bearing minerals in basin sediments, such as ankerite, pyroxene, and rhodochrosite (Peterson, 1962), account for this background concentration. Subreach Mn concentrations were reduced by this background value to isolate the mass resulting from groundwater transport from the mined area.

A significant difference in Mn concentrations between the fine- and coarse-grained sediment groups was not detected by the randomization test using a 90-percent confidence level. The bulk Mn concentrations of the sediments composed of coarse-grained material may have been increased by two factors, reducing the concentration difference between the two sediment groups. First, the underrepresentation of particles greater than 100 mm in diameter would lessen the role of these particle-size concentrations in diluting bulk sample concentrations. Second, sediments in coarse-grained areas had more evident coatings of Mn oxides than

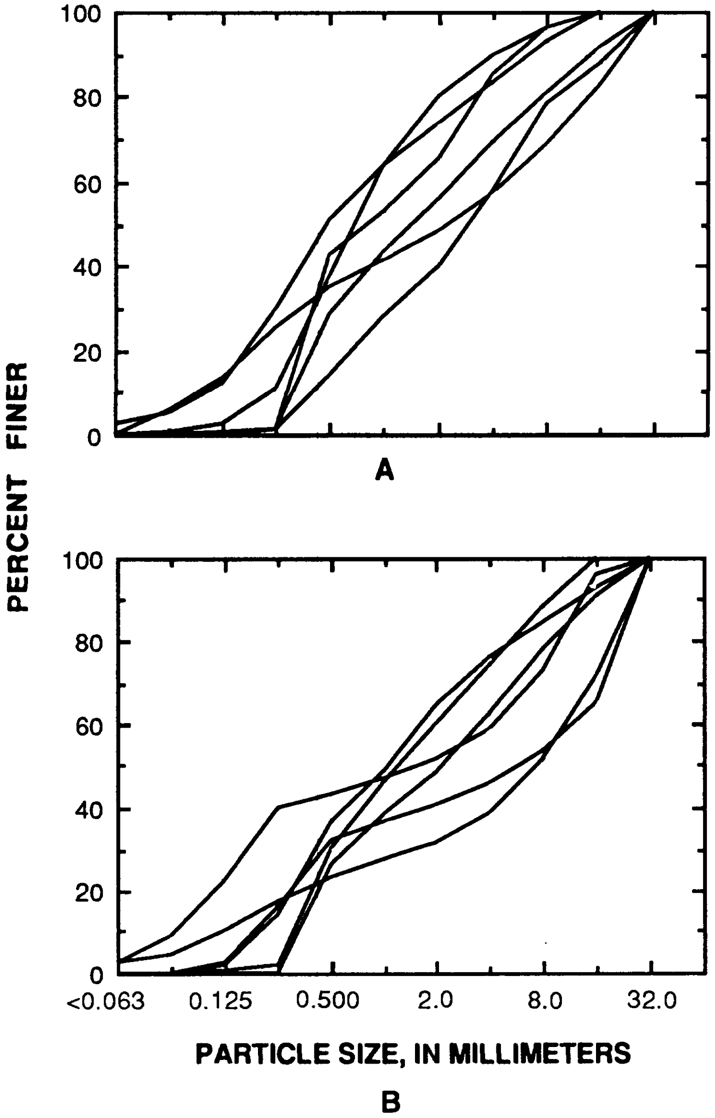

Figure J-13.—Particle-size distribution curves for the 10 subreach samples and two manganese concentration grain-size samples divided into the cross sections of fine-grained sediment (A) and the cross sections of coarse-grained sediment (B).

sediments in fine-grained areas. Therefore, elevated concentrations in individual particle-size fractions in the coarse-grained samples would increase bulk sediment concentrations.

The mean base-flow channel of the study reach was 4.1 meters wide, whereas the flood-plain width averaged 10.1 meters (table J-3). The larger width of the base-flow channel and flood-plain in the upper, braided reach reflects a valley that is not restricted by bedrock outcrops.

The total mass of Mn in Pinal Creek was calculated using Mn concentration, sediment density, and volumetric channel dimensions. Average Mn concentrations in each subreach (table J-3) multiplied by mean subreach sediment density provided the subreach mass of Mn per volume of sediment. These subreach values multiplied by subreach channel volume dimensions (the product of subreach length, average flood-plain width, and 60-mm sampling depth) yielded subreach mass. The total mass of Mn in perennial channel sediments (the sum of subreach values) is estimated to be 37 Mg (megagrams); this minimal value represents sediments in general.

The mass of Mn contained in sediments along channel margins was computed because Mn oxides are very evident in these sediments. The two channel margin samples from the Mn variability cross section (fig. J-12) provided an

Table J–3.—*Channel characteristics and manganese concentrations*

Subreach	Length (meters)	Base-flow width (meters)	Bar-deposit width (meters)	Average manganese concentration (milligrams per gram)
1	1,260	4.1	9.0	4.90
2	2,890	4.0	8.5	3.50
3	1,350	3.7	9.4	3.35
4	950	3.9	9.4	2.95
5	6,460	5.0	14.1	3.55

average concentration of 13.2 mg/g for margin areas. Calculation of sediment mass (product of average sediment density and channel volume) included only the width of channel margins, approximated at 5 percent of the average floodplain width. Deposits in the margins account for 10 Mg and increase the total Mn mass in stream sediments to 47 Mg. The background mass of Mn is estimated at 20 Mg. Therefore, upstream mining activity has resulted in a 135 percent increase in the mass of Mn in channel sediments.

Estimates of total Mn mass do not include Mn-coated sediment transported through the channel system before sediment collection in September 1987. In subreach 4, sediment transport processes are evidenced by the breakup of a ledge of Mn-cemented sediments about 10 meters long and 0.4 meter wide between April and August 1987, during which the largest peak discharge was 25 m^3/s (cubic meters per second). Between September 1979, when stream discharge measurements began at the gaging station, and September 1987, 15 floods occurred with peak discharges greater than 25 m^3/s. Thus, an undetermined amount of Mn has been removed from temporary storage in the stream environment by sediment-transport processes.

SUMMARY

The movement of dissolved Mn through the ground-water system has resulted in the deposition of an estimated minimum of 37 Mg of Mn on channel sediments in the perennial-flow segment of Pinal Creek. Estimated total mass of Mn, including increased Mn concentrations in channel margins, is 47 Mg. This Mn is related to mining activities in the Pinal Creek basin. Areas of extensive sediment cementing by Mn oxides, particularly along channel margins, have been disrupted, and Mn-coated particles have been transported during flood events. Sediment in the stream channel is only a temporary sink for Mn oxides because transport processes limit residence time in this segment of the environmental system.

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RESEARCH ACTIVITIES RELATED TO ACIDIC WATER NEAR GLOBE, ARIZONA

By James H. Eychaner[1]

ABSTRACT

In an area contaminated by acidic water related to copper mining, many geochemical reactions involving metals may be studied in ground and surface water. Drilling is planned near Globe, Arizona, to determine whether predicted secondary minerals form in a complex field environment as pH rises from less than 5 to more than 6 and metal concentrations decrease from milligrams to micrograms per liter. Solid-solution minerals or coprecipitates may be formed, and bacteria may mediate the process. Recent elimination of a major contaminant source may establish a second transition zone and allow further evaluation of geochemical models. Sampling methods for metallic colloids in ground water are to be tested, and reconnaissance sampling is planned for tritium, organic compounds, and alpha radiation. Within a 12-kilometer reach of a perennial stream, changes in concentration of several elements by as much as 50 percent could be studied without mixing with uncontaminated streamflow. Breakthrough of several metals to the stream is expected within about 6 years.

INTRODUCTION

In the Globe, Ariz., copper-mining district, acidic water has contaminated a ground-water flow path 15 km (kilometers) long to a depth of at least 50 meters during at least 40 years. General hydrology and geochemistry of the contaminant plume are described by Eychaner (1989, this Proceedings) and Stollenwerk and Eychaner (1989, this Proceedings). The plume lies along a valley, largely in unconsolidated alluvium that contains some cobbles and boulders. The water table is 1 to 10 meters below land surface and varied by as much as 6 meters during 1985-87. Average ground-water velocity in the alluvium is about 5 m/d (meters per day). The core of the plume has a pH of less than 4 and 90 mmol/L (millimoles per liter) sulfate, 50 mmol/L iron, 10 mmol/L aluminum, 2.5 mmol/L copper, 1.6 mmol/L silica, 1.4 mmol/L manganese, and less than 0.5 mg/L (milligram per liter) oxygen. Other constituents are listed in table J-1 of Eychaner (1989, this Proceedings). The longitudinal and vertical variation of chemistry and head have been sampled at 23 wells in 6 clusters. A zone of neutralization reactions is advancing through the aquifer at about 0.5 m/d and is expected to reach a perennial stream in about 6 years. The perennial reach begins in the lower part of the valley, where impermeable rocks truncate the aquifer and force the entire flow of 0.2 to 0.3 m^3/s (cubic meters per second) to the surface. Stream discharge and chemistry have been measured since 1979 at a gaging station about 6 km downstream from the head of perennial flow (Eychaner, 1989, this Proceedings, figs. J-1 and J-2). Dissolved manganese at the gage increased from 0.5 mg/L in 1979 to more than 30 mg/L in late 1987; manganese oxides are deposited on the streambed in a 12-km reach upstream from the confluence of Pinal Creek with a major river.

The purpose of this paper is to describe research opportunities in both the ground-water and surface-water parts of the plume. Several activities are in progress or just beginning, and others are being planned. In addition, reconnaissance samples are to be collected in 1988 for other lines of potential research. Activities in each stage could benefit by the involvement of additional investigators.

ONGOING RESEARCH

A hydraulic simulation of the flow field in the Pinal Creek area is to be completed by September 1988 (Neaville, 1989, this Proceedings). In the conceptual model, most ground-water flow occurs in the alluvium, whose width, thickness, and hydraulic gradient are known. Concurrent measurements of ground-water levels and stream discharge at several locations have been made (Eychaner, 1989, this Proceedings, fig. J-3) as well as several pumping tests. A local resident reported that the head of perennial flow in 1985 was the farthest upstream in about 50 years and also reported its most downstream location.

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

Conditional solubility constants for reactions occurring in the field are being formulated using the geochemical model PHREEQE to analyze field observations and laboratory column experiments (Stollenwerk, 1989, this Proceedings). PHREEQE is to be coupled with a solute transport model to predict future behavior of the solutes.

An attempt was made to track the velocity of the reaction zone or individual metals over several decades using cores from 23 cottonwood trees growing above the plume. Certain cores showed a major reduction in growth rate that might be related to an arrival of acidic ground water, but the annual growth boundaries were so obscure and so inconsistent between cores from nearby trees or opposite sides of the same tree that specific dates could not be determined. Despite the absence of firm dates, three cores were analyzed by proton-induced X-ray emission spectroscopy for metal concentrations. The results were inconclusive but suggest that elevated metals concentrations correspond to growth reductions. Because no other useful tree species grows above the plume, this aspect of the study has ended.

Methods for sampling mobile metals in ground water that may contain colloids are to be compared in June 1988. The work, in cooperation with U.S. Environmental Protection Agency R.S. Kerr Environmental Research Laboratory, will involve about 10 wells that span the range of chemistry in the plume. Each well is to be pumped at a low rate with a bladder pump and at a higher rate with a submersible pump. Water samples will be collected unfiltered or by using one of several filters with different pore sizes. The water will either be isolated from or exposed to atmospheric oxygen during sampling.

Concentrations of several constituents are known to decrease through the perennial reach of Pinal Creek as low-oxygen ground water is exposed to the atmosphere, generally without mixing with uncontaminated streamflow. More than 50 mg/L of dissolved manganese has been measured at one point, decreasing to less than 25 mg/L about 10 km downstream. Precipitated manganese minerals are to be characterized during 1988. Stream pH increases from 6.4 to 8.2 in the reach; concentrations of calcium, sulfate, and silica decrease about 10 percent; and concentrations of barium, iron, nickel, and zinc, though small, decrease about 50 percent. In addition to monthly samples at the gaging station, concurrent samples were collected at four locations along the stream on two dates in 1987. A periodic sampling program at a point 5 km upstream from the gage is to begin in June 1988 in order to monitor increasing metal concentrations as the water first enters the stream and to quantify changes along the stream. Breakthrough of several contaminants to the stream is expected in about 6 years (Eychaner, 1989, this Proceedings).

PLANNED RESEARCH

A cooperative project is planned with U.S. Environmental Protection Agency Athens Environmental Research Laboratory to drill several wells in the major reaction zone during fiscal year 1989 in order to identify and quantify reactive minerals, secondary minerals formed in the reactions, and associated changes in solution chemistry. The objective is a demonstration or test of equilibrium geochemical models, specifically MINTEQ. In the initial phase, acidic water will be passed through a laboratory column of alluvium. The column contents will be disassembled and secondary minerals identified to guide drilling plans. The study will require methods development for sampling in loose, rocky, low-oxygen, saturated material for minerals that are amorphous, unstable, or a small fraction of the total mass. Size distribution may be as important as chemistry, and colloids or solid-solution minerals may be present. Both the laboratory and field phases should provide opportunities for coordinated research in a zone with large changes in pH and metal concentrations.

POTENTIAL RESEARCH

Metal concentrations in ground water vary with pH, but only iron appears to be near a simple solubility limit. Other metals are below saturation with respect to simple minerals. These metals may sorb on fresh ferric hydroxide or precipitate as impurities or solid solutions in gypsum, jarosite, or siderite. Gypsum crystals that formed near a major contaminant source are to be analyzed to identify a possible solid solution. Bacteria may facilitate mineral formation, but bacteria samples have not been collected.

A wastewater reservoir that in 1986 contained 5.5×10^6 m^3 (cubic meters) of water at pH 2.7 was drained by May 1988 to eliminate a major contaminant source. Removal of contaminated water from the upstream part of the aquifer also is underway. These changes in the upstream contaminant load should create a new transition zone as lesscontaminated water moves through the system and could provide another opportunity to test geochemical models. In addition, electromagnetic induction measurements through nonmetallic well casings could measure changes in solution conductivity through the entire thickness of the plume.

Knowledge of the age of ground water in various parts of the aquifer may help to define flow velocities or apparent vertical dispersion. Tritium was selected for reconnaissance samples to be collected in June 1988 because estimated flow velocities and the date of initial contamination both indicate ages of less than 100 years.

Organic carbon concentrations in ground water are less than 5 mg/L in the plume and about 1.5 mg/L in uncontaminated water. Even so, the transport of some metals may be accelerated by organic compounds, and identification of specific compounds may allow tracking of contamination from specific sources. Reconnaissance samples for identification of organics are to be collected by the University of Arizona during June 1988. Tracking specific waters may also be possible by measuring extremely low concentrations of many elements using an ion-coupled plasma mass spectrometer.

