MOVEMENT AND FATE OF CREOSOTE WASTE IN GROUND WATER, PENSACOLA, FLORIDA: U.S. GEOLOGICAL SURVEY TOXIC WASTE-GROUND-WATER CONTAMINATION PROGRAM

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Edited by HAROLD C. MATTRAW, Jr., and BERNARD J. FRANKS

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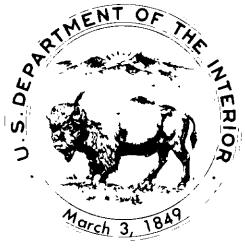

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PREFACE

Relatively little is known about the processes controlling the fate and transport of the many toxic compounds associated with industrial wastes, and even less is known about how various inorganic and organic compounds interact after entering the ground-water system. A more thorough understanding of the processes affecting contaminants in the subsurface is needed to assess future problems of contamination and to effectively contain and clean up contaminated ground waters. Analysis and selection of appropriate and cost-effective remedial measures to contain and restore contaminated ground water rely on a thorough understanding of the many factors that affect transport and transformation of contaminants that have entered an aquifer.

To improve understanding of these factors, the U.S. Geological Survey's Office of Hazardous Waste Hydrology is conducting three major research demonstration efforts addressing hazardous-waste contamination of ground water. These national interdisciplinary field studies have developed important applied, developmental, and theoretical research findings that have expanded our knowledge of ground-water contamination transport processes.

This series of technical papers presents the research conducted at a creosote works site in Pensacola, Fla. The papers were originally presented at the Toxic Waste–Ground-Water Contamination Program symposium in Tucson, Ariz., in March 1984.

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Conversion Factors

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

Multiply SI unit	By	To obtain inch-pound unit
meter (m)	3.281	foot (ft)
meter per day (m/d)	3.281	foot per day (ft/d)
square meter (m^2)	0.0002471	acre
hectare (ha)	2.471	acre
cubic meter (m^3)	0.0008107	acre-foot (acre-ft)
cubic meter per day (m^3/d)	0.0008107	cubic foot per day (ft^3/d)
liter (L)	0.2642	gallon (gal)
liter (L)	1.0567	quart (qt)
gram (g)	0.0022	pound (lb)
milligram (mg)	0.0000353	ounce (oz)
milligram per liter (mg/L)	1.0	parts per million (ppm)
centimeter per second (cm/s)	0.0328	foot per second (ft/s)

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

$$°F = 1.8°C + 32$$

Additional Abbreviations

amu	atomic mass unit
$\delta^{13}C$	del carbon
eV	electron volt
GCMS	gas-chromatography mass-spectrometry
kg	kilogram
km	kilometer
mL	milliliter
mm	millimeter
mM	millimole per liter
MPN	most probable number
m/Z	mass to charge ratio
µA	microamperes
µg/kg	microgram per kilogram
µg/L	microgram per liter
µL	microliter
µM	micromole
µm	micrometer
ng/µL	nanogram per microliter
nm	nanometer
nM/L	nanomole per liter
PAC	polycyclic aromatic compounds
PAH	polyaromatic hydrocarbons

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

Chapter A. Description of Hazardous-Waste Research at a Creosote Works, Pensacola, Florida

By Harold C. Mattraw, Jr., *and* Bernard J. Franks

Abstract

Ground- and surface-water contamination by pesticides used in the wood-preserving industry is widespread in the United States. Pine poles were treated with wood preservatives from 1902 to 1981 at a creosote works near Pensacola, Florida. Diesel fuel, creosote, and pentachlorophenol were discharged to two unlined impoundments that had a direct hydraulic connection to the sand-and-gravel aquifer. Evidence of wood-preserving waste contamination appears to be confined to the upper 30 meters of the aquifer. The waste plume extends downgradient approximately 300 meters south toward Pensacola Bay.

In 1983, the creosote works site was selected by the U.S. Geological Survey's Office of Hazardous Waste Hydrology as a national research demonstration area to apply the latest techniques for characterizing hazardous waste problems. The multidisciplinary research effort is aimed at studying processes that affect the occurrence, transport, transformations, and fate of the toxic contaminants associated with wood preservatives in the environment. Clusters of two to five wells were constructed at different depths at nine sites to define the depth of contamination. Research studies are investigating sorption, dispersion, dilution, chemical reactions, bacterially mediated transformations, quality assurance, plume hydrodynamics, and the ultimate fate of these complex organic wastes.

INTRODUCTION

Creosote, the most extensively used industrial wood preservative in the United States (Rumker and others, 1975), is a complex mixture of almost 200 organic compounds: 85 percent (by weight) polynuclear aromatic compounds, 12 percent phenolic compounds, and 3 percent heterocyclic nitrogen, oxygen, or sulfur compounds. It is estimated that there are 631 wood-preserving plants in the United States and that collectively these plants utilize over 454,000 metric tons of creosote annually. As a result of the high volume of creosote and other wood preservatives used by industry, there is great interest and concern with how these contaminants are transported, transformed, and attenuated in ground and surface waters.

In 1983, the site near Pensacola, Fla., was selected by the U.S. Geological Survey's Office of Hazardous Waste Hydrology as one of three national research demonstration areas to develop understanding of hazardous-waste processes. The criteria governing the selection of this site included (1) the relatively simple mineralogy of the surficial sand-and-gravel aquifer, (2) the apparently straightforward flow system within the sand-and-gravel aquifer at the site, and (3) the availability of a preliminary data base on the flow system, extent of contamination, and water chemistry.

The multidisciplinary U.S. Geological Survey effort is designed to study the processes that affect the occurrence, transport, and fate of toxic contaminants associated with wood preservatives in the environment. The research being conducted at the Pensacola site is designed to (1) characterize the geology and hydrology of the study area; (2) determine which organic compounds are selectively transported in ground water; (3) describe and quantify the physical, chemical, and biological processes affecting the attenuation of these compounds; (4) develop a solute-transport model capable of simulating the various processes that affect the movement of selected contaminants in ground waters; and (5) determine the impact of selected toxic compounds on aquatic organisms.

The research site also has become a field laboratory for additional studies dealing with the practicality of using nested bundles of narrow tubing set in a single hole for water-level and water-quality measurements at different depths, precision of long-term ground-water-quality monitoring data, movement of two-phase contaminants through the flow system, and tidal effects on contaminant movement. The large volume of creosote and pentachlorophenol (PCP) used in the United States and the large num-

ber of wood-preserving plants ensure that these research results will have great transfer value.

Pine poles had been treated with wood preservatives for nearly 80 years (1902-81) prior to the closing of the Pensacola site in December 1981. Prior to 1950, creosote was used exclusively to treat poles; however, the use of PCP as a wood preservative steadily increased from 1950 to 1981. The plant used approximately 95 m^3 of creosote per month and a similar quantity of PCP prior to closing. It is estimated that approximately 53 m^3 of blowdown, the residual wastewater from the pressure chambers used to treat the wood, were discharged to surface impoundments each month.

In May 1982, the creosote works declared bankruptcy and became eligible for remedial action under the U.S. Environmental Protection Agency (USEPA) Superfund Program. A private USEPA contractor is currently (1984) conducting a Remedial Investigations/Feasibility Study to define the extent of the contamination problem and develop appropriate remedial measures. The U.S. Geological Survey research group is coordinating its work with USEPA to maximize information transfer and avoid costly duplication of effort.

Purpose and Scope

The purpose of this chapter is to provide the factual and conceptual framework upon which the investigations discussed in subsequent chapters were carried out. The operational history and procedures of the creosote facility are summarized, the geology and hydrology of the creosote site are described, the concepts of waste transport that underlie the overall research program are outlined, and the interconnection between the specific investigations is delineated.