Silicate minerals in the aquifer have been exposed to a pH of less than 4 for periods ranging from months to decades. Dissolution rates could be studied by using penetration depths or size distributions at different points in the valley. Minerals at shallow depth have been alternately saturated and unsaturated, exposed and unexposed to oxygen because of annual water-level variations of more than 2 meters. Minerals deeper in the plume have been continuously saturated with nearly anoxic water.

Granite in the ore body may be a source for elevated uranium and its daughter nuclides. Reconnaissance measurements of gross alpha radiation in three previous water samples are to be made at the University of Arizona during 1988.

SUMMARY

This paper describes research opportunities in an area contaminated by acidic water related to copper mining. Most potential topics relate to geochemistry of metal transformations in ground and surface water, but developments in sampling methods also are included. Drilling is planned to determine whether secondary minerals predicted by an equilibrium geochemical model actually form in a complex field environment. Coordinated studies with other investigators are possible in an aquifer with large changes in pH and metal concentrations. The formation of solid-solution minerals or coprecipitates is possible, and bacteria may be important in the reactions. Recent elimination of a major contaminant source may establish a second transition zone in the aquifer and allow further evaluation of models. Sampling methods for metallic colloids in ground water are to be tested, and reconnaissance samples for several lines of potential research are to be collected in 1988. Transformations of low-oxygen contaminated water exposed to the atmosphere in a perennial stream could be studied, and breakthrough of several metals to the stream is expected within about 6 years.

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(p. 603 follows)

CHAPTER K – TOXIC SUBSTANCES IN GROUND AND SURFACE WATERS – POSTER PRESENTATIONS

Page

METAL LOADINGS INTO THE ARKANSAS RIVER FROM THE LEADVILLE, COLORADO, AREA

By Bryan D. Nordlund[1] and Briant A. Kimball[2]

ABSTRACT

Contributions of metals to the Arkansas River by tributaries in the upper Arkansas River basin near Leadville, Colorado, mostly are from two sources, the Leadville Drain and California Gulch. Massflow calculations indicate the effect of these contributions on Arkansas River water quality as functions of downstream travel distance and of streamflow magnitude. Constituents analyzed for massflow are iron, manganese, cadmium, copper, chloride, and sulfate. Preliminary calculations indicate that the majority of metal loading is from California Gulch. The contribution of these constituents from the Leadville Drain, upstream of California Gulch, also is significant. The data base used for the calculations has been collected as part of the Upper Arkansas Surface Water Toxics project.

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[1] Gresham, Ore.
[2] U.S. Geological Survey, Lakewood, Colo.

MINERALOGY OF FLOCCULANT CONSTITUENTS IN ST. KEVIN GULCH, LEADVILLE, COLORADO

By Joan J. Fitzpatrick[1]

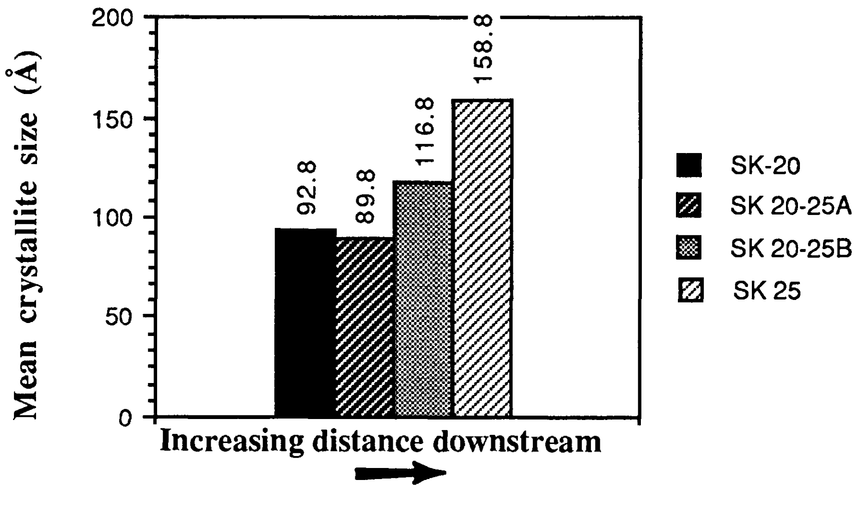
ABSTRACT

The mineralogy of flocculants that form in the surface waters of St. Kevin Gulch, an acid-mine drainage site near Leadville, Colorado, was investigated using X-ray powder diffraction techniques. Goethite (α–FeO(OH)) and ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$) were identified in four samples taken on a 0.4-kilometer reach near the confluence of Shingle Mill and St. Kevin Gulches.

Standard sample preparation and mounting techniques for powder X-ray diffraction do not generally yield diffraction patterns that display good enough peak-to-background characteristics to permit identification of these poorly crystallized phases. Consequently, a plate from a single crystal of quartz, cut on a nondiffracting crystallographic plane, was used as a low background substrate. Samples were loaded as a slurry and allowed to air dry. After drying, samples were step-scanned at 0.02° 2Θ with a 20-second integration time over the range 2°–70° 2Θ. The resultant X-ray diffraction patterns showed linear backgrounds of less than 5 counts per second in intensity and excellent peak-to-background characteristics, even on milligram quantities of material.

Diffraction peaks of goethite and ferrihydrite were easily distinguished from those of detrital phases (quartz, kaolinite, illite/smectite) on the basis of their large, full widths at half maximum (FWHM), that is, peak widths. The large FWHM's, all greater than 1° 2Θ, indicate small coherent X-ray domain size ("crystallinity"). The strongest peak of goethite, at approximately 4.18 Å, was deconvoluted and profile-fitted using a gaussian peak shape for all samples. The retrieved FWHM's were then used to calculate an average "crystallinity" using a simple Debye approximation (no strain). The results of this calculation indicate a rapid coarsening in the coherent domain size of the goethite with distance downstream as shown in the figure below.

Mean crystallite size for goethite from St. Kevin Gulch



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

STATUS REPORT ON A STUDY OF THE EFFECTS OF ACID MINE DRAINAGE ON VEGETATION NEAR LEADVILLE, COLORADO

By Barbara M. Erickson[1]

ABSTRACT

Moss, grass, and soil samples were collected from 8 sites along St. Kevin Gulch, Leadville, Colorado. Samples of sedge, horsetail, and cow manure also were collected where present. The sampling sites were located from above the area of mine drainage downstream to where St. Kevin enters a wetland. Field work in 1988 will concentrate on the wetland--determining the major ecotypes, establishing permanent sampling plots, and beginning the sampling on a seasonal basis.

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

A MODEL FOR PHOTOLYTIC DECOMPOSITION OF TOXIC MATERIALS ADSORBED ONTO IRON OXYHYDROXIDES IN SURFACE WATERS

By K.M. Cunningham[1] and M.C. Goldberg[1]

ABSTRACT

Photoredox reactions are known to occur in aqueous suspensions that contain iron oxyhydroxide particles. Such reactions occur between Fe(III) at the lattice-aqueous solution interface and adsorbed species that may be either organic or inorganic compounds. In these reactions, the adsorbed species loses an electron to Fe(III), which then is reduced to Fe(II). The experimentally observed generation of Fe(II) in the absence of organic compounds implies that OH and(or) CO_3^{2-} (if present) undergo photoredox to produce OH and CO_3^- radicals, respectively. In the presence of organic compounds, these radicals also can be generated by a second route in which Fe(II) generated by a Fe(III)-organic photoredox reaction is oxidized through the Haber-Weiss mechanism. Whether OH and CO_3^- radicals are generated in significant quantities in surface-water environments containing iron oxyhydroxides is an important question because they will affect the mechanism of reactions that cause the destruction of toxic substances, and the reactions of natural dissolved organic matter.

In order to better understand radical interactions in the iron oxyhydroxide/water/organic system, we have developed a kinetic model for the specific aqueous system alanine adsorbed onto goethite (alpha-FeOOH). The kinetic model incorporates rate constants either obtained from the literature or estimated, and is based on the assumption that a diffusion-controlled surface adsorption reaction of the organic solute occurs. The known reactions are expressed as a set of differential equations that include the important stable and postulated radical species. The model calculation results in a set of concentrations of these species as a function of photolysis time, taking into account important parameters like pH and dissolved oxygen concentration. The model can approximate the experimental results for the alanine plus goethite system, and it emphasizes the major role of adsorption of Fe(II) on the goethite surface and of the formation of CO_3^- radicals as determining the observed concentration of Fe(II). A similar approach should be applicable to other aqueous systems that contain goethite and organic compounds.

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

EVALUATION OF LITHIUM, SODIUM, CHLORIDE, AND SULFATE AS TRACERS TO INVESTIGATE HYDROLOGIC ASPECTS OF ACIDIC, METAL-RICH STREAMS

By Gary W. Zellweger[1],Kenneth E. Bencala[1], Briant A. Kimball[2], and Diane M. McKnight[2]

ABSTRACT

In small, acidic, metal-rich streams measurable and significant chemical reactions occur over distances as short as tens of meters and times on the order of minutes. Tracer reactivity in such stream environments is a concern recently raised in the context of both acid mine drainage and acid rain. Continuous injections of ionic tracers have been used to investigate spatial and temporal discharge variation, stream dispersion characteristics, and transport time in acidic streams. Lithium, sodium, chloride, and sulfate, have been judged as nominally nonreactive tracers in six injections studies of the water chemistry of Snake River, (Summit County, Colorado), St. Kevin Gulch, (Lake County, Colorado), and Leviathan Creek, (Alpine County, California). Injections lasting from 6 to 48 hours were made in streams that ranged in pH from 3.2 to 4.9 and in discharge from 6 to 900 liters per second. The study reaches were up to 4,381 meters long. They had high dissolved concentrations of iron, aluminum, zinc, copper, and other metals associated with acid-mine drainage. Estimates of relative discharge of tributaries at confluences and estimates of downstream discharge based on solute dilution were calculated. Comparison of these values from multiple tracer injections indicates that the ionic tracers behaved relatively conservatively over 4,381 meters of stream and for as long as 11 hours. The practical limitations of ion injection studies (determined by the total volume of injectate, injection rate, or cost) were evaluated. Within these limits, conservative ionic tracers can be used to aid in the study of acidic streams.

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

EXCHANGE BETWEEN STREAM AND SUBSTREAM FLOWS—IMPLICATIONS FOR POLLUTANT TRANSPORT AND NUTRIENT CYCLING THROUGH A FORESTED WATERSHED

By Kenneth E. Bencala[1], Frank J. Triska[1], Vance C. Kennedy[1], Gary W. Zellweger[1],
John H. Duff[1], and Ronald J. Avanzino[1]

ABSTRACT

Within a watershed, pollutants and nutrients are exposed to differing physical, chemical, and ecological environments. An approximation of watershed processes may include the view of solutes flowing with water from subsurface environments into streams. This view envisions the subsurface as a source for solute input to streams. In some watersheds, exchange of pollutants and nutrients between the subsurface and the stream, in both directions, may continue over significant lengths of the stream. Studies of this exchange are ongoing in the watershed of Little Lost Man Creek, located in Redwood National Park along the northern coast of California. Tracer experiments have demonstrated rapid transport of solutes from the stream into subsurface zones. Nutrient concentrations within the subsurface reflect the existence of a variety of ecological environments. At substream sampling sites within several meters of the boundary of the stream channel nutrient concentrations have been observed to be lower, higher, or equivalent to instream concentrations. Thus, the subsurface serves as both a sink and source for the stream as well as a lateral extension of the stream. Strongly sorbing tracers have been used to demonstrate the implications for enhanced capacity of the watershed to retain sediment-binding pollutants through continued interaction with subsurface environments. Assessment of the environmental fate of pollutants and nutrients within a watershed may need to extend beyond the limited concepts of "soil water," "ground water," or "stream water". An inclusive consideration of interactions among multiple environmental zones may be appropriate.

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

RECORDS OF FALLOUT CS–137 IN LAKE OAHE RESERVOIR, SOUTH DAKOTA

By Edward Callender[1], John A. Robbins[2], and Nancy R. Morehead[2]

ABSTRACT

The distribution of Cs–137 (half-life equals 30.2 years) was determined in a sediment core collected in the summer of 1986 from an arm of the Oahe Reservoir, about 25 kilometers from the mouth of the Cheyenne River, south-central South Dakota. All sections (2-centimeter intervals) of a nearly 2-meter length of core have a Cs–137 activity well above detection limits with peak activity of about 4.5 disintegrations per minute per gram at a depth of 130 centimeters. The profile of Cs–137 in the sediment core is generally coincident with the history of deposition of radiocesium from atmospheric nuclear testing and indicates a mean sediment accumulation rate of 5.7 centimeters per year since the mid-1960's. Because the sedimentation rate is high, the annual cycle of Cs loading is apparent as periodic "spikes" in the profile. From the location of the spikes, the mass-sediment-accumulation rate is calculated and is shown to have decreased gradually from 7 to 1 grams per square centimeter per year since filling of the reservoir in 1959.

These data are used to calculate the flux of arsenic and other contaminants to the Cheyenne River Arm of Lake Oahe. The distribution of Cs–137 in the core is quantitatively predicted by a model that includes direct transfers from the atmosphere plus contributions that are integrated as a result of long-term storage in the upper Missouri River drainage basin and possibly elsewhere within the Oahe Reservoir. At this site, the contribution of Cs–137 from the Cheyenne River watershed is minimal.

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

[2] Great Lakes Environmental Research Laboratory, NOAA, Ann Arbor, Mich.

BIOCONCENTRATION OF HYDROPHOBIC ORGANIC COMPOUNDS IN STREAM BIOTA IN THE CALCASIEU RIVER ESTUARY

By W.E. Pereira[1], C.E. Rostad[1], and C.T. Chiou[1]

ABSTRACT

Historically, water-quality assessments have been based on the nature and concentration of chemical species found in solution. Hydrophobic organic contaminants are often present in the water column at trace concentrations that are below the detection limits of conventional analytical methods. Many of these compounds are toxic to aquatic species such as algae and fish. Because of their relatively high octanol-water partition coefficients (K_{ow}), they are sorbed strongly by sediment organic matter and bioconcentrate in the tissue of stream biota. Concentrations of these compounds in sediments and biota may be orders of magnitude greater than levels in the water column. Therefore, sediments and biota may serve both as sinks and sources for hydrophobic organic contaminants, and play an important role in their fate and transport in aquatic environments.

Studies being conducted in the Calcasieu River Estuary, Louisiana, have indicated that halogenated organic compounds are discharged into Bayou d'Inde, which drains into the Calcasieu River. Because the river is tidally affected, these compounds are transported both upstream and downstream, and are distributed in different compartments of the system including the water column, bottom and suspended sediments, and several species of biota, such as catfish, blue crabs, Atlantic croakers, spotted sea trout, and marshgrass. The objectives of this study were to (a) determine the distributions of halogenated organic compounds in the different compartments, and (b) determine the bioavailability of halogenated organic compounds to stream biota.

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

APPLICABILITY OF CONVENTIONAL METHODS FOR ANALYSIS OF TRACE-LEVEL ORGANIC CONTAMINANTS IN NATURAL WATERS

By Larry B. Barber, II[1], James A. Lewis[1], Michael P. Schroeder[1], and Jacob Gibs[2]

ABSTRACT

Organic contaminants in natural waters are frequently present at trace levels. This study evaluates several analytical methods for recovery and identification of 22 target compounds from distilled and natural river water matrices, at concentrations of less than 1 microgram per liter. The isolation/concentration methods studied were purge and trap, closed-loop stripping, and liquid extraction. Gas chromatography was used for compound separation. Mass spectrometry, flame-ionization, electron capture, electrolytic conductivity, photo-ionization, and nitrogen phosphorus detectors were used for identification and quantitation. Recovery results were interpreted with respect to the compound's Henry's Law constant and water solubility. Although there was some overlap, each extraction method was variable with respect to percent recovery, precision, and compounds detected. Recovery from the distilled water matrix was slightly greater than that for the river water, with the exception of several positive interferences resulting from the presence of target compounds in the river. Precision for the two matricies was similar. The universal detectors (mass spectrometry, flame-ionization) performed similarly in the simple distilled water matrix, but in the complex river water, the mass spectrometry provided more reliable identifications. The class specific detectors had greater sensitivity for some compounds but yielded less information about the total water sample.

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

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

RESPONSE OF ANIONIC DETERGENTS AND THEIR CARBOXYLATED DEGRADATION PRODUCTS TO THE METHYLENE-BLUE-ACTIVE SUBSTANCES TEST

By Jennifer A. Field[1,2] and Jerry A. Leenheer[2]

ABSTRACT

Methylene-blue-active substances (MBAS) have been routinely measured at the Cape Cod Ground Water Toxic Waste Research Site as an indicator for anionic detergents. The sulfonic acid group of anionic detergents, such as linear (LAS) and branched-chain (ABS) alkylbenzene sulfonic acids forms a blue-colored complex with methylene blue, a tertiary amine dye. The color complex is extracted into chloroform and measured spectrophotometrically.

Infiltration of secondary treated sewage has resulted in a plume of MBAS approximately 3,500 meters in length. ABS has been identified at a distance of 3,000 meters from the infiltration beds. In this zone, MBAS is a reliable indicator for detergents; ABS isolated at neutral pH on Amberlite[3] XAD–8 and analyzed by carbon–13 (^{13}C) nuclear magnetic resonance spectrometry (NMR) is comparable to that predicted by the MBAS test. This observation is consistent with the well-documented resistance of ABS to biodegradation, as further evidenced by detection of ABS after more than 25 years of transport in the aquifer. However, the correlation between MBAS and LAS is less clear. For wells near the infiltration beds that would be expected to contain LAS, the LAS does not account for all of the MBAS response. Independent analyses by high-pressure liquid chromatography (HPLC) have shown that the concentration of LAS in the effluent is equivalent to MBAS (approximately 250 micrograms per liter). However, 200 meters downgradient from where the MBAS value was 200 micrograms per liter, results from the HPLC, XAD–8 isolation, and ^{13}C NMR characterization did not detect LAS, and ABS was not expected. Because LAS generally is considered biodegradable, the high MBAS response downgradient leads to the hypothesis that LAS degradation products may be contributing to the MBAS response.

LAS degradation products are formed by a microbial beta-oxidation process that results in carboxylation of the hydrocarbon end of the LAS molecule while leaving the anionic sulfonic acid group intact. These molecular characteristics could lead to a positive MBAS response but will inhibit LAS degradation product isolation by Amerlite XAD–8. LAS and ABS, which have 1 ionic functional group to 18 carbons units, are effectively concentrated at neutral pH on Amberlite XAD–8 resin by a hydrophobic mechanism. However, LAS degradation products are much more hydrophilic (a maximum of 1 ionic group to 9 carbon units for a 12-carbon unit degradation product at neutral pH) and would not be expected to isolate on Amberlite XAD–8 at neutral pH.

To test LAS degradation product response to the MBAS test, a series of synthesized sulphophenyl carboxylic acid (SPC) analogs of LAS degradation products, ranging in chain length from 1 to 10 carbon units, were subjected to the MBAS test and the response compared to LAS and ABS standards. The acidic solutions (pH 1.5) of the MBAS test affects the protonation of the carboxylic end group, which decreases the hydrophilic character of the molecule, thereby increasing the extraction efficiency of the methylene blue-SPC complex. It was found that the MBAS response varied as a function of chain length. No response was detected for a SPC less than 8 carbon units. At 8 carbon units, the response was 30 percent of that for an equimolar concentration of standard LAS. At 10 carbon units, the response increased to 70 percent. It can be presumed that a 12-carbon SPC would be on the order of the intact parent surfactant response.

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

[2] Colorado School of Mines, Golden, Colo.

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

This empirical evidence of a MBAS response near the infiltration beds despite the apparent lack of anionic surfactants may be explained, in part, by the presence of LAS degradation products. MBAS accurately predicts LAS in the sewage effluent and in the zone where ABS is present. However, in the zone with the greatest microbial activity near the infiltration beds, LAS may be undergoing biodegradation which gives rise to SPCs. If the SPCs have a hydrocarbon chain length greater than 6, MBAS response may remain high while the parent surfactant (LAS) may be degraded below limits of detection. New isolation and characterization techniques are being developed to determine LAS degradation products. Because LAS generally is accepted as biodegradable, definitive evidence for SPCs at the Cape Cod Ground Water Toxic Waste Research Site would open for question the ultimate fate of LAS in ground water.

(p. 617 follows)

COLLECTION AND ANALYSIS OF UNSATURATED-ZONE SOIL GAS FOR VOLATILE ORGANIC COMPOUNDS

By James A. Kammer[1] and James A. Smith[2]

ABSTRACT

A new method to sample and analyze quantitatively soil gas for the presence of volatile organic compounds is described. Soil gas is removed from the unsaturated zone through stainless-steel tubing and collected in 125 milliliter glass sampling bulbs. After sample collection, a vapor surrogate standard, bromochloromethane, is added by syringe through a septum on the side of the bulb. The sampling bulbs are transported to the laboratory where the entire contents of each bulb are purged onto an adsorbent trap and then thermally desorbed into a gas chromatograph for compound separation and quantitation. Benefits of the method include its low cost, its low analytical detection limit, its high precision, and the ability to monitor sample recovery by use of a field-spiked surrogate standard.

INTRODUCTION

The analysis of volatile organic compounds in soil gas plays an important role in ground-water quality studies where an understanding of contaminant fate and distribution are needed to define the extent and movement of ground-water solute plumes. Existing analytical methodologies include syringe sampling of soil gas followed by the direct injection of the sample into a gas chromatograph (GC) onsite and the collection of soil gas in Tedlar[3] bags, in stainless-steel canisters, or on adsorbent traps for later analysis. Spittler and others (1985), Kerfoot (1987), and Marrin and Thompson (1987) all describe methods requiring onsite gas chromatographs. The method described in this paper does not require onsite GC analysis, allows the addition of a field surrogate to monitor sample recovery, and is designed to be implemented using the same analytical equipment required by the U.S. Environmental Protection Agency protocols for the analysis of purgeable organic compounds in water.

Specifically, this paper details the method of collection and analysis of soil-gas samples from the unsaturated zone. Data on sample stability and precision for laboratory and field samples are presented. Picatinny Arsenal, in Morris County, N.J., was selected as the test site for implementation of the method. Details of the location of sample collection points, results of the soil-gas analyses, and site history can be found elsewhere (Fusillo and others, 1987; Smith and others, 1989, this Proceedings).

EXPERIMENTAL SECTION

A schematic diagram of the sampling configuration is shown in figure K-1. The soil-gas samples were collected from the unsaturated zone using probes constructed of 3-mm (millimeter) inner-diameter, stainless-steel tubing cut to the desired sampling depth. The bottom 6 cm (centimeters) of each probe was slotted and covered with a fine-mesh stainless-steel screen. Three probes were typically installed in the unsaturated zone at each sampling site by augering a 5-cm-diameter hole to the desired sampling depth. The deepest vapor probe was inserted into the hole, and general-purpose sand was added to surround the screened interval of the probe. Two additional probes were placed at different intervals above the deepest probe in each borehole. A 30-cm layer of bentonite was placed between the screened intervals of the probes to minimize vertical transport of soil gas during sampling. At land surface, the vapor probes were fitted with Swagelok connectors and caps to maintain a gas-tight seal.

Samples were collected by drawing soil gas from the probes through two 125-mL (milliliter) glass sampling bulbs with Teflon stopcocks at both ends. The sampling bulbs were connected in parallel to the vapor probe using Tygon tubing and a glass "Y" joint. The soil vapors were drawn through the bulbs using a peristaltic pump which displaced 225 mL of gas per bulb per minute.

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

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

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

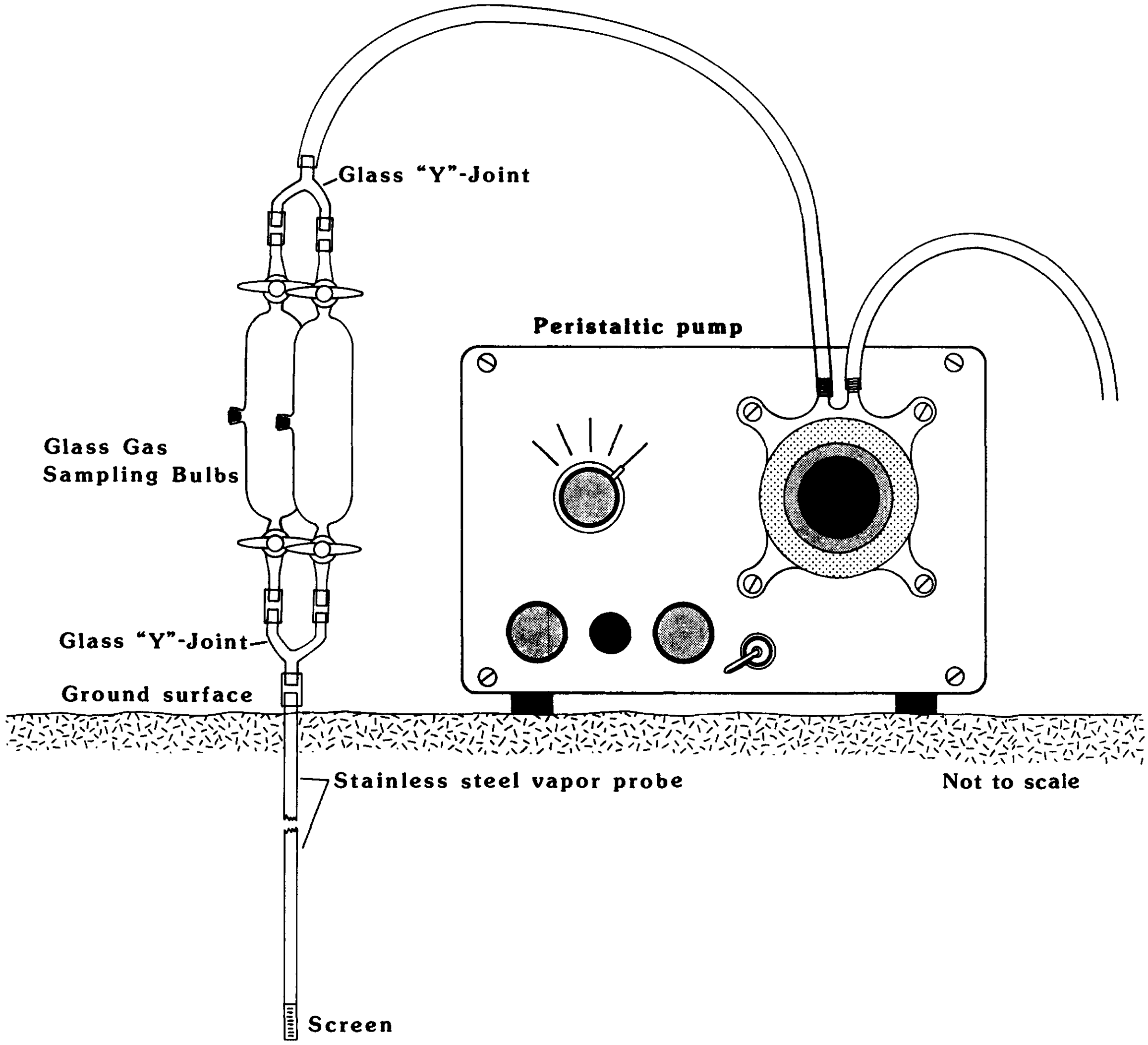

Figure K-1. – Soil-gas sampling configuration.

After a minimum of 1,000 mL of soil gas passed through each bulb, the stopcocks were closed and 4 µL (microliters) of a gaseous field surrogate, bromochloromethane, were added to the bulbs through a half-hole plug septum in the side. A trip blank and ambient air sample were also included as part of each sampling trip.

Immediately after collection, the stopcocks on each bulb were tightened. This procedure was repeated approximately 15 minutes later after the bulbs had equilibrated with the temperature in the field van (20–25 °C (Celsius)). Samples were then transported to the laboratory in the dark at room temperature and were analyzed within 9 hours of collection.

Prior to their initial use, the glass sampling bulbs were washed in water containing a nonionic detergent, rinsed consecutively with distilled water and reagent-grade methanol, and baked at 110 °C for a minimum of 4 hours. Thereafter, the bulbs were flushed with high-purity helium for 5 to 10 minutes at a flow rate of about 400 mL per minute. Periodically, the bulbs were rewashed, rinsed, and baked out as described above, but experience indicates that even bulbs containing high concentrations of compounds are cleaned effectively by simply purging the bulb with helium. Bulbs were periodically checked for organic contaminants by GC analysis.

The analytical equipment used for this method includes a Tracor 540 GC equipped with a photo-ionization detector (PID) and a Hall electrolytic conductivity detector (HECD), a 60-meter-long, 0.75-mm inner-diameter Volcol capillary chromatography column, a Tekmar Model 4000 purge-and-trap concentrator, and two Shimadzu CR3-A microprocessor integrators. The sampling bulb was attached to the purge-and-trap unit at the sample bulkhead by an externally heated nickel sample line and at the purge bulkhead by a Teflon line.