Background

In July 1981, the Florida District of the U.S. Geological Survey entered into a 2-year cooperative study with the Florida Department of Environmental Regulation to assess the susceptibility of the surficial sand-and-gravel aquifer in western Florida to contamination from surface impoundments. The purpose of the investigation was to determine the extent of movement of contaminants in the aquifer and the effect of the local hydrogeology on contaminant attenuation and movement. The study site was selected because of its long, uninterrupted history of discharging wood preservative wastewaters to unlined surface impoundments (1902–81), site accessibility, and the nature of the chemical compounds associated with wood-preserving wastewaters.

The results from the 1981 field investigation have been summarized by Troutman and others (1984) and indicate that the plume, as defined by total phenol, is confined to a relatively small area generally less than 30 m in depth and extending less than 300 m downgradient from the surface impoundments (north of Pensacola Bay). Migration of the phenols in the plume is, therefore, considerably less than the theoretical extent of plume migration that should be, on the basis of calculations of groundwater velocities, 4 to 5 km downgradient from the site beneath Pensacola Bay.

Attenuation of phenols in contaminated ground waters at the Pensacola research site probably occurs as a result of physical processes including dilution, dispersion, and ground-water discharge and microbial processes. These initial findings led to the formulation of additional hypotheses regarding the transport, transformation, and fate of other toxic contaminants in surface and ground water and are currently being tested by researchers at the Pensacola research site.

SITE DESCRIPTION AND HYDROLOGY

The research site is located in Escambia County within the city of Pensacola, Fla., at and adjacent to the site of an abandoned wood-preserving plant (fig. 1). The 7.3-ha plant site is situated approximately 550 m north of Pensacola Bay, an important commercial fishery, and near the entrance to Bayou Chico (fig. 1). The site contained two unlined surface impoundments: a northern impoundment or recirculation pond and a southern impoundment used as an overflow pond for additional storage.

The wood-treatment process consisted of removing as much of the cellular moisture as possible from the poles and replacing the moisture with either creosote or PCP. The poles were delivered to the plant, debarked, and allowed to air dry. They were then loaded on a tram and placed in airtight cylinders where they were steam heated under pressure to burst the wood cells. A vacuum was applied to the chamber to remove the cellular moisture. The airtight chamber was then pressurized and flooded with preservative. After several hours, the preservative that had not been sorbed by the wood fiber was pumped from the chamber to the recirculation pond and the treated poles removed to an outside storage area for eventual shipping.

The wastewaters discharged to the recirculation impoundment consisted of moisture extracted from the poles in the dewatering process and any residual PCP, creosote, and diesel fuel remaining in the chamber subsequent to treatment. The diesel fuel provided a "carrier effect" that increased the solubility of creo-

Figure 1. Location of the creosote works and vicinity, Pensacola, Fla.

sote and PCP and, consequently, their ability to penetrate into the wood fiber.

The recirculation impoundment occupied 7,700 m^2 and held 9,400 m^3 of wastewater. The southern impoundment, constructed in 1954, was used as an overflow pond for additional storage. It occupied 3,240 m^2 and held 4,000 m^3 of wastewater. Both impoundments were constructed of clay embankments approximately 1 m high on all sides. The average depth of both surface impoundments was 1.2 m. The south embankment of the recirculation pond also formed the northern boundary of the overflow pond.

Prior to 1970, whenever water levels in the impoundments became high, wastewater spilled over a small dam and flowed south through a natural depression discharging directly into the entrance to Bayou Chico. Subsequent to enactment of the Clean Water Act in 1970, in an effort to control water levels in the impoundments, wastewaters were periodically drawn off and allowed to evaporate in designated areas north of the recirculation pond and south and east of the overflow impoundment (fig. 2). The depression to the south has since been channelized into a stormwater drainage ditch to convey runoff from the basin north of the plant site.

In October 1983, under the USEPA emergency response program of Superfund, wastewaters were drained from the two surface impoundments and the sludge in the pond was dewatered by using a mixture of lime and fly ash. A clay cap was emplaced over the entire area once occupied by the surface impoundments and evaporation areas.

The surface impoundments were unlined and in direct hydraulic contact with the sand-and-gravel aquifer. The aquifer, the principal source of water supply in the area, consists of deltaic, fine to coarse quartz sand deposits, interrupted by discontinuous silts and clays, which locally confine the aquifer

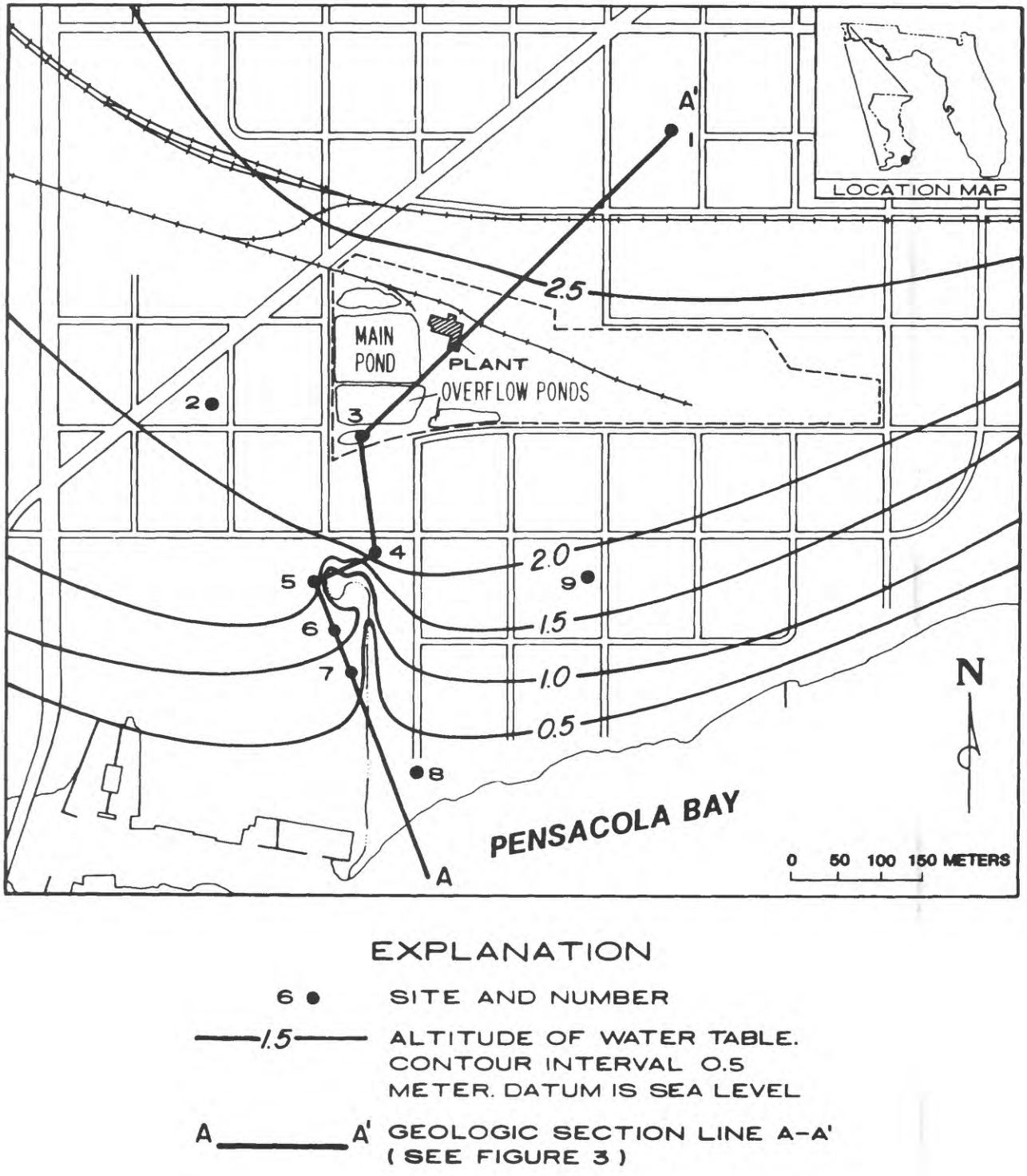


Figure 2. Shallow ground-water-level contours (March 1984) around the drainage stream at the creosote works site.