The contents of the sampling bulb were analyzed by attaching the heated sample line and the purge line to the entrance and exit ports of the sample bulb. These two lines were held in place by Teflon-butyl plug septa. After opening the stopcocks on the sample bulb, the purge and trap concentrator was placed into the "purge" setting. The sample was flushed across an adsorbent trap containing Tenax, charcoal, and silica gel. After the sample had been purged for 15 minutes at a rate of 40 mL/min (milliliters per minute), the contaminants on the trap were thermally desorbed onto the chromatographic column. The column was heated at a programmed rate to achieve adequate separation of the analytes. The eluted compounds were detected with the PID and HECD connected in series and interfaced with two integrators. Details of the operating conditions for the GC and purge and trap concentrator are given in table K-1.

Table K–1. – *Chromatographic conditions*

[–, not applicable; °C, degrees Celsius; °C/min, degrees Celsius per minute; min, minute; mL/min, milliliters per minute; HECD, Hall electrolytic conductivity detector; PID, photo-ionization detector; V, volt]

	Flow rates (mL/min)		
Gas	Column	Purge and trap	HECD
Helium		40	–
Carrier	5	–	–
Makeup	35	–	–
Hydrogen	–	–	30

Temperature program		**Purge and trap settings**	
Initial temperature	10 °C	Trap temperature	< 30 °C
Initial hold	7.5 min	Purge time	15.0 min
Ramp rate	4.5 °C/min to 95 °C	Desorb temperature	180 °C
Hold	0.2 min	Desorb time	4.0 min
Final ramp	15 °C/min to 160 °C	Bake temperature	205 °C
Final hold	2.1 min	Bake time	15 min
Total run time	33.1 min	**Detector settings**	
HECD	250 °C	HECD solvent flow	5 mL/min
PID	225 °C	HECD reactor temperature	850 °C
Inlet	110 °C	PID voltage	0.15 V

The precision of the analysis method is in part dependent on the consistency of the displacement of the soil gas in the sampling bulb by the purge gas (helium). To determine the percentage of the soil gas sample that was discharged from the sampling bulb, 10 sampling bulbs were analyzed twice consecutively. In all cases, the second analysis of a sample bulb yielded a detector response for each organic compound that was less than 1 percent of the initial analysis. This indicates that the purge rate and time are sufficient to displace greater than 99 percent of the soil gas from the sampling bulb.

When the concentration of an organic compound in a soil-gas sample collected from the field exceeded the upper limit of the standard curve (typically 650 ng/L (nanograms per liter)), the soil-gas sample was diluted. When dilutions were made, 5- and 25-mL glass gas-tight syringes were used to withdraw 1.25 and 12.5 mL of sample for 1/100 and 1/10 dilutions, respectively. After the appropriate amount of sample was withdrawn into the syringe (through the half-hole septa on the bulb), one of the stopcocks on the sampling bulb was opened before the syringe was removed to equalize the pressure within the bulb. The contents of the syringe were then added to a clean sampling bulb for subsequent analysis by the above methodology.

Gaseous standards were prepared weekly by the static-dilution bottle method. A clean, 2-liter static-dilution bottle containing approximately fifteen 3-cm glass beads and a glass stirring bar was purged with high-purity helium, capped with a Mininert valve, and heated in an oven to 65 °C. The cap on the dilution bottle was tightened twice during heating. The dilution bottle was then removed from the oven and placed on a magnetic stirrer while 2 μL of each of the neat liquids were injected into the bottle through the Mininert valve. Specifically, trans-1,2-dichloroethylene (trans-DCE), cis-1,2-dichloroethylene (cis-DCE), bromochloromethane (BCM), trichloroethylene (TCE), and tetrachloroethylene (PCE) were added to the dilution bottle for the purposes of this study. Aliquots of the gaseous standard were transferred from the static dilution bottle to the glass sampling bulbs by a gas-tight syringe. A 5-μg/L (micrograms per liter) per liter certified gaseous vinyl chloride standard was added directly to the glass sampling bulb using a gas-tight syringe. The contents of the sampling bulb were then discharged to the adsorbent trap for subsequent detection as described previously. When not in use, the static-dilution bottle was stored in the dark at 65 °C. Figure K-2 presents a sample chromatogram from both the PID and HECD of a gaseous standard.

RESULTS

Data describing method precision were generated at concentrations ranging from 100 to 113 ng/L for each compound of interest. The precision data are presented in table K-2. The observed standard deviation for the field surrogate, BCM, is presented in table K-2 for both laboratory precision data and field surrogate recovery data.

Table K–2.—*Method precision at approximately 100 nanograms per liter for seven replicate samples.*

Compound	Coefficient of variation (in percent)
Vinyl chloride	2.86
trans-1,2-dichloroethylene	3.43
cis-1,2-dichloroethylene	4.27
Bromochloromethane (laboratory)	9.98
Bromochloromethane (field recovery)	8.96
Trichloroethylene	3.49
Tetrachloroethylene	4.16

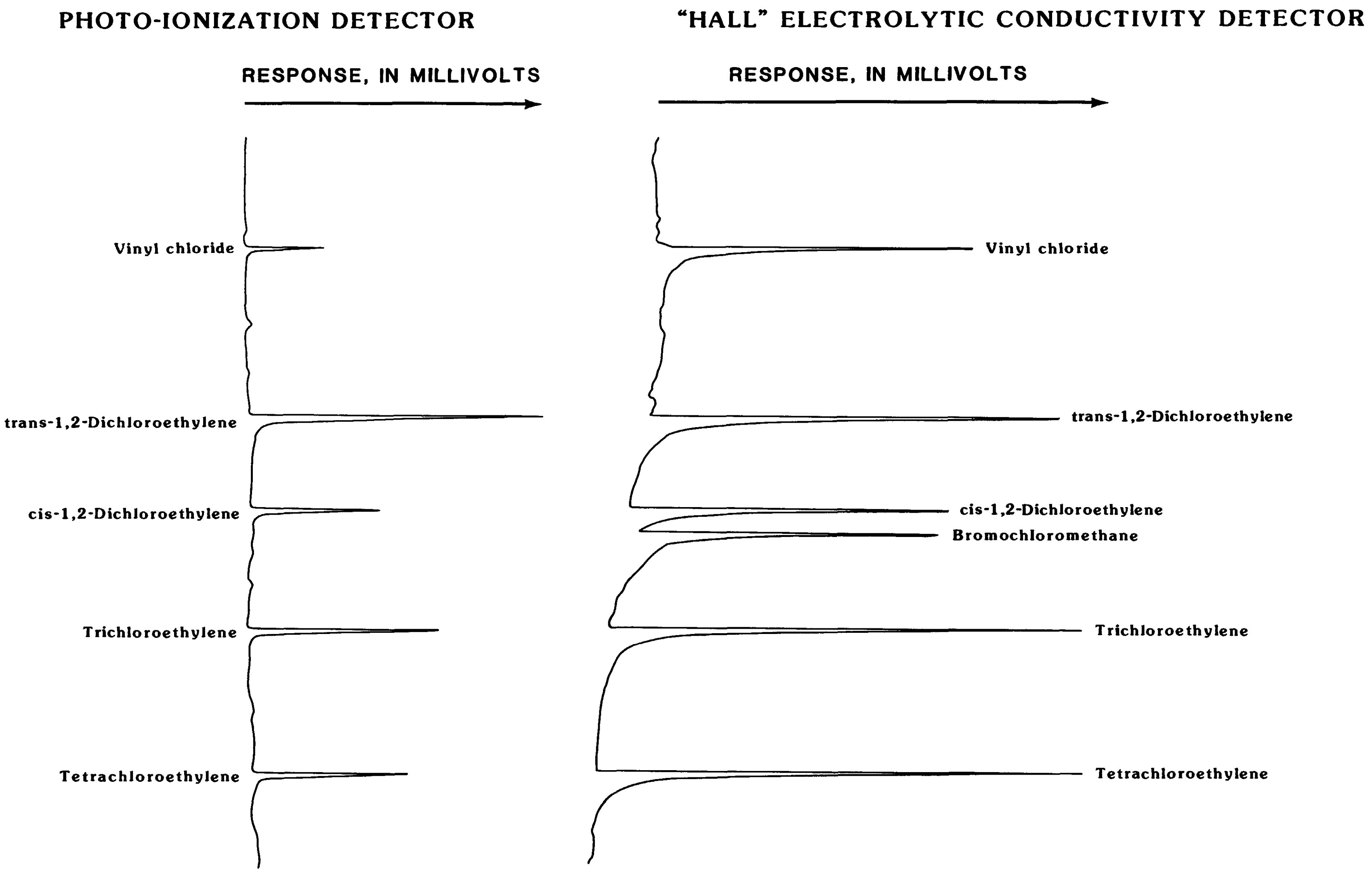

Figure K-2.—Sample chromatograms from the photo-ionization and Hall electrolytic conductivity detectors.

Recoveries of the field surrogate were quite consistent. Duplicate sample analyses yielded remarkable consistency when the response fell within the boundaries of the standard curve (approximately 40–650 ng/L). Dilutions were made for samples containing compound concentrations exceeding the upper boundary of the standard curve and duplicate dilution concentrations were consistently within 5 percent of each other.

To determine a maximum sample holding time, the following experiment was conducted. Nine glass sampling bulbs were spiked simultaneously with equal amounts of the gaseous standard containing vinyl chloride, trans-DCE, cis-DCE, BCM, TCE, and PCE. The contents of one bulb was analyzed immediately. The remaining bulbs were stored in the dark at room temperature. These bulbs were consecutively analyzed over a 20-hour period. Figure K-3 presents the results of this experiment for BCM and TCE, and indicates that the maximum sample holding time for a quantitative soil-gas analysis is approximately 9 hours from the time of collection. Samples stored for more than 9 hours showed a significant decrease in the concentration of BCM and TCE. Very similar results were observed for vinyl chloride, cis-DCE, trans-DCE, and PCE. Based on these results, all field samples were analyzed within 9 hours of collection.

DISCUSSION

The potential for interferences in the analytical method necessitates certain precautions, especially when attempting to quantify the concentration of volatile organic compounds below a level of 500 ng/L. Compounds present in the ambient air of either the laboratory or the field site can adversely affect the analysis. Flushing the bulbs with helium helps to minimize potential contamination from laboratory air prior to sampling. Tightening the stopcocks on the bulbs after flushing with helium and again after sampling helps to minimize contamination from laboratory/ambient air and loss of sample. Air blanks collected in the laboratory will verify any contamination of the sample by the laboratory air.

The soil-gas collection and analysis methodology described in this paper offers three distinct advantages over other methods currently in use. First, the method employs a field surrogate to monitor sample recovery after transport to the laboratory. Second, the large sample size (125 mL) discharged to the chromatographic column results in a low analytical detection limit. Third, because the method involves the transport of gas samples from the field to the laboratory, onsite portable analytical equipment is not a requisite, and the cost of the analysis is reduced.

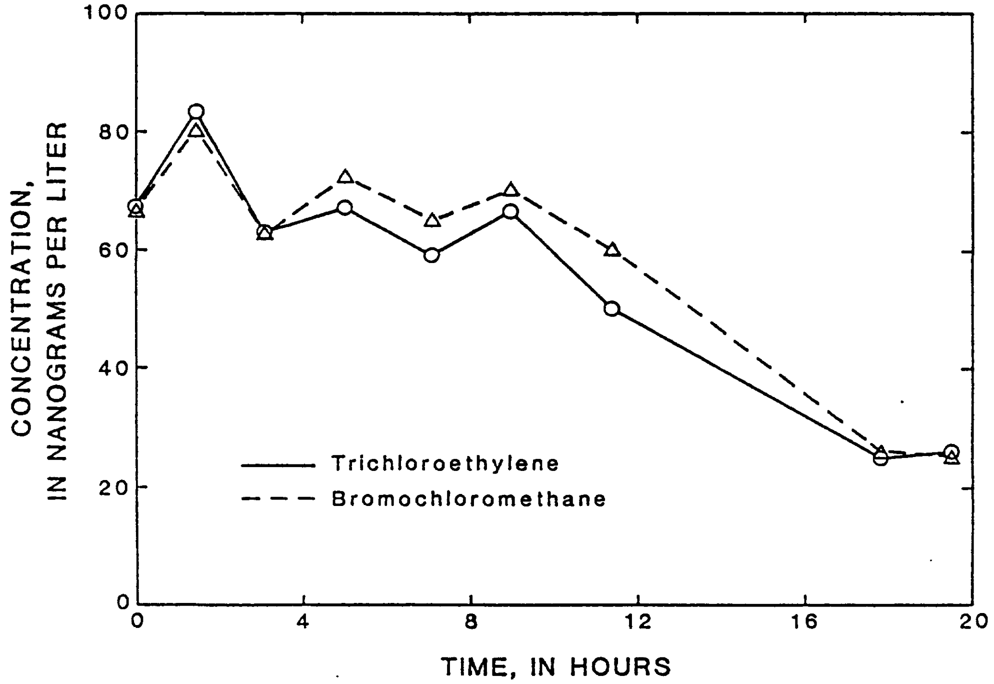

Figure K–3. – Vapor concentration of two compounds as a function of sampling bulb storage time.

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(p. 625 follows)

ACTIVITIES OF THE U.S. GEOLOGICAL SURVEY'S HYDROLOGIC INSTRUMENTATION FACILITY IN SUPPORT OF HAZARDOUS- AND TOXIC-SUBSTANCES PROGRAMS

By James H. Ficken[1] and Doreen Y. Tai[1]

ABSTRACT

The Hydrologic Instrumentation Facility has nationwide responsibility within the U.S. Geological Survey for hydrologic instrumentation research, development, testing, evaluation, procurement, warehousing, distribution, repair, and calibration. Support activities for the Survey's hazardous- and toxic-substances programs include warehouse operations, electronic and mechanical shops, test and evaluation services, instrument development and application, and information dissemination.

Facility support of field activities fall into several areas. Personal protective gear, including breathing apparatus; field gas chromatographs; portable gas analyzers; toxic-gas monitors; and sampling pumps are stocked in the warehouse and are available to Survey field personnel. Personnel at the Facility have recently built mechanical prototypes of dewatering equipment, such as centrifuges and filters. Testing and evaluation performed at the Facility ensure that instrumentation available is capable of meeting Survey data-collection requirements. Sampling pumps have been designed that can prevent contamination of water during pumping. A standpipe and well have been installed to evaluate ground-water samplers and other instrumentation. As part of instrument development and application, pressure transducers and water-quality instrumentation are being evaluated in conjunction with a recently developed downhole sampler and data logger. Facility publications communicate technical information to the field.

INTRODUCTION

The Hydrologic Instrumentation Facility (HIF) was established in 1979 and given nationwide responsibility for the research, development, testing, evaluation, procurement, warehousing, distribution, repair, and calibration of hydrologic instrumentation[2] of the U.S. Geological Survey. Emphasis at the HIF is placed on technical assistance to field activities. The HIF staff includes individuals with field experience in surface water, water quality, ground water, and hydrometeorology, as well as engineers with training in chemical, electronic, electrical, and mechanical engineering.

This paper describes HIF activities in support of the Survey's hazardous- and toxic-substances programs. The development of instrumentation and equipment concerned with the data-collection and sampling activities in these programs is included. Only general descriptions are given of the instrumentation, equipment, and testing programs.

SUPPORT ACTIVITIES

Various sections and units within the HIF are involved in activities in support of hazardous- and toxic-substances programs.

The warehouse stocks approximately 950 items of hydrologic equipment and instrumentation for sale or rent. Included are protective gear and clothing (fig. K-4) for protection of personnel working in hazardous areas. Items stocked include wearing apparel and breathing apparatus that provide differing degrees of protection. Eyewash/shower decontamination equipment is available. Most items are listed in the WRD (Water Resources Divison) Instrumentation Catalog[3] and are purchased or rented through use of any Survey computer terminal throughout the country. Some of the instrumentation and equipment, available for use in the field, that can be rented from the HIF are described in the following paragraphs.

Field Gas Chromatograph.—HIF has three organic vapor analyzers. These are portable gas chromatographs (GC) with flame-ionization

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[1] U.S. Geological Survey, Stennis Space Center, Miss.

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

[3] U.S. Geological Survey personnel may order equipment through the HIF Computerized Support System (HIF–CSS). Employees of other Federal agencies may contact the Chief, Field Service and Supply Section, HIF, for ordering information. The HIF may not rent or sell equipment to non-Federal agencies.

Figure K–4. – Protective apparel for field personnel in hazardous areas.

detectors (FID) and are powered by rechargeable batteries. The basic instrument consists of two major assemblies: the probe/read-out assembly and side-pack assembly. A recorder can be attached for GC operations. The output-meter and alarm-level adjustments are incorporated in the probe/read-out assembly. A telescoping probe, having a 22- to 30-inch range, can be attached to the read-out probe for hard-to-reach areas. The side-pack assembly contains the operating controls, indicators, electronic circuitry, detector chamber, hydrogen supply, and battery power supply. This instrument can be used to measure most trace-organic vapors in the air or in the headspace of water samples.

Portable Photo-ionization Analyzer.—This trace-gas analyzer can be used to measure the concentration of a variety of trace gases in industrial areas. The analyzer is based on the principle of photo-ionization. The sensor consists of a sealed ultraviolet (UV) light source that emits photons with an energy high enough to ionize many trace organics. Ions formed by the absorption of photons are driven to the collector electrode. The current produced is then measured and the corresponding concentration displayed on a meter directly, in milligrams per liter. The analyzer consists of a probe, read-out assembly, and a battery charger. The analyzer is very easy to use and will operate from the battery for more than 10 hours.

Portable Gas Monitor.—This portable gas monitor can be used to monitor toxic levels of carbon monoxide or hydrogen sulfide and levels of combustible gases and oxygen deficiencies within a confined space. This meter is designed for personal use. It should be used by workers when entering or working in a confined space or hazardous area. This meter basically uses two different sensing elements: a gas-sensitive, metallic-oxide semiconductor element for toxic- and combustible-gas detection and an electrochemical fuel cell for detecting oxygen deficiency.

Sampling pumps are available for rent. Figure K-5 shows a helical-rotor pump, which operates on 12-volt direct current. This pump can lift

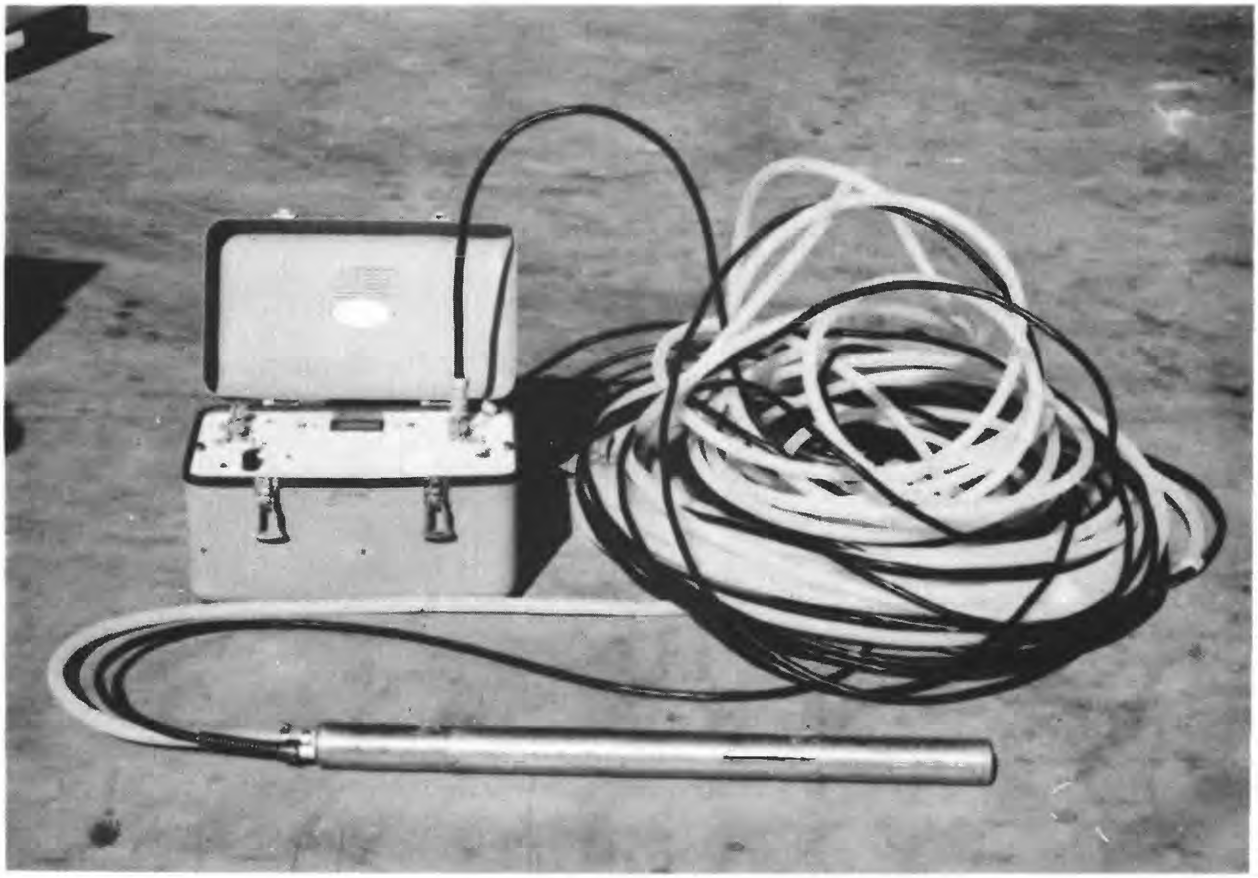

Figure K–5.—The helical-rotor pump for downhole sampling.

water higher than 100 feet through fluorocarbon plastic tubing, which prevents contamination of the water during pumping.

The HIF's electronic shop can repair and calibrate most electronic equipment and instrumentation, and the mechanical shop can fabricate prototype equipment and specialized items. One recent project was the procurement and assembly of centrifugal units for evaluation of their usefulness in dewatering suspended sediment under the surface-water toxics program. Figure K-6 shows a back-flushing filter recently assembled for evaluation as a dewatering unit. Testing and evaluation is conducted at the HIF to ensure that data-collection requirements are met and scientific credibility continues.

A stainless-steel standpipe (fig. K-7) was constructed in March 1988, to test ground-water samplers. The standpipe is 5 inches in diameter and 100 feet in height. Two stainless-steel mixing tanks with a total capacity of 260 gallons are connected to the standpipe. The tanks are equipped with mixers and a stainless-steel floating top, which prevents the volatilization of organic compounds from water. Three temperature probes are installed in the pipe to record water temperatures automatically. The standpipe has 14 sampling ports from which samples can be withdrawn at the same time and at the same position as samples collected by the sampler. This sampling technique offers a highly accurate evaluation of the ability of the samplers to collect a representative sample.

Two wells (fig. K-8), 100-foot deep, were constructed in February 1988. Polyvinyl chloride (PVC) casing was used for both wells. One well has a 6-inch nominal diameter and a sealed bottom, and water has to be pumped in or out. Another well, fed by ground water, has a 2-inch nominal diameter and a screened interval at the bottom. These wells are used to test water-level instruments and water-quality monitors. The wells are adjacent to one another and are located just outside of the HIF's Water-Quality Instrument Laboratory. All data loggers and monitors can be placed in the laboratory.

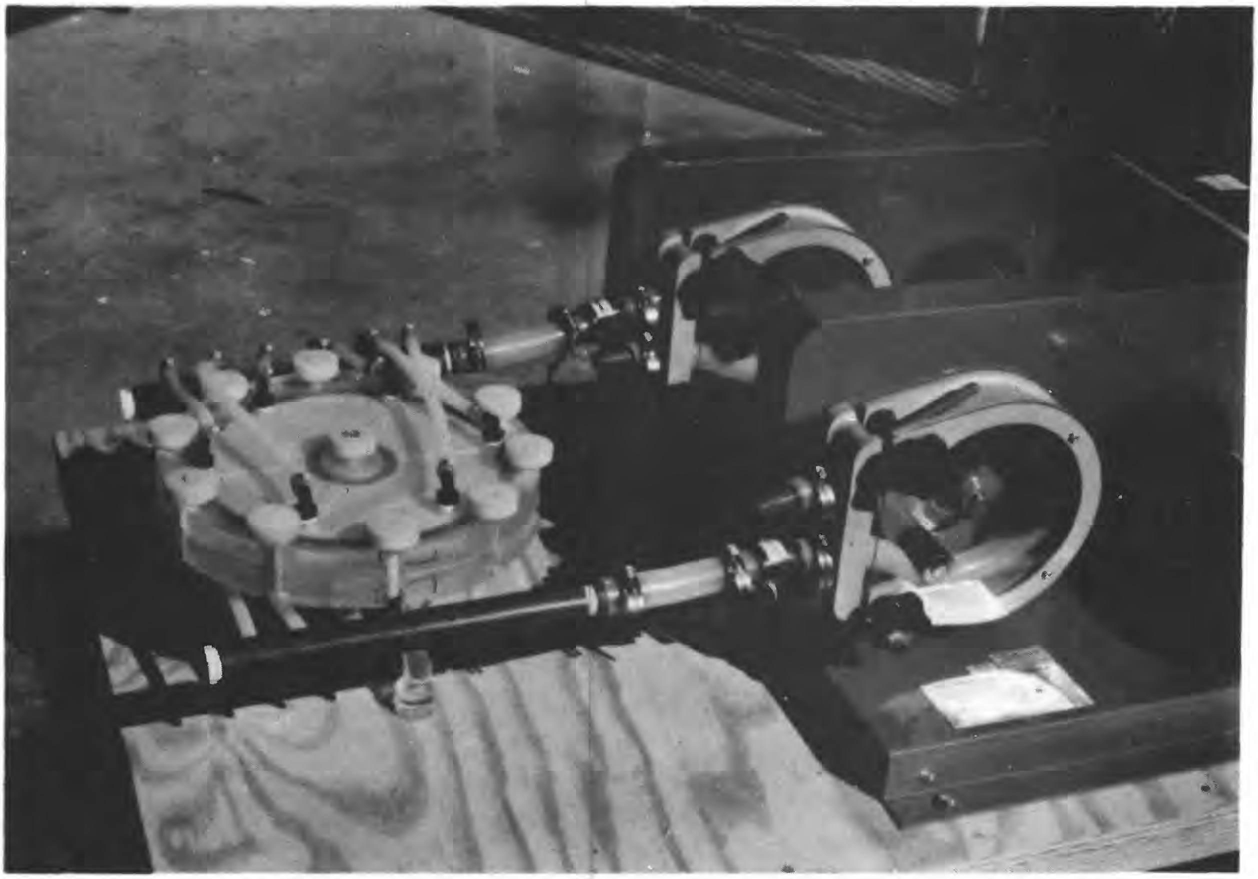

Figure K-6. — Back-flushing filter for dewatering sediment.

Figure K–7.—Stainless-steel standpipe for testing water samplers.

Figure K–8.—Hydrologic Instrumentation Facility wells for testing water-level and water-quality instrumentation.

Some commercially available instruments have application to surface and ground water. Water-quality instrumentation for downhole measurement of various water-quality characteristics is being evaluated. Extensive testing is being done to develop systems that use pressure transducers to satisfy Survey requirements for the accurate measurement of water stage and well levels.

Figure K-9 shows some of the recent developments in sampling equipment and data loggers for downhole applications. A piston sampler for collecting sealed samples down to 150 feet and a HIF-developed downhole recorder are shown. The recorder can measure and record or store maximum, minimum, and average daily well levels for 1 year. Other areas in which the HIF can provide experienced technical assistance are the preparation of specifications and advertisement and procurement of specialized instrumentation and equipment.

The HIF publishes the WRD Instrument News—a quarterly publication with a 2,500-copy circulation throughout the Survey. This publication communicates important technical information and acts as a forum for the discussion of instrumentation problems and other items of interest. In addition, the HIF contributes to the Instrument Continuum on the Survey's Computer Network and has a hydrologic-instrumentation data base accessible on its computer system.

SUMMARY

The HIF supports the equipment needs of the Survey's hazardous- and toxic-substances programs. The HIF is involved in warehouse stocking of protective wearing apparel, breathing apparatus, and hazardous- and toxic-substances detection equipment; electronic and mechanical shops for equipment repair and calibration; test and evaluation services; instrument development and application; and information dissemination.