(Franks, 1982). Near the site, the sand-and-gravel aquifer is about 90 m in total thickness. Only the upper 30 m seem to be affected by contamination by wood-preserving wastes. Figure 3 indicates the hydrogeology along a generalized south to north section (fig. 2), located approximately along a flow line passing south from the source of contamination through the affected part of the aquifer. The aquifer is very permeable but clay lenses locally impede the movement of water.

Ground-water flow is generally to the south towards Pensacola Bay (fig. 2). Flow velocities are on

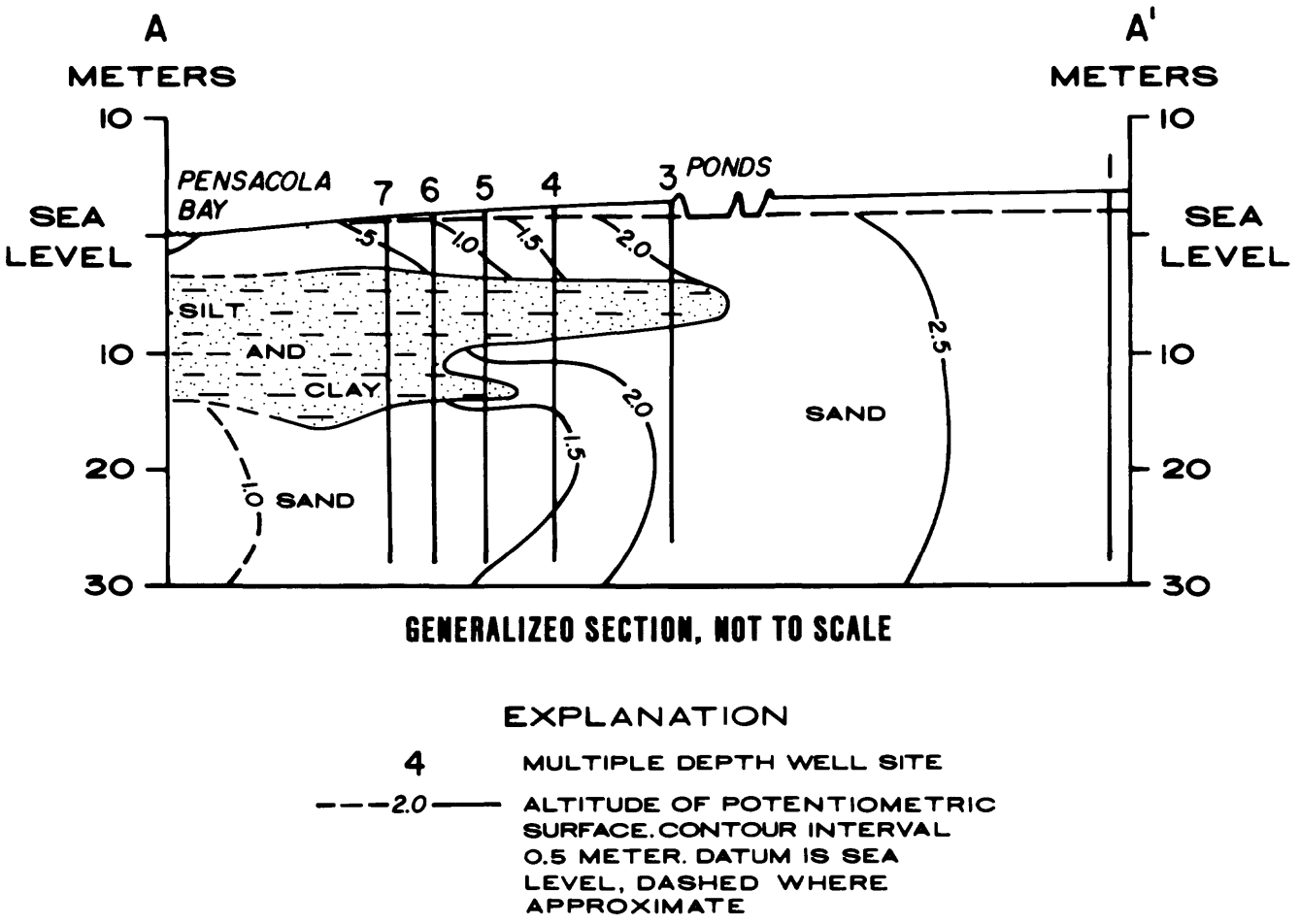


Figure 3. Geologic cross section showing lines of equal head and approximate potentiometric surface, January 1984.

the order of 0.3 to 1.2 m/d, with lower velocities in the deeper parts of the aquifer. Discontinuities in the confining silts and clays, as well as the stormwater drainage ditch that intercepts the shallow ground water, complicate the flow system. At its headwater the ditch receives a continuous flow of water from a storm drainage system originating upgradient from the site.

Pumpage in the vicinity of the study area has fluctuated considerably throughout the last 80 years, largely as a result of varying industrial pumping. For example, withdrawal rates at a nearby chemical company have ranged from over 30,000 m^3/d in the 1930's (Jacob and Cooper, 1940, p. 60) to the present day minimum of 1,700 m^3/d (S.D. Leach, written commun., 1983). Jacob and Cooper (1940, p. 63) conclude that heavy industrial water use was responsible for inducing downward gradients in the area. Present vertical gradients (1984), on the contrary, are generally upward (fig. 3), thus reducing the probability of significant downward transport of the contaminant plumes.

Well-Drilling Program

Test holes were drilled upgradient from the plant site and in a line between the surface impoundments and the bay as shown in figure 2. To reduce the possibility for cross contamination, test wells were drilled in the following sequence: sites 1, 7, 6, 5, 4, and 3—beginning at an upgradient (background) site and ending closest to the contaminant source. The drilling equipment was steam cleaned between drilling of each site. Sites 2, 8, and 9 were drilled later to define lateral plume migration. Test holes were drilled by using 95 mm stainless steel hollow-stem auger, with minimal amounts of native aquifer water used as the only lubricant. Wells were completed by inserting casing into the hollow auger stem and removing the auger flights, allowing the unconsolidated sands to collapse around the casing. Most wells discussed in this report were constructed of either 25.4 mm or 50.8 mm diameter galvanized pipe with a 0.91 m stainless steel screen to economically minimize effects of well construction on water chemistry (table 1). The pipe and screen were steam cleaned

Table 1. Well construction data

[Casing and screen type: GS, galvanized steel; PVC, polyvinylchloride; SS, stainless steel]