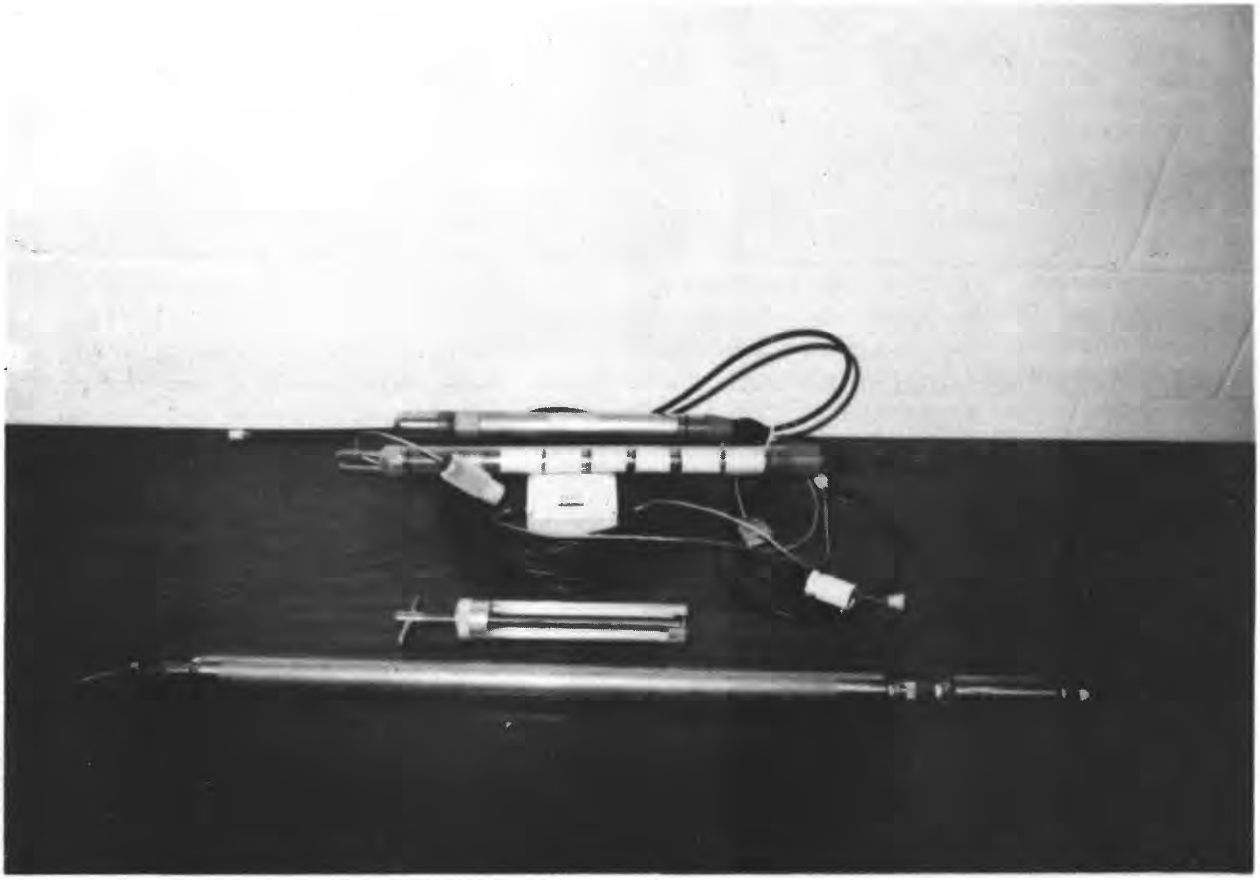

Figure K-9. – Downhole piston sampler and R200 downhole water-level recorder.

The equipment provided by the HIF serves numerous functions. Detection equipment can protect Survey field personnel. Samplers and pumps help improve the accuracy of data collection. Portable gas chromatographs with flame-ionization detectors can be used to measure most trace-organic vapors in the air or in the headspace of water samples. The portable photo-ionization analyzer, a trace-gas analyzer, can be used to measure the concentration of a variety of trace gases in industrial areas. The portable gas monitor can be used to monitor toxic levels of carbon monoxide or hydrogen sulfide, combustible gases, and oxygen deficiencies within a confined space. The sampling pumps can lift water higher than 100 feet through fluorocarbon plastic tubing to prevent contamination of the water during pumping.

Instrument evaluation activities include water-quality instrumentation for downhole measurement of various water-quality characteristics and pressure transducers that accurately measure water stage and well levels. An available downhole recorder can measure and record or store maximum, minimum, and average daily well levels for 1 year.

The WRD Instrument News, published quarterly and sent to 2,500 Survey personnel, updates field personnel on latest instrumentation news and acts as a forum for instrumentation problems and solutions. The WRD Instrumentation Catalog describes equipment available from the HIF warehouse.

USE OF A STANDPIPE TO EVALUATE GROUND-WATER SAMPLERS

By Doreen Y. Tai[1]

ABSTRACT

A stainless-steel standpipe, 5 inches in diameter and 100 feet in height, was constructed to test ground-water samplers. Water containing organic compounds is prepared in two stainless-steel mixing tanks, having a total capacity of 260 gallons, and is fed to the bottom of the standpipe by gravity. The standpipe has 14 sampling ports from which samples can be withdrawn at the same time and elevation as samples collected by a sampler lowered in the standpipe. This technique offers a reliable evaluation of the samplers for collecting ground-water samples.

Test solutions were made by dissolving five volatile chlorohydrocarbons in water at two ranges of concentrations: 10 to 30 micrograms per liter and 100 to 200 micrograms per liter. A gas chromatograph interfaced with a purge and trap system was used for analyses. Twenty repetitive analyses of the test solutions collected from the sampling ports showed relative standard deviations ranging from 0.4 to 1.2 percent. The three downhole samplers showed the recoveries in the range of 92.2 to 103.5 percent, and the three pumping samplers showed the recoveries in the range of 97.6 to 101.5 percent.

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[1] U.S. Geological Survey, Stennis Space Center, Miss.

PRELIMINARY RESULTS OF THE DEPARTMENT OF THE INTERIOR'S IRRIGATION DRAINAGE STUDIES

By Marc A. Sylvester[1], Jonathan P. Deason[2], Herman R. Feltz[3], and Richard A. Engberg[4]

ABSTRACT

Responding to increasing concern about the quality of irrigation drainage and its potential effects on human health, fish, and wildlife, the Department of the Interior, in 1986, began irrigation drainage studies in nine areas in seven Western States. These studies were done to determine whether irrigation drainage has caused or has the potential to cause harmful effects on human health, fish, and wildlife, or might reduce the suitability of water for beneficial uses. Results of the seven studies completed in 1987 are presented and are compared to baselines, standards, criteria, and other guidelines helpful for assessing the potential of observed constituent concentrations in water, bottom sediment, and biota to result in physiological harm to fish, wildlife, or humans. Selenium is the constituent most commonly found at elevated concentrations in water, bottom sediment, and biota in the study areas. Yearly variation in precipitation and streamflow, geologic sources of trace elements, arid to semiarid climate, internal drainage basins, irrigation drainage, and pesticide usage were the factors that affected concentrations of constituents in water, bottom sediment, and biota in the study areas.

[1] U.S. Geological Survey, Menlo Park, Calif.
[2] Department of the Interior, Irrigation Drainage Program, Washington, D.C.
[3] U.S. Geological Survey, Reston, Va.
[4] U.S. Geological Survey, Iowa City, Iowa

SEASONAL VARIATION AND VERTICAL DISTRIBUTION AND MOVEMENT OF HERBICIDES AND NITRATE IN UNSATURATED AND SATURATED ALLUVIUM UNDERLYING A CROPPED FIELD, IOWA COUNTY, IOWA

By Mark G. Detroy[1]

ABSTRACT

The occurrence and movement of atrazine, alachlor, cyanazine, and nitrate is being evaluated for the unsaturated and saturated alluvial sediments underlying a corn field located near the Iowa River in Iowa County, Iowa. At one well nest, four lysimeters and seven wells are used to describe the seasonal variation and vertical distribution of water quality at depths from 3 to 40 meters before and after the application of herbicides and nitrogen fertilizers. Samples were collected during the growing seasons (April to August) of 1986 and 1987. Atrazine and alachlor were applied on the corn field in 1986, whereas alachlor and cyanazine were applied in 1987. The behavior of these constituents are evaluated with respect to rainfall timing, moisture content of the unsaturated zone, water-table position, and concentration of organic carbon in ground water.

The summer of 1986 was one the wettest on record in Iowa, and provided ample rainfall to promote the leaching of herbicides and nitrate. Concentrations of atrazine and nitrate differed markedly throughout the spring and summer of 1986. Atrazine concentrations of 0.10 to 0.23 microgram per liter (equal to or slightly greater than the detection limit) were detected only briefly immediately after application and rainfall. Alachlor also was observed at similar concentrations, however detections were few and sporadic. Atrazine was not detected again until August when concentrations in shallow ground water were above 1.0 microgram per liter. Concentrations of nitrate in shallow ground water, however, differed moderately with those for atrazine. Seasonal depth profiles for 1986 indicate that atrazine is leached more slowly than nitrate, and its presence late in the summer suggests that (1) residual atrazine remains in the soil, (2) atrazine is less soluble than alachlor, and (3) atrazine is partially leached by each pulse of infiltrating water. Nitrate concentrations increased rapidly (maximum of about 20 milligrams per liter as nitrogen) in shallow ground water (depth of 3 to 7 feet) immediately after application and with the first post application rains. These increases were of short duration as nitrate concentrations in the shallow ground water just below the water-table surface decreased to about the detection limit (0.1 milligram per liter as nitrogen) in late July. Spring inputs of nitrate move or are transformed rapidly in shallow ground water at this site.

The spring and summer of 1987 was extremely dry and provided a contrast to the wet summer of 1986. Preliminary data for 1987 indicate dissimilar seasonal variations and vertical distributions of herbicides and nitrate. The concentrations of alachlor and cyanazine measured in 1987 were larger than concentrations of atrazine measured in 1986 and are observed at greater depths; however, observation of detectable concentrations of alachlor were again sporadic as seen in 1986. Cyanazine was detected in the unsaturated zone from just after application in May through September at concentrations as much as 14 micrograms per liter. Concentrations of cyanazine in shallow ground water were as much as 3.0 micrograms per liter at a depth of 12 feet. Concentrations of atrazine also were consistently observed in 1987 at concentrations from 0.10 to 1.0 microgram per liter. The sources of atrazine presumably are either the residuals from past application or leachate from adjacent fields on which atrazine was applied in 1987. Nitrate concentrations in the unsaturated zone were as much as 9.5 milligrams per liter as nitrogen after application in May and remained at about 2.0 milligrams per liter as nitrogen into mid-August.

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[1] U.S. Geological Survey, Iowa City, Iowa.

HERBICIDE TRANSPORT IN THE CEDAR RIVER, IOWA–IMPORTANCE OF HYDROLOGY AND GEOCHEMISTRY IN NONPOINT-SOURCE CONTAMINATION

By Paul J. Squillace[1] and E.M. Thurman[2]

ABSTRACT

Concentrations of alachlor, atrazine, cyanazine, metolachlor, metribuzin, and dissolved and suspended organic carbon were monitored at six surface-water sites from May 1984 through November 1985 in large subbasins (777–15,540 square kilometers) within the Cedar River drainage basin of Iowa and Minnesota. A computer model separated the Cedar River hydrograph into approximate contributions from ground water and overland flow. The contribution of herbicides from shallow ground water, including field tile drains and possibly bank storage in the alluvium was normally less than 1 microgram per liter during the application season. During the remaining part of the year only atrazine was consistently greater than the detection limit (0.1 microgram per liter) at concentrations of about 0.2 microgram per liter. Based on the estimated quantity of ground water contributed to streamflow and the concentrations of atrazine detected during base flow, a conservative estimate of atrazine in the Cedar River transported by ground water is calculated to be 6 percent of the mass of annual transport. In contrast, overland-flow contributions were 94 percent of the mass with atrazine concentrations exceeding 16 micrograms per liter during high flow in the spring. During 1984, 70 percent of the annual transport occurred in June. Virtually all of the herbicides (99 percent) were in the dissolved phase on the basis of chemical analysis and theoretical considerations of sorption onto suspended sediments. Maximum concentrations of dissolved herbicides were 21 micrograms per liter for alachlor, 16 micrograms per liter for atrazine, 8.7 micrograms per liter for cyanazine, 11 micrograms per liter for metolachlor, and 3 micrograms per liter for metribuzin. Mass-balance calculations for atrazine indicate that 1.5 to 4.0 percent of the herbicides applied during 1 year ultimately were exported from the basin. A significant correlation ($r = 0.86$) was determined between the log of the herbicide concentration and the log of discharge divided by area of drainage for May, June, and July in 1984 and in 1985. Thus, transport of herbicides is critically associated with time of application and the seasonal runoff of dissolved herbicides associated primarily with overland flow.

Additional research has begun in the Cedar River basin that involves 3 months of weekly sampling for nitrate-nitrogen and herbicides at seven surface-water sites and two tile drain sites. Four well nests of three wells each were installed in alluvium in an unfarmed area to determine whether herbicides in the river move into the alluvial aquifers during high river stage and then are released during base flow. The well nests are located from 10 to 80 meters from the river and the three wells at each nest range in depth from 3 to 10 meters. During base flow, the geographic contribution of herbicides and nitrate to the river will be delineated by water-quality sampling and the determination of discharge at 50 sites throughout the basin.

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[1] U.S. Geological Survey, Iowa City, Iowa

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

EFFECTS OF HUMAN ACTIVITIES AND HYDROGEOLOGY ON WATER QUALITY IN THE UNCONFINED COASTAL-PLAIN AQUIFERS OF NEW YORK AND NEW JERSEY—A PLAN OF STUDY

By Steven F. Siwiec[1], William A. Battaglin[2], Eric F. Vowinkel[2], and Edward T. Oaksford[1]

ABSTRACT

Water quality in unconfined aquifers is significantly affected by the complex interactions of human activities and local hydrogeologic conditions. Suburban development, industrial and commercial growth, and agricultural practices can result in the introduction of contaminants at or near the land surface from point or nonpoint sources. Once a contaminant has entered the system, its transport and fate are determined by physical, chemical, and biological processes. Human activities, such as ground-water withdrawal by pumping, can alter the ground-water flow regime and partially control the rate and direction of contaminant transport. These activities, and the hydrogeologic properties of the unsaturated zone and underlying unconfined aquifer, need to be quantified before their effect on ground-water quality can be predicted.

This study will apply a statistical approach in conjunction with a geographic information system (GIS) to develop models that describe relations between ground-water quality and factors that influence it in the unconfined aquifers of the New York and New Jersey coastal plain. Statistical models developed and tested in previous phases of study show significant correlations between the detection of volatile organic compounds in ground water and specific human-related factors, such as population density and land use. Although these models are statistically valid over areas of tens to hundreds of square miles, their validity over larger areas and transfer potential to new areas have yet to be evaluated.

Ground-water-quality data are spatially discontinuous and commonly categorical, whereas human activities and hydrogeologic properties may be expressed as spatially continuous variables and used as polygon features in a GIS. Statistical procedures specifically designed for these types of data, such as logistic regression, analysis of variance, contingency table analysis, and selected nonparametric tests can be applied in this study to evaluate relations between and among these data. The relative importance of each factor and the possible scale dependencies inherent to this type of approach can then also be evaluated.

The study will entail estimating recharge areas that contribute to wells selected for statistical analysis and water-quality modeling through analytical or numerical methods. Definition of recharge areas to wells requires consideration of ground-water flow, hydrogeologic conditions, and well characteristics. This approach will allow for representative characterization of variables to describe human activities and hydrogeologic properties at each well.

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[1] U.S. Geological Survey, Syosset, N.Y.

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

AN INTERIM ASSESSMENT OF REGIONAL AND LOCAL FACTORS AFFECTING THE OCCURRENCE, MOVEMENT, AND FATE OF 1,2-DIBROMOETHANE IN THE SUBSURFACE, CENTRAL FLORIDA

By Brian G. Katz[1] and Anne F. Choquette[1]

ABSTRACT

The soil fumigant (nematicide) 1,2-dibromoethane (EDB) continues to be detected in ground water in Florida at least 4 years after its last known application. Contamination of ground water by EDB is not surprising because of two factors: (1) its chemical properties (moderate aqueous solubility, low sorption affinity for soils, and relatively low vapor pressure); and (2) its application in farming areas to sandy soils that are highly permeable and contain little organic material. The persistence of EDB in ground water is, however, unexpected because of reported half-life values of 1.5 to 2 years for hydrolysis reactions and 2 to 3 months for the microbiological degradation of EDB.

Data on EDB concentration in water from 350 wells distributed over a 100-square-mile study area in central Florida are being related statistically to key hydrogeologic, soil, climatological, and land-use factors. For smaller scale study areas (1-2 square miles), the chemical, biological, and physical processes are being evaluated that are controlling the movement and fate of EDB and other fumigants in ground water and in the unsaturated zone. Laboratory experiments are being performed to investigate the mechanism(s) responsible for the binding and release of EDB from soil and unsaturated zone material. In addition, a mass-balance model that accounts for the partitioning of EDB in the subsurface is being developed. Comparison of the results from the multiscale investigations are expected to provide information on data requirements and sampling strategies for regional-scale assessments of EDB and other agricultural contaminants in ground water.

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

THE EFFECTS OF INFILTRATION AND TRANSPORT MECHANISMS ON NITRATE AND CHLORIDE CONCENTRATIONS BENEATH A SMALL WATERSHED NEAR PLAINS, GEORGIA

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

ABSTRACT

Ground-water contamination from agrichemicals is a growing concern in the United States. A study was initiated by the U.S. Geological Survey and the U.S. Department of Agriculture, Agricultural Research Service, to improve an understanding of ground-water recharge mechanisms that may affect agrichemical transport in the unsaturated and saturated zones. The study site is a 267-hectare watershed near Plains, Sumter County, in the western Georgia Coastal Plain.

Water samples collected in the watershed during an 18-month period from 58 wells that penetrate the surficial Claiborne aquifer indicate that concentrations of nitrate and chloride decreased from 4 to less than 1 milligram per liter and from 5 to 1 milligram per liter, respectively, in the general direction of ground-water flow. Concentration gradients seem to be related to recharge characteristics and land-use practices in the watershed. Concentrations of nitrate and chloride in ground water are higher in the farmed upland areas than in the forested lowland areas.

Lithologic profiles determined from drill cores, geophysical borehole logs, and ground-penetrating radar indicate that, recharge to the Claiborne aquifer in the watershed passes through 3 to 15 meters of overburden that consists of sandy loam, sandy-clay loam, and clay. However, because of differences in lithology, recharge rates are spatially variable. In the interstream areas of the watershed, vertical recharge is inhibited by clay-rich residuum at a depth of about 2 to 5 meters that redirects part of the flow laterally downslope. The clayey residuum progressively thins in the midslope areas, and is absent in the lower part of the midslope areas and in the toe-slope areas where the overburden consists of permeable sandy loam. Here, the potential is high for water that moves laterally downslope, or infiltrates from the surface to percolate rapidly into the upper part of the Claiborne aquifer.

Samples of runoff from a field in an interstream area had substantially lower concentrations of nitrate and chloride than ground-water samples collected upgradient from the field. Analysis of geohydrologic data suggests that recharge may be rapid in the lower part of the midslope and in the toe-slope areas of the drainage. Thus, dilution of the ground water by recharge water containing low concentrations of nitrate and chloride may be a probable explanation for the decrease in the concentrations that are observed downgradient in the Claiborne aquifer. It is hypothesized that more intense agricultural activity than is currently occurring in the midslope and toe-slope parts of the watershed would result in recharge waters higher in concentrations of dissolved agrichemicals and would increase chemical loading to the aquifer.

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

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

APPLICATION OF A MODEL TO EVALUATE AGRICHEMICAL LOADING TO GROUND WATER AT THE PLAINS, GEORGIA, RESEARCH SITE

By R.A. Leonard[1] and W.G. Knisel[1]

ABSTRACT

The GLEAMS model (Ground water Loading Effects of Agricultural Management Systems) is an extension of an earlier model developed by the U.S. Department of Agriculture, Agricultural Research Service. The original model was used to evaluate chemicals, runoff, and erosion from agricultural management systems (CREAMS). GLEAMS consists of three major components: hydrology, erosion/sediment yield, and pesticides. Front-end and back-end software facilitate model use on personal computers.

In addition to simulating surface runoff of pesticides, GLEAMS couples pesticide and water movement using a storage-routing technique to simulate pesticide transport within and through the plant-root-soil zone. The model also simulates pesticide uptake by plant roots and pesticide redistribution resulting from evaporation at the soil surface. GLEAMS can be used to track pesticide intermediates or metabolites produced during sequential first-order degradation reactions. Simulation of up to 10 pesticides, or metabolites, can be conducted simultaneously for periods of up to 50 years. If desired, the model will compute and apply irrigation quantities necessary to manage soil water within prescribed limits.

Extensive testing of GLEAMS has been conducted, particularly under conditions in the southeastern Coastal Plain of the United States. Pesticide-loading potential was simulated with GLEAMS using soils common to the Plains, Georgia, area. On the basis of results of 50-year simulations, exceedance percentages (probabilities for leaching) were developed for a range of soils and pesticides. In addition, relations were developed for 50-year, mean-leaching losses as a function of pesticide half-life to Koc ratios. Unsaturated-zone models are being developed by ARS cooperators and linked with GLEAMS. The Plains, Georgia, research site will provide additional test data for model development and calibration.

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

NITRATE TRANSFORMATIONS IN THE RECHARGE AREA OF THE CLAIBORNE AQUIFER NEAR PLAINS, GEORGIA

By D.C. Obenhuber[1] and R.R. Lowrance[1]

ABSTRACT

Twelve replicate, 20-liter, flow-through microcosms were constructed using aquifer material and ground water collected from the Claiborne aquifer near Plains, Georgia. Adenosine triphosphate, acridine orange direct counts, and standard plate counts were used to monitor microbial numbers and biomass in conjunction with the analysis for nitrate and chloride in the effluent from the microcosms. Microbial denitrification was determined by most probable number, acetylene-block, and denitrification-enzymeactivity. Nitrate and glucose additions were performed on subsets of the microcosms to determine the effects on the stability of the microbial community and the amount of assimilation or degradation of nitrate occurring in the microcosms. Nitrous oxide levels in the microcosms and in ground water also were determined. Microbial biomass and most probable numbers remained relatively constant throughout the experiment. Nitrate concentrations in microcosms receiving ground water with 10 milligrams per liter nitrate as nitrogen (NO3 – N) were reduced about 1 percent per day to approximately 5 milligrams per liter NO3 – N in the effluent by the addition of 10 milligrams per liter glucose carbon. Nitrate disappearance correlated with increases in most probable number denitrifiers, nitrous oxide concentration, dissolved oxygen, and pH, thus suggesting biological denitrification. This experiment indicates that the remediation of nitrate-contaminated aquifers by organic infusion is a function of microbial-denitrification potential.

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

MICROBIAL MINERALIZATION OF ATRAZINE IN SURFACE SOIL AND AQUIFER MATERIAL DURING ALTERNATING AEROBIC AND ANAEROBIC INCUBATION

By D.C. Obenhuber[1]

ABSTRACT

The oxygen content of surface soil and aquifer material often varies seasonally between aerobic and anaerobic conditions depending on rainfall, chemical application, depth, and so on. Research was designed to determine the rate of microbial mineralization of atrazine during periodic variations in oxygen content. It was hypothesized that aerobic mineralization rates would be enhanced by periodic incubation under anaerobic conditions as a result of varying oxygen requirements of the atrazine-microbe system.

The mineralization rate of atrazine was determined by radioactive carbon dioxide-14 evolution. Samples of soil and aquifer material were incubated under aerobic, anaerobic, and alternating aerobic-anaerobic (1:1) conditions. Preliminary results suggest an atrazine half-life of 556, 2,632, and 669 days for aerobic, anaerobic, and alternating aerobic-anaerobic conditions, respectively. The rate of mineralization during alternating aerobic-anaerobic incubation is significantly greater than the sum of the two processes combined, thus suggesting synergistic microbial degradation.

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

ROLE OF ION EXCHANGE IN THE TRANSPORT OF AMMONIUM THROUGH A CONTAMINATED SAND AND GRAVEL AQUIFER

By Marnie L. Ceazan[1], Richard L. Smith[1], and E. Michael Thurman[2]

ABSTRACT

Ion exchange of ammonium in a shallow sand and gravel aquifer was evaluated using field data, forced-gradient tracer experiments, and batch-sorption experiments with aquifer solids. Ground water was sampled along a longitudinal transect through a 4-kilometer long contaminant plume that resulted from on-land disposal of secondary sewage effluent. The relative distributions of ammonium and nitrate in the ground water suggested that the migration velocity of ammonium was 50 percent of that of nitrate in the transporting ground water. Batch experiments with aquifer solids showed that ammonium was distributed between the aqueous and solid phases. Forced-gradient tracer tests conducted in an uncontaminated part of the aquifer demonstrated that ammonium and potassium transport was retarded by cation exchange. Injected ammonium and potassium replaced calcium and magnesium on aquifer solids. Conversely, nitrate separated from ammonium and potassium and was transported at the mean rate of ground-water flow in the tracer tests. A retardation factor of 2.5 was calculated from an experimental distribution coefficient to determine the influence of sorption on transport of ammonium. This was similar to the estimated retardation factor of 2.0 that was determined on the basis of the ammonium distribution in the contaminant plume. These results demonstrated that transport of ammonium through a sand and gravel aquifer with low exchange capacity is substantially affected by cation-exchange processes.

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[1] U.S. Geological Survey, Denver, Colo.
[2] U.S. Geological Survey, Lawrence, Kans.

THE MINIPIEZOMETER AS A RECONNAISSANCE TOOL IN GROUND-WATER CONTAMINATION INVESTIGATIONS

By B. Pierre Sargent[1], Richard L. Walker[1], and William H. Ellis, Jr.[1]

ABSTRACT

Ground-water contamination investigations generally begin at the contaminant source and continue downgradient to delineate the extent of the contaminant plume. If the exact location of the contaminant source is unknown or if an area contains multiple sources, much time and money may be spent on installing and sampling wells that may or may not yield useful results. An alternative approach is to begin an investigation in a ground-water discharge area, or sink, and search back toward the source. The minipiezometer, a temporary hand-driven well, has been found to be a useful tool for investigating the ground-water/surface-water relations at the point where ground water enters a stream. The purpose of this paper is to report the successful use of minipiezometers as a reconnaissance tool to aid in the definition of a contaminant plume at Picatinny Arsenal, in Morris County, New Jersey.

The minipiezometer is a portable, hand-driven device. It consists of an approximately 5-foot-long, 1/4-inch inner-diameter pipe containing a 1/4-inch outer-diameter steel tube and screen. A 3-foot-long drive sleeve screws into one end of the pipe. The unit is driven into the ground by a pipe that slides over the drive sleeve and strikes a coupling on the drive sleeve. It can be used in a discharge area to determine water levels and to collect water-quality samples; these samples can be used to detect contaminated ground water moving from the water-table aquifer to a stream.

In the Picatinny study, the minipiezometer was used at seven stream transects. At each transect, a left bank, right bank, and center stream site was chosen. Transects began at a point known to be uncontaminated, progressed upstream across the contaminant plume, and continued until contamination was undetectable. Depths of the screen ranged from 4 to 6 feet below the stream level. Measurements of hydraulic head indicated an upward gradient from the aquifer to the stream; differences of head between the stream and the sampling point ranged from 0.05 to 0.30 foot. Analysis of water samples detected trichloroethylene, the major contaminant (maximum concentration, 2,750 micrograms per liter), and cis-1,2-dichloroethylene, a degradation product (maximum concentration, 1,430 micrograms per liter). In the center of the stream and on the bank away from the contaminant source, a trichloroethylene concentration greater than 3 micrograms per liter was not detected. The field reconnaissance determined that a contaminant plume approximately 400 feet wide had intersected the stream. This provided a basis for further investigation in the direction of the contaminant source.

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

CAN TRANSIENT FLOW CAUSE APPARENT TRANSVERSE DISPERSION?

By Daniel J. Goode[1] and Leonard F. Konikow[1]

ABSTRACT

Large-scale dispersion of solutes in ground water results from spatial variations in the velocity field caused largely by variability in aquifer properties. Some theoretical analyses indicate that longitudinal dispersivity is scale-dependent in porous media and that transverse dispersivity is small; resultant solute plumes are long and thin. However, some observed plumes are relatively wide and can be interpreted as resulting from a large transverse dispersivity. For example, chloride and tritium plumes at the Idaho National Engineering Laboratory have been estimated to have a transverse dispersivity of about 140 meters, which is 1.5 times larger than the longitudinal dispersivity.

Aquifers exhibit not only spatial variability in the velocity field, but also temporal variability caused by changes in recharge, water use, barometric pressure, and other factors. This temporal variability includes both changes in the magnitude of velocity, and changes in the direction of flow. Previous studies from the literature indicate that fluctuations in velocity magnitude alone do not significantly affect longitudinal dispersion, hence, our study focuses on changes in flow direction.

This paper presents results of numerical experiments to investigate the effects of temporal velocity fluctuations on apparent dispersion. Two-dimensional simulations were performed using a method-of-characteristics solute-transport model. Aquifer properties were assumed to be uniform, and hydraulic boundary conditions were changed over time to induce temporal variability in potentiometric heads and velocities. Dispersion of an initial slug of solute mass was compared for steady-state flow fields and for flow fields with temporal velocity fluctuations. Examples also are presented for constant-source conditions.

The response time of an aquifer is characterized by its hydraulic diffusivity, the ratio of transmissivity to storativity (or storage coefficient). Aquifers with high diffusivity respond quickly to changing hydraulic conditions and are likely to exhibit significant velocity fluctuations. Aquifers with low diffusivity respond very slowly and can often be modeled as steady-state systems for transport. Important transients are those that occur over a time period long enough for a change in flow direction to propagate to the solute-plume location.

Numerical results show that the increase in apparent transverse dispersivity primarily is a function of the extent of change in flow direction and the ratio of longitudinal to transverse dispersivity. For a 20:1 ratio of longitudinal to transverse dispersivity, apparent transverse dispersivity is shown to increase by a factor of six in the examples analyzed. Thus, flow-field transients that are not recognized or accounted for in transport simulations may result in significant overestimates of transverse dispersivity. Furthermore, changes in the nature of the hydraulic transients will significantly affect the predictive accuracy of simulations using a transverse dispersivity that was calibrated to an erroneously high value.