Site No.	Site identification No.	Well No.	Depth, in feet below land surface datum	Depth, in meters below land surface datum	Casing		Screen	
					Diameter, in millimeters	Type	Length, in meters	Type
1	302423087140402	120	20.5	6.2	51	GS	0.9	GS
	302423087140401	160	58.2	17.7	51	GS	.9	SS
	302423087140400	100	98.6	30.0	51	PVC	1.5	PVC
	302423087140403	199	23.1	7.0	Bundle consisting of five			
	302423087140404		36.0	11.0	16-mm diameter polypropylene tubes			
	302423087140405		55.8	17.0	surrounding a 25-mm diameter			
	302423087140406		70.9	21.6	polyvinylchloride core			
	302423087140407		98.1	29.9				
2	302415087142501	220	21.4	6.5	51	GS	.9	SS
	302415087142502	260G	64.2	19.6	51	GS	.9	GS
	302415087142503	260P	60.2	18.4	51	PVC	1.5	PVC
	302415087142504	260S	60.2	18.4	51	SS	.9	SS
	302415087142500	200	99.7	30.4	51	GS	.9	GS
3	302413087141903	320	20.0	6.1	25	GS	.9	SS
	302413087141904	340	39.8	12.1	25	GS	.9	SS
	302413087141905	360	60.1	18.3	25	GS	.9	SS
	302413087141906	380	77.3	23.6	25	GS	.9	SS
	302413087141902	300	97.7	29.8	25	GS	.9	SS
4	302408087141704	420	20.6	6.3	25	GS	.9	SS
	302408087141703	440	40.1	12.2	25	GS	.9	SS
	302408087141707	480	79.3	24.2	25	GS	.9	SS
	302408087141705	400	101.7	31.0	25	GS	.9	SS
5	302407087142001	520	15.2	4.6	51	GS	.9	SS
	302407087142002	540	37.8	11.5	51	GS	.9	SS
	302407087142003	560	59.6	18.2	51	GS	.9	SS
	302407087142004	580	78.2	23.8	51	GS	.9	SS
	302407087142000	500	100.0	30.5	51	GS	.9	SS
6	302405087142001	620	21.3	6.5	51	GS	.9	SS
	302405087142002	660	58.4	17.8	51	GS	.9	SS
	302405087142000	600	99.3	30.3	51	GS	.9	SS
7	302404087142001	720	19.4	5.9	51	GS	0.9	SS
	302404087142002	760	64.4	19.6	51	GS	.9	SS
	302404087142000	700	100.0	30.5	51	GS	.9	SS
8	302400087141601	820	21.7	6.6	51	GS	.9	SS
	302400087141600	800	99.6	30.4	25	GS	.9	GS
9	302407087140901	920	22.3	6.8	25	GS	.9	SS
	302407087140902	960	58.9	18.0	25	GS	.9	SS
	302407087140900	900	99.0	30.2	102	PVC	1.5	PVC

and then rinsed with methanol and distilled water just prior to installation in the test hole. At each site, a cluster of two to five wells was constructed, with each well set at a different depth. The first digit of the three-digit well number in table 1 refers to the site number and the last two digits represent the approximate well depth in feet (for example, well 160 is a 60-ft (18.3 m) well at site 1; well 200 is a 100-ft (30.5 m) well at site 2). Prior to sampling each well, at least three casing volumes were removed with a peristaltic

pump. Natural gamma, gamma-gamma, and neutron borehole logs were run on selected wells. The logs confirmed the existence of a relatively impermeable shallow confining bed in the study area.

Concepts of Waste Transport

Effluent from the treatment process was water, diesel fuel, creosote, and PCP. The chemically complex, organic-rich brew was discharged to the shallow, unlined waste disposal ponds and from there seeped to the shallow water table. An unknown fraction of organic waste did not move downgradient—selected compounds were either trapped in the pond sediments, degraded, or possibly sorbed immediately below the ponds. The lighter-than-water fractions have migrated downgradient at or near the water table. The water soluble and more dense organic phases entered the ground-water system and were transported along flow paths above and below a prominent clay layer near and downgradient of the disposal ponds (fig. 3). The clay and sand materials in the shallow sand-and-gravel aquifer may have sorbed a part of the organic waste under the reducing conditions. Soluble organic wastes and dissolved inorganic chemicals were dispersed and diluted downgradient. The waste plume is smaller than one would expect, on the basis of measured ground-water gradients and previously published transmissivities for the deeper parts of the sand-and-gravel aquifer.

In addition to physical processes, the reduction of organic components in a ground-water system may also be related to chemical reactions or microbial transformation. Both processes are heavily influenced by the oxidation-reduction state (poise) of the ground-water system. This is an interactive process whereby specific microbial metabolites or chemical reactions affect the oxidation-reduction state of the ground-water environment. Aerobes operate in the unsaturated zone and the shallow parts of the aquifer to oxidize refractory organic compounds. Deeper in the aquifer, where there is little oxygen because of the organic waste load entering the system, anaerobes degrade certain phenolic compounds to methane and carbon dioxide (Ehrlich and others, 1982).

Although many of the expected waste components are absent or extremely dilute near Pensacola Bay, a dark sludge band that has been observed on the beach at low, low tide suggests transport to the bay through the ground-water system. Another phenomenon is the appearance of sludge globules in the storm drainage ditch, usually after heavy rains. The ultimate fate of these materials and the impact on the Pensacola Bay marine ecosystem is largely undetermined.

SYNOPSIS OF RESEARCH ELEMENTS

The initial effort was to design and develop a data-collection network that meets diverse objectives of specialized research goals. The preliminary work of Troutman and others (1984) included installation of nine wells that were used to define the approximate area of ground-water contamination. In the current research program, a set of nine additional well clusters was installed to provide further insight into site geology, hydrology, and downgradient plume migration. An extensive characterization of the dissolved inorganic species and the oxidation-reduction relations is presented in chapter B (Baedecker and Lindsay). Water-quality analyses for organic compounds from these wells appear in chapter E (Pereira and others) and chapter G (Goerlitz and others).

The best cross-sectional representation of the current location of the plume is presented in chapter B (Baedecker and Lindsay). Their work with unstable constituents reveals five water-quality zones in the surficial sand-and-gravel aquifer between the disposal ponds and Pensacola Bay. Their definition of the most strongly reducing zone also marks the location of an excess of iron described by Hearn and others (chapter C). Using energy dispersive X-ray fluorescence on polished soil samples, Hearn and others discovered evidence for recent siderite (iron carbonate) precipitation. Iron in excess of sulfide formed this secondary mineral under the highly reducing conditions created by bacterially mediated oxidation of organic wastes.

The transformation of the organic constituents begins in the pond. Heterocyclic nitrogen compounds, particularly quinoline, have been investigated by Bennett and others (chapter D). Aerobic pseudomonads degrade quinoline to 2-quinolinone, which then migrates into the ground water. The high concentrations of this compound in the ground water at five of the new well sites was demonstrated by Pereira and Rostad (chapter E). Their work revealed approximately 80 specific organic contaminants in the aquifer system. Selected phenolics, polycyclic aromatic hydrocarbons, nitrogen heterocycles, sulfur heterocycles, and oxygen heterocycles were quantified by using gas-chromatography mass-spectrometry (GCMS) analysis.

An improved technique of sampling ground water for many of these hazardous organic compounds was developed by Rostad and others (chapter F). A cyclohexyl bonded phase column was used successfully in the field to recover different functional organic groups from 50-mL samples. This procedure is recommended for similarly contaminated waters because of the advantages in reduced time, lower

cost, increased safety, and simplicity. The reduced possibility of chemical transformations after sample collection suggests that bonded phase columns will be used more widely in the future.

The original analyses of creosote and PCP in 1981 were performed by Goerlitz (Troutman and others, 1984) with high performance liquid chromotography and GCMS. This initial characterization of the contamination led to the placement of the nine well clusters used in the current research. Goerlitz has designed a series of column sorption studies (chapter G) that indicate that dimethylphenols are not sorbed or degraded by sand-and-gravel aquifer materials. This group of compounds appears to be the best organic tracers of contaminant plume development.

Godsy and Goerlitz tested 19 individual phenolic and related compounds in anaerobic digestors with bacterial populations from the Pensacola site (chapter H). Only five were biodegradable. Sequential steps for the degradation of phenol and methyl phenol, identified in the laboratory, are consistent with chemical analyses and bacterial consortiums found in a "bioreactor zone" at sites 3, 4, and 5. The research begins to explain the reduction of phenolic concentrations below concentrations attributable to such physical processes as dilution, dispersion, and sorption.

Transport of organic contaminants by surface water down the storm drain and by shallow ground water result in contamination of sediments and water in Pensacola Bay. Elder and Dresler (chapter I) are evaluating creosote byproduct bioaccumulation in mollusks as well as testing the effect of contamination on species diversity in the freshwater drainage ditch and the estuarine system.

A detailed ground-water flow model is presently under development for the site. The model is based on hydrologic data from the initial wells (Troutman and others, 1984) and the 9 well sites that further define the flow field. The recognition of the influence of the drainage ditch on shallow flow has greatly influenced the flow-model development. The three-dimensional finite-difference model (McDonald and Harbaugh, 1984) chosen for simulation of the ground-water flow system accounts for the impacts of the drainage ditch and also for tide effects in wells near Pensacola Bay.

Development of a solute transport model by coupling simulations of flow with estimates of selected water-quality processes is planned. This transport model will have significant transfer value in understanding the movement and fate of contaminants derived from creosote in ground-water systems.

SELECTED REFERENCES

Ehrlich, G.G., Goerlitz, D.F., Godsy, E.M., and Hult, M.F., 1982, Degradation of phenolic contaminants in ground water by anaerobic bacteria, St. Louis Park, Minn.: Ground Water, v. 20, no. 6, p. 703–710.

Franks, B.J., ed., 1982, Principal aquifers in Florida: U.S. Geological Survey Water-Resources Investigations Open-File Report 82–255, 4 sheets.

Jacob, C.E., and Cooper, H.H., Jr., 1940, Report on the ground-water resources of the Pensacola area in Escambia County, Florida: U.S. Geological Survey Open-File Report FL–40001, 89 p.

Marsh, O.T., 1966, Geology of Escambia and Santa Rosa Counties, western Florida panhandle: Florida Division of Geology Bulletin 46, 140 p.

McDonald, M.G., and Harbaugh, A.W., 1984, A modular three-dimensional finite-difference ground-water flow model: U.S. Geological Survey Open-File Report 83-875.

Musgrove, R.H., Barraclough, J.R., and Grantham, R.G., 1965, Water-resources of Escambia and Santa Rosa Counties, Florida: Florida Geological Survey Report of Investigations 40, 102 p.

Rumker, Rosmarie von, Lawless, E.W., and Meiners, A.F., 1975, Production, distribution, use and environmental impact potential of selected pesticides: U.S. Environmental Protection Agency, EPA 540/1–74–001, 439 p.

Trapp, Henry, Jr., 1978, Preliminary hydrologic budget of the sand-and-gravel aquifer under unstressed conditions, with a section on water-quality monitoring, Pensacola, Florida: U.S. Geological Survey Water-Resources Investigations 77–96, 57 p.

Troutman, D.E., Godsy, E.M., Goerlitz, D.F., and Ehrlich, G.G., 1984, Phenolic contamination in the sand-and-gravel aquifer from a surface impoundment of wood treatment wastes, Pensacola, Florida: U.S. Geological Survey Water-Resources Investigations Report 84–4230, 36 p.

Chapter B. Distribution of Unstable Constituents in Ground Water Near a Creosote Works, Pensacola, Florida

By Mary Jo Baedecker *and* Sharon Lindsay

Abstract

Ground water downgradient from a wood-treatment plant near Pensacola, Florida, contains contaminant plumes having high concentrations of unstable organic compounds, particularly phenols and polyaromatic hydrocarbons. Unstable constituents distributed in ground water downgradient of the treatment plant's disposal ponds delineate five zones: (1) an anaerobic contaminated zone that has all constituents present in concentrations greater than background levels; (2) a more contaminated zone where methane concentrations are high, carbon isotopes show the most fractionation, and dissolved organic carbon, ammonia, and iron concentrations are high; (3) a zone having two areas of high methane and sulfide production in which there are high dissolved organic carbon concentrations and highly fractionated carbon isotopes; (4) a deeper zone having high iron concentrations; and (5) a shallow zone that has high ammonia, iron, and manganese concentrations, with the presence of methane, but not hydrogen sulfide.

INTRODUCTION

The generation of anaerobic leachate and its movement have a significant impact on the water chemistry of an aquifer. Bicarbonate, sulfate, hydrogen sulfide, methane, ammonia, iron, manganese, dissolved oxygen, and dissolved organic carbon are reactants or products in oxidation-reduction reactions, and their concentrations show marked variations over relatively short distances in contaminated aquifers. In addition, microbial processes result in the fractionation of stable isotopes. In particular, methanogenesis alters the distribution of carbon 13 to carbon 12 ratios of carbon species dissolved in water. Variations in concentrations of these constituents and changes in the distribution of isotopes may indicate the extent of leachate migration and may provide information about the progress of reactions.

A description of the study site and the hydrogeology of the surficial sand-and-gravel aquifer is discussed in chapter A (Mattraw and Franks). The direction of ground-water flow is generally south toward Pensacola Bay (fig. 4). Immediately south of the disposal ponds, the sand aquifer is separated into two parts by a discontinuous confining layer of silt and clay, interbedded with sand, that thickens toward the bay. This divides the leachate into two plumes—a shallow plume and a deeper plume. The hydrologic data show that at depths greater than 25 m below land surface, water may move upward from deeper parts of the aquifer and discharge to the bay. Part of the contaminated ground water in the upper plume is discharged to a stream within 300 m of the disposal ponds. Data for this study are presented on a cross section from site 1 upgradient and northeast of the creosote plant to site 8 about 450 m downgradient (fig. 4).

The uncontaminated ground water is a Na-HCO_3-Cl type with dissolved solids generally less than 50 mg/L, which is typical for a shallow quartz sand-and-gravel aquifer. In the contaminated water the concentrations of all constituents are higher and the dissolved solids are about 200 mg/L. Higher chloride concentrations are from the effluent, and because these sediments do not contain carbonates, higher alkalinities result from the degradation of organic material. An increase in the relative abundances of calcium, magnesium, and potassium to sodium in the contaminated water may be an input from the source of contaminants or may result from ion exchange or the weathering of clays.

ANALYTICAL METHODS

A summary listing of the analytical methods used and the limits of detection for individual constituents is given in table 2. Water equal to the volume of at least two well casings was removed from the wells with a peristaltic pump before samples were collected. Temperature, pH, alkalinity, dissolved ox-

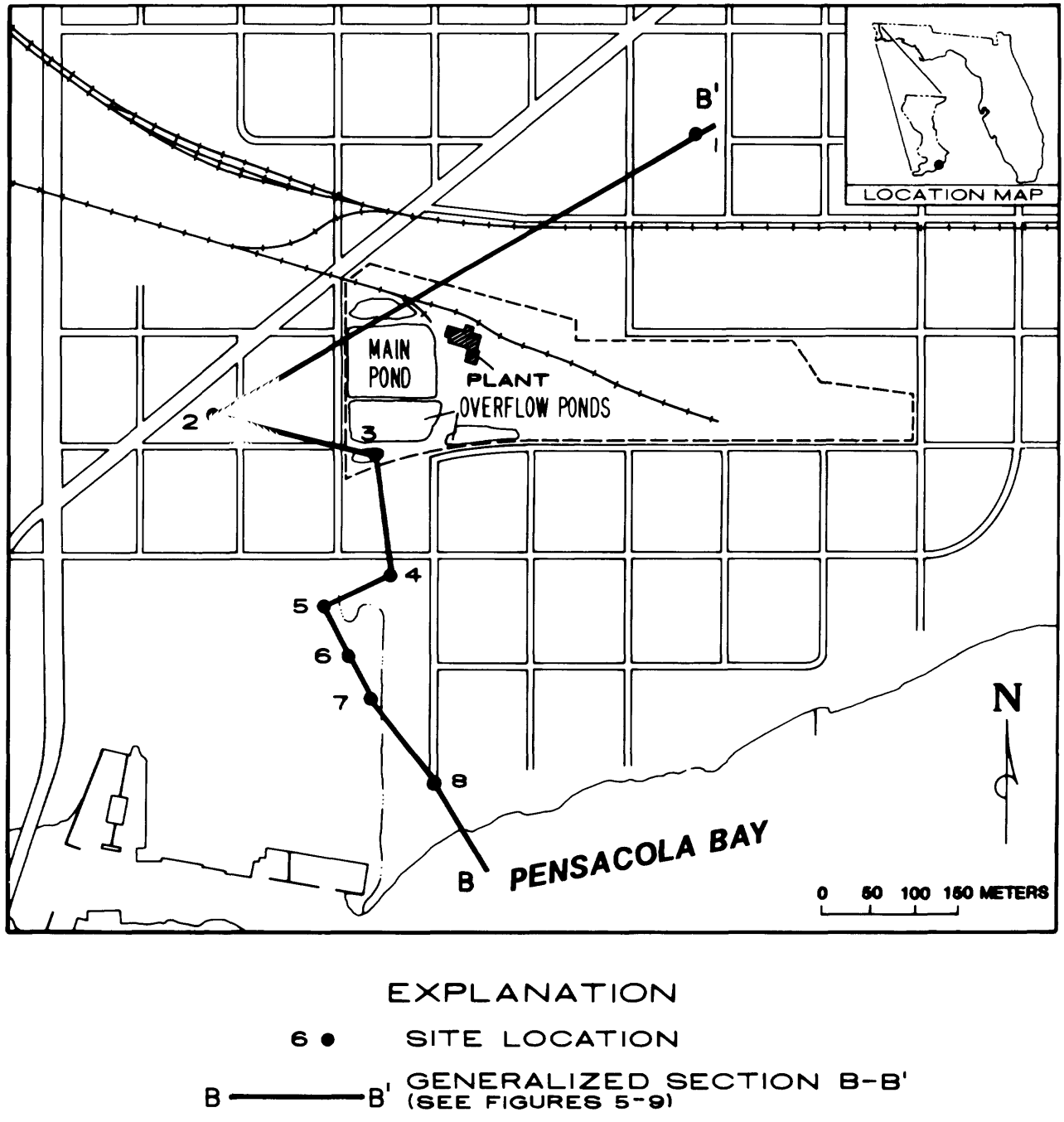


Figure 4. Location of the creosote works, disposal ponds, and a trace connecting the wells used in the generalized sections B–B'.

ygen, and sulfide were measured in the field immediately upon collection of the water sample. Oxygen was determined by the standard Winkler method and sulfide was determined by a methylene blue procedure (Cline, 1969) with modifications. Samples for analysis of dissolved organic carbon were sealed in ampules within 24 hours of collection and analyzed by the wet oxidation technique. Samples were chilled and analyzed for methane by gas chromotography and for ammonia by electrode within 7 days of collection. Samples for analysis of iron and manganese were filtered in the field through a 0.1-micron filter, acidified to pH 2, and analyzed by atomic absorption.

Collection of water samples with a peristaltic pump caused some outgassing. Future sampling should be done with a small submersible pump that would reduce the loss of dissolved gases.

Table 2. Methods used and limits of detection for unstable constituents

Constituent	Sampling	Analysis	Detection limit, micromoles per liter
Oxygen (O_2)	Unfiltered	Winkler (field)	1.60
Ammonia (NH_4^+)	0.4 µm filtered, chilled	Electrode	1.00
Hydrogen sulfide (H_2S)	Unfiltered	Modified methylene blue (field)	.310
Methane (CH_4)	Unfiltered, chilled	Gas chromatography	.190
Iron (Fe^{++})	0.1 µm filtered, acidified	Atomic absorption	1.8
Manganese (Mn^{++})	0.1 µm filtered, acidified	Atomic absorption	.550
Del carbon-13 ($\delta^{13}C$)	$SrCO_3$, precipitation	Mass spectrometry	40.0 Σ CO_2
Dissolved organic carbon (DOC)	0.4 µm filtered	Wet oxidation (ampules prepared in field)	8.50

RESULTS

Values of pH of the ground water in the area of study ranged from 5.2 to 6.4 units with two exceptions, at depths of 30 m below land surface where the pH measurements were 6.9 and 8.0 units. Although the water was slightly more acidic in the vicinity of the plume, this shift, which may be due to the presence of organic compounds, was generally less than 0.3 pH units.

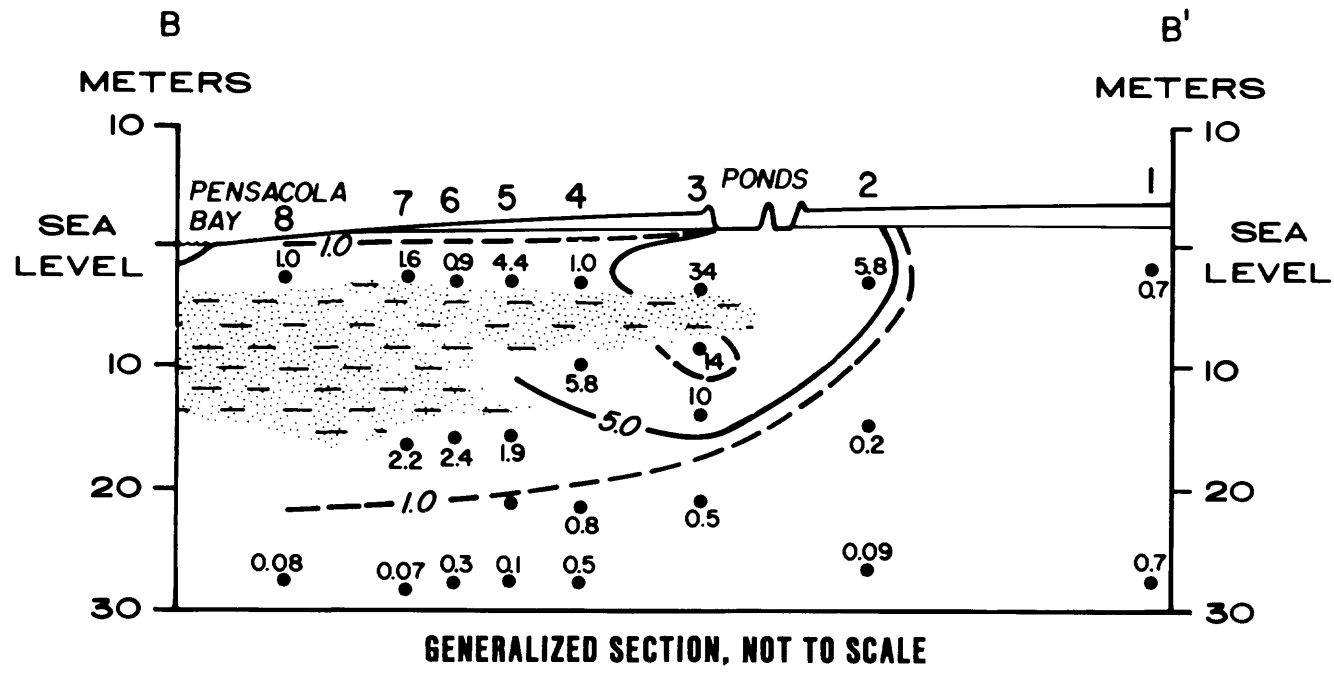
Concentrations of alkalinity ranged from 0.3 to 5 mM. These concentrations are low because of the lack of calcareous materials and the lack of an organic-rich soil zone to supply carbon dioxide to the aquifer. The higher values were found in areas of contamination. Several studies (Golwer and others, 1977; Baedecker and Back, 1979) showed that low-molecular weight organic acids contribute to the alkalinity in ground water, often in significant amounts. Goerlitz and others (chapter G) identified several organic acids in water immediately downgradient from the disposal ponds (sites 3 and 4). These acids contribute up to 63 percent of the measured alkalinity. The highest alkalinity value of 5 mM was found at site 8 near the bay, which suggests that the source of inorganic carbon may be from seawater rather than from degradation of organic compounds in the contaminated water.

The highest concentration of dissolved organic carbon (DOC), 34 mM, was in ground water beneath the ponds (fig. 5). DOC in concentrations greater than 1 mM, well above background levels of 0.1 mM, indicates that contaminants are present in water about 450 m downgradient of the ponds. The concentration of organic carbon decreased rapidly away from the source. However, the outer boundary of the plume toward the bay was not delineated by the present data.

An anaerobic zone extended beneath the ponds to depths greater than 30 m and laterally about 450 m downgradient (fig. 5). Dissolved oxygen concentrations outside the anaerobic zone ranged from 1 to 70 µM. The higher concentrations were at greater depths, however, the number of points sampled in the deeper part of the aquifer were not sufficient to establish baseline values.

Ammonia values were generally low, less than 50 µM, except at three sites (fig. 6). Ammonia was detected in concentrations greater than 3 µM in the contaminant plume and the occurrence resembles the distribution of DOC. The highest concentration of ammonia was in water from a shallow depth near the bay. As in the case of alkalinity, the source of ammonia in water near the bay is probably from seawater rather than effluent contamination.

Concentrations of hydrogen sulfide (H_2S) ranged from 0 to 65 µM (fig. 6), and the highest concentrations were found above and immediately below the silt- and clay-rich sands. Unlike the distribution of other constituents, the higher values were not found in the most contaminated zones, such as immediately beneath the ponds at site 3. Also, H_2S was not detected in water at site 8 (near the bay), although the water was anaerobic and contained high concentrations of other constituents. Concentrations



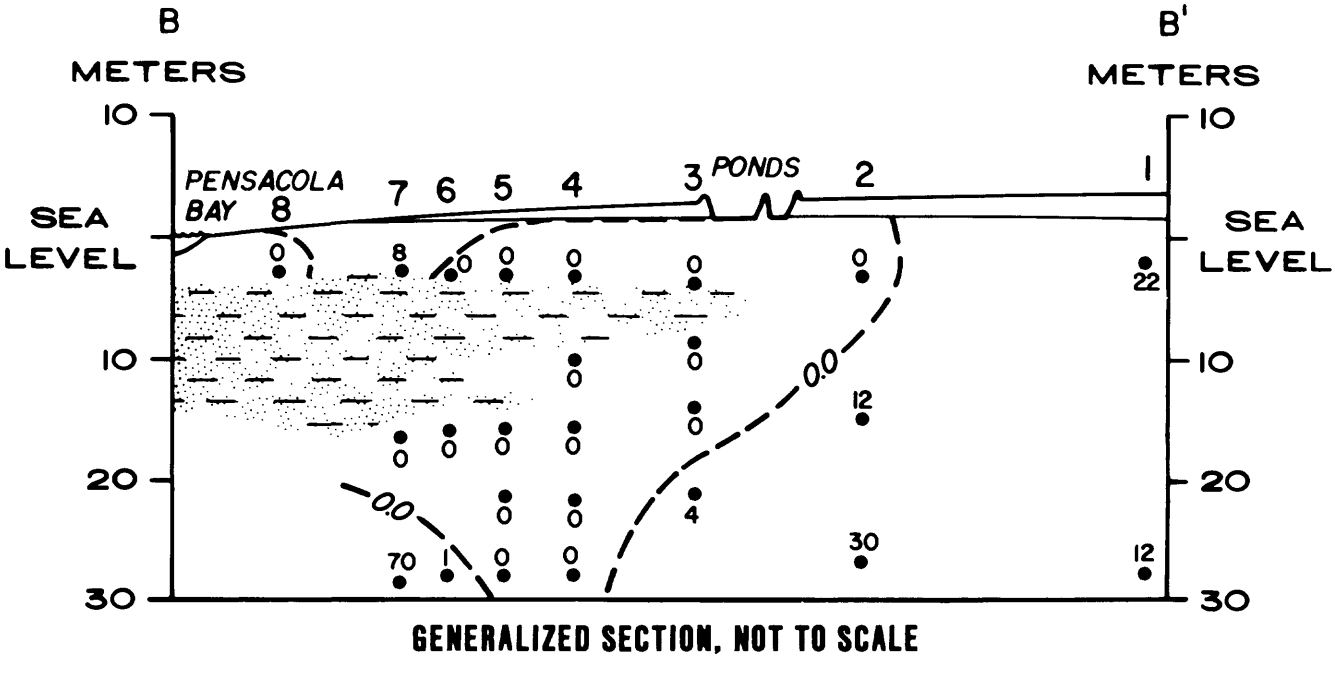
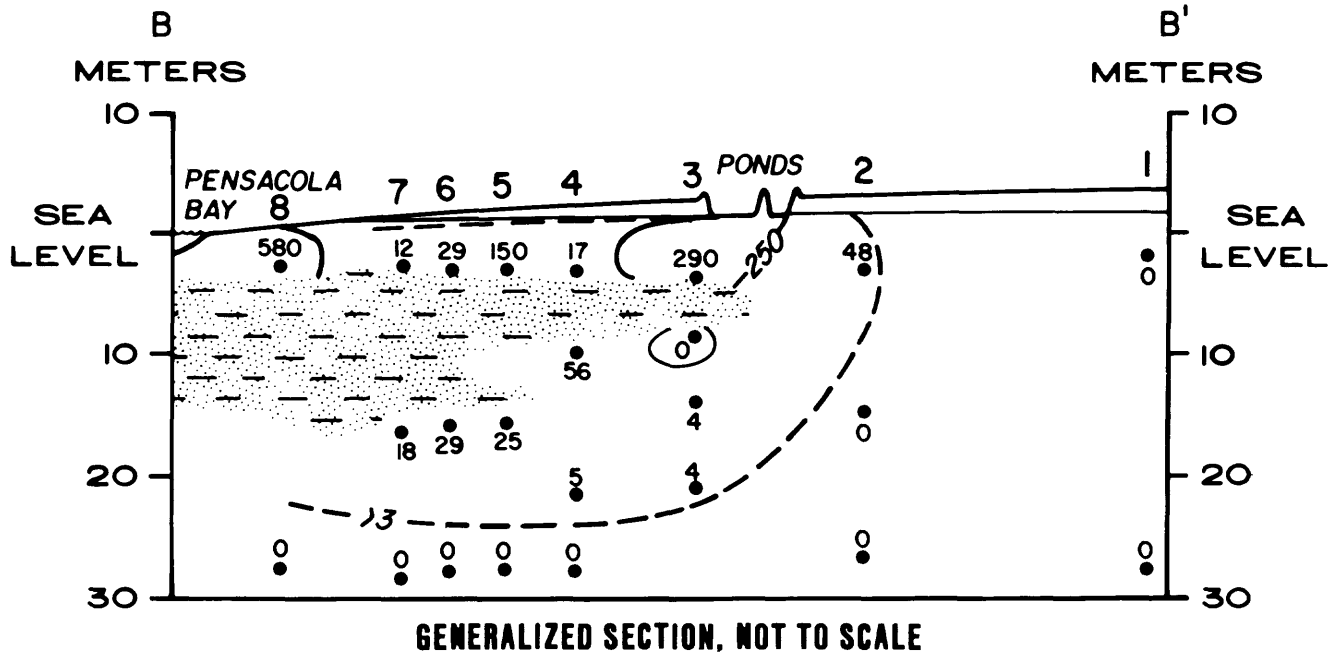


Figure 5. Distribution of organic carbon and oxygen dissolved in ground water, generalized section B–B'.



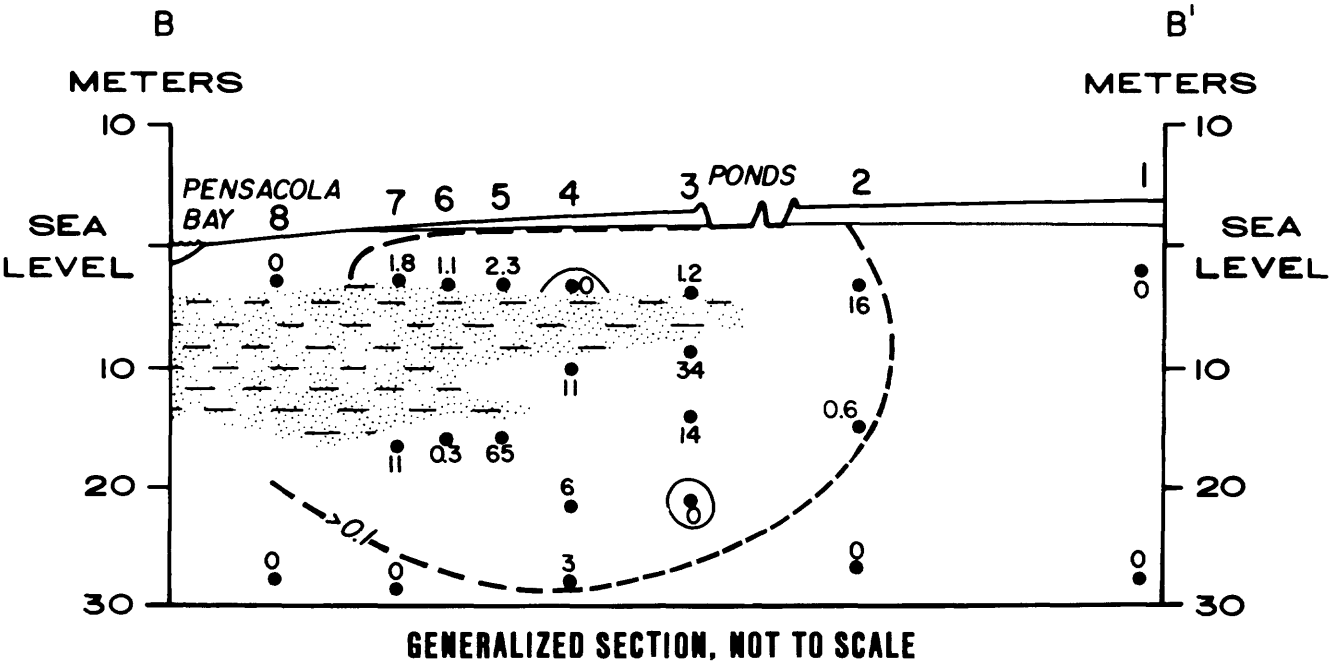


Figure 6. Distribution of ammonia and hydrogen sulfide dissolved in ground water, generalized section B–B'.

of sulfate (SO_4) in water from the study area ranged from 1 to 240 μM and the higher concentrations were generally in water that was less contaminated. Two sites within the contaminated zone had concentrations of H_2S less than the detection limit and sulfate concentrations of 1 μM. It is likely that all the SO_4 was reduced at these sites, and the H_2S that formed was removed from solution by precipitation, leaving low dissolved H_2S. High concentrations of iron in parts of the aquifer suggest that an important control on the concentration of H_2S is its removal by precipitation as iron sulfides. Pyrite was found in some, but not all, samples of aquifer material by Hearn and others (chapter C).

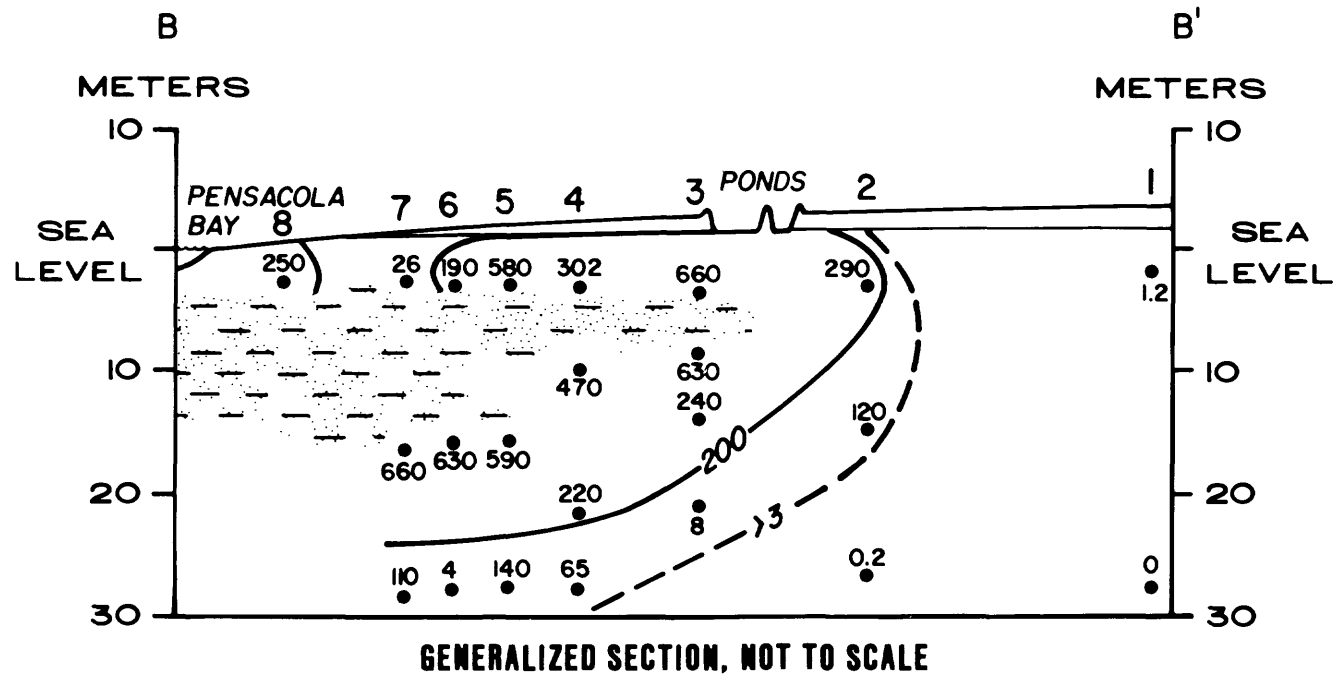
Concentrations of methane were high in the ground water, even at depths greater than 30 m and at distances 450 m downgradient (fig. 7). However, the boundaries of the methane plume were not defined. Godsy and Goerlitz (chapter H) showed that methanogenesis is a major process in the degradation of phenolic compounds. As a result of methanogenesis, the stable isotopes of carbon are fractionated. The lighter isotopes preferentially form methane and the inorganic carbon becomes enriched in the heavier isotopes. The carbon 13 to carbon 12 ratio values were heaviest immediately beneath the ponds (fig. 7), which indicates that a significant quantity of methane has formed there. The values became increasingly lighter with depth and distance away from the source of contamination. The values at site 1, which were heavier than background values, provide additional evidence that this site was probably contaminated, but from a source other than the disposal ponds.

The distribution of iron and manganese in the ground water is different from that of the other constituents (fig. 8). The values for iron ranged from 2 to 420 μM; the lower values were in water upgradient of the ponds. Iron concentrations were greatest in the shallow plume above the less permeable clay layer and also beneath the layer, but not in the more contaminated zone of the lower plume (near sites 3 and 4). Several possibilities could explain this distribution: (1) the iron-containing minerals or coatings may have been leached or these phases may be absent in parts of the aquifer, (2) iron may be removed from solution by precipitation, and (3) some water in the lower zone of greater iron concentrations may be from lower depths. Manganese concentrations were low throughout this part of the aquifer. Values were less than 1 μM except in the shallow plume (fig. 8). The highest iron and manganese concentrations were near the bay.

CONCLUSIONS

The distribution of unstable constituents in ground water downgradient of the disposal ponds indicates that five zones are delineated (fig. 9): (1) a contaminated zone that is anaerobic and has all constituents present in concentrations greater than background levels; (2) a more contaminated zone immediately beneath the ponds at shallow depths of less than 6 m, where methane concentrations are high, carbon isotopes show the most fractionation, and dissolved organic carbon, ammonia, and iron concentrations are high; (3) two areas of high methane and sulfide production, one above and one below the clay layer, where dissolved organic carbon concentrations are high and carbon isotopes show significant fractionation; (4) a lower zone that has high iron concentrations although, in most cases, the concentrations of other constituents