Unrecognized flow-field transients that change the direction of flow in the solute plume cause an apparent increase in transverse dispersion because the higher longitudinal dispersivity is acting in a direction not parallel with the assumed mean flow direction. If flow-field transients are symmetric in time and space, resultant plumes closely resemble plumes in uniform steady-flow fields. Asymmetric transients (for example, those caused by pumping or recharge only along one side of the flow field) may significantly increase the spreading of the plume in a direction transverse to the assumed mean flow direction by advection alone, but this effect may be discernible from the plume shape and position.

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

SEDIMENT TEXTURE AND MINERALOGY OF CLAY-RICH BEDS IN A CONTAMINANT PLUME AT PENSACOLA, FLORIDA

By Thomas M. Stodd[1,2] and Joseph F. Donoghue[2]

ABSTRACT

Clay lenses within the saturated heterogeneous sand-and-gravel aquifer near an abandoned creosote wood-treatment plant at Pensacola, Florida, may be directly affecting the attenuation of creosote-related constituents in the contaminant plume over time. Textural and mineralogic analyses of the clay lenses show that the clays have a high potential for contaminant absorption. Size distributions of fine-grained particles, obtained with an electrozone particle counter and sizer, were used to determine the surface area available for media-contaminant interaction. The surface area available for interaction in the clay-rich layers was shown to be an order of magnitude larger than in the sand-dominated layers. The clay mineralogy of the sand-and-gravel aquifer was determined by an automated X-ray diffractometer using heat treatment and glycolation to improve identification of the expandable clay minerals. Internal standards were used to quantify the relative abundances of each clay mineral present. The clays within the sand units are predominantly kaolinite, with some smectite, illite, and chlorite. The clays within the clay units are kaolinite and smectite, with some illite and chlorite. The clay lenses also contain substantial amounts of organic matter that enhance their absorptivity, whereas only trace amounts of organic matter are present in the sand lenses.

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

[2] Department of Geology, Florida State University, Tallahassee, Fla.

SIGNIFICANCE OF CREOSOTE DEGRADATION ON THE GEOCHEMISTRY OF A SURFICIAL AQUIFER[1]

By Isabelle M. Cozzarelli[1], Mary Jo Baedecker[1], Jessica A. Hopple[1], and Bernard J. Franks[2]

ABSTRACT

The geochemistry of a surficial sand-and-gravel aquifer in Pensacola, Florida, was investigated from 1984 to the present to determine changes in the aquifer caused by the degradation of creosote and to identify the processes controlling these alterations. Ground water immediately downgradient from creosote disposal ponds is anoxic and has high concentrations of dissolved organic carbon (230 milligrams per liter). Most organic contaminants associated with creosote are attenuated or degraded within 270 meters downgradient from the source. Anaerobic degradation of organic matter results in elevated concentrations of total inorganic carbon (up to 80 milligrams per liter) and methane (up to 14 milligrams per liter) in the leachate plume. Carbon dioxide and methane outgas from the anaerobic ground water.

Concentrations of dissolved iron and hydrogen sulfide are as much as 25 milligrams per liter and 5 milligrams per liter, respectively. Iron is mobilized during the oxidation of organic matter, and hydrogen sulfide originates from microbially mediated sulfate reduction. Iron mobilization and sulfate reduction processes result in supersaturation of ground water with respect to iron sulfide minerals. Altered clays and authigenic framboidal pyrite were found in soil samples from the contaminated part of the aquifer.

Although creosote and its degradation products are largely organic, they influence the inorganic consitutents in the ground water and aquifer material. Significant geochemical alterations occur over short vertical and horizontal distances. Microbial processes proceed rapidly because of the presence of oxidizing agents in the ground water and the large amounts of organic carbon from the creosote waste. These processes cause changes in the aquifer that occur much more rapidly than in undisturbed natural systems.

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

[2] Woodward-Clyde Consultants, Plymouth Meeting, Penn.

BIODEGRADATION OF METHANOL AND TERTIARY BUTYL ALCOHOL IN SUBSURFACE SYSTEMS

By Kevin D. White[1]

ABSTRACT

Recently, many investigations have revealed the existence of significant microbial populations in the subsurface environment and the capability of these populations to metabolize a variety of organic chemicals commonly used in industrial processes. Knowledge of the rate of natural microbial degradation is important for ground-water protection and cleanup strategies. The response of this subsurface microbial population to influxes of alcohols or other soluble organics will determine the potential for both natural and enhanced biological reclamation of contaminated aquifers and help establish some predictive capability.

Laboratory microcosms, using actual aquifer material and ground water from two sites in the eastern United States, were designed to obtain biodegradation data for two soluble organic compounds. Methanol and tertiary butyl alcohol (TBA), common gasoline additives, were used as substrates in this study. The microcosms were incubated in the dark at 10 degrees Celsius, the approximate ground-water temperature, and monitored for contaminant concentration on a weekly basis.

Soil-extract plate counts and epifluorescence direct counts revealed the existence of significant populations of bacteria at all sites studied. In general, methanol was readily biodegradable and followed a typical batch response. Complete degradation (1,000 milligrams per liter) was accomplished in a 1- to 2-month period of time, which indicates that native subsurface bacteria have an inherent capability for metabolizing methanol.

TBA degradation followed two distinct degradation patterns. Typically, TBA biodegradation proceeded very slowly. The rate was constant throughout the monitoring period, up to 3 years in some cases, and appeared to be zero-order. However, this zero-order rate was directly proportional to the initial substrate concentration over a range of initial concentrations from 1 to 1,000 milligrams per liter.

TBA biodegradation was also observed in microcosms composed of subsurface soil from an aquifer that had been previously contaminated with gasoline containing TBA. Degradation at this contaminated site did not follow the zero-order pattern. Instead, the degradation rate paralleled that of the uncontaminated systems for a short period before increasing in rate dramatically. This degradation pattern suggests a growth-type response, possibly resulting from acclimation. Complete degradation of TBA (1–100 milligrams per liter) in the contaminated system was accomplished in 2 to 4 months. The presence of prior contamination, therefore, does not adversely affect degradation rates, and may actually contribute to an acclimation process.

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[1] U.S. Geological Survey, Louisville, Ky.

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STATUS REPORT ON A STUDY OF THE EFFECTS OF ACID MINE DRAINAGE ON VEGETATION NEAR LEADVILLE, COLORADO

By Barbara M. Erickson[1]

ABSTRACT

Moss, grass, and soil samples were collected from eight sites along St. Kevin Gulch, Leadville, Colorado. Samples of sedge, horsetail, and cow manure also were collected where present. The sampling sites were located from above the area of mine drainage downstream to where St. Kevin enters a wetland. Fieldwork in 1988 will concentrate on the wetland--determining the major ecotypes, establishing permanent sampling plots, and beginning the sampling on a seasonal basis.

INTRODUCTION

Many environmental-pollution-control efforts in the past involving vegetation have concentrated only on finding species that will grow on the waste materials after burial and not on the subsequent uptake by the vegetation (Redente and Cook, 1981, p. 36).

The current trend is toward the use of natural or manmade wetlands as self-maintaining, long-term, passive-treatment systems for water-quality improvement (Guertin and others, 1985, p. 59; Brodie and others, 1986, p. 2). Most wetland research thus far conducted has been limited to the assessment of the plant introductions and the effects the wetlands have had on the removal of the metal ions from the water--not on the fate of the metals in the sediments or their potential subsequent uptake by plants or redistribution in the environment, especially in food for wildlife. Are metals accumulating to toxic levels, or are the wetlands a bottomless sink?

Since the "opening of the west," one-third of the original wetland areas of the Rocky Mountains has been lost (Windell and others, 1986, p. 237). Emerick and others (1987, p. 95), after studying the effects of diverted acid mine water on a wetland ecosystem and the metal content of the vegetation growing on the wetland, agree there is much work to be done before wetlands are "rubber stamped" as an environmental cure-all.

A study is underway to assess the effect of mine drainage on the vegetation along St. Kevin Gulch and on the alpine wetland vegetation receiving the mine drainage. This research will interface with research on the chemical changes in the inflow and outflow waters of the wetland and the substrate chemistry currently (1988) under investigation. This paper describes the purpose and general methodology of work conducted along St. Kevin Gulch in 1987 and the work planned for the wetland in the 1988 field season.

Thanks are given to Rebecca J. Coel (University of Texas, graduate student) for her assistance both in the field and in the laboratory, and her supervisor, James G. Crock; the sample collection and preparation could not have been accomplished without her.

SAMPLING DESIGN

Eight sampling sites were established in August 1987, along St. Kevin Gulch (fig. B-39). Site 1 was located as far upstream from the major mine drainage area as possible. The second site was downstream at the junction of St. Kevin Gulch and Shingle Mill Gulch. The mine drainage flowing into St. Kevin Gulch does not enter Shingle Mill Gulch, and, therefore, the third site was established on Shingle Mill for comparison. Sites 4, 5, 6, and 7 were located farther downstream. Site 8 was located where the flow in St. Kevin Gulch turns north and disperses into the wetland.

The vegetational gradient along St. Kevin Gulch changes from a pine-dominated forest at sites 1 and 2 to a conifer-deciduous forest at sites 3 to 6. Site 7 is predominantly grass and site 8 is dominated by sedges. At each of the eight sites, two sampling points were randomly chosen, and samples of moss, grass, and soil were collected for analysis. Moss and grass were chosen as the sampling media for this part of the study because they were present at all sites in the various

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

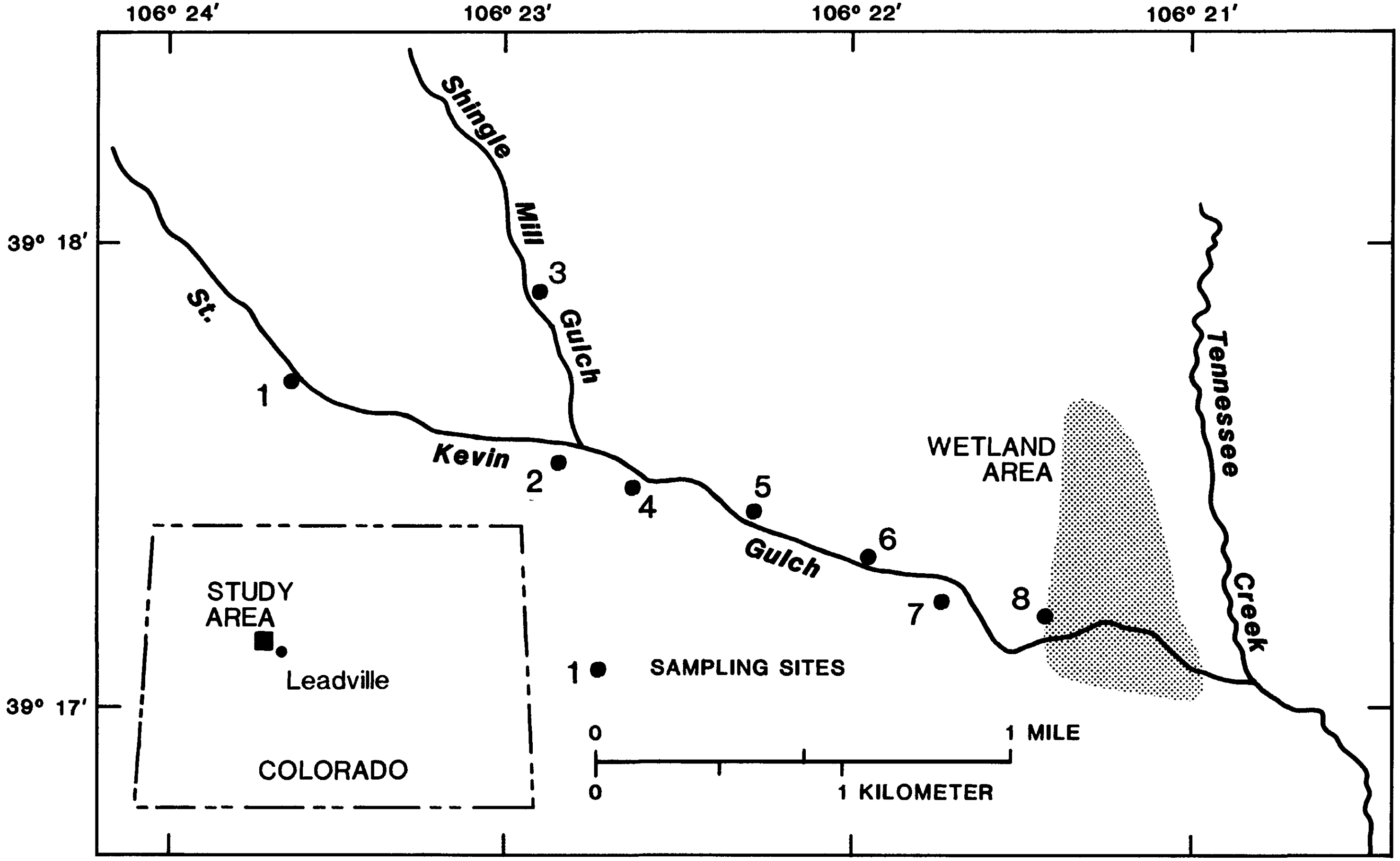

Figure B-39.—Vegetation and soil sampling sites along St. Kevin Gulch, Leadville, Colorado, 1987.

vegetation zones. Close to site 5, a sample of horsetail (arsenic indicator) was collected. At sites 6 and 7, samples of sedge and cow manure also were collected.

SAMPLING METHODS

The composite samples of grass and horsetail were collected by clipping, with stainless-steel clippers, enough material of the above-ground part to fill a 20 x 30 cm (centimeter) cloth bag. Mosses were "peeled" off the sediment to fill a 15 x 20 cm sealable plastic bag. The cow manure was picked off the surface and transported in cloth bags. The soils were collected as close as possible to the grass samples at each site by first scraping off the surface debris and then collecting the top 10 x 12 cm and storing in cloth bags. All samples have been prepared and submitted to the Branch of Geochemistry Laboratories (U.S. Geological Survey, Denver) for inductively coupled plasma-atomic emission spectroscopy (40 element) and atomic absorption (As, Hg, Sb, and Se) analyses.

FUTURE WORK

The preliminary work conducted in 1987 will be expanded to include sampling of more plant species along St. Kevin Gulch and to begin work on the wetland. The wetland boundaries and major ecosystems will be defined and permanent sampling plots installed. Seasonal sampling of the vegetation will be started to determine the distribution and concentration of metals within the wetland throughout the growing season. Also, the vegetation samples will be divided into their respective parts (leaves, roots, and so forth) to determine where the metals are accumulating within the plants. Vegetative sampling also will be conducted in conjunction with peat sampling to define metal flux in the wetland ecosystem.

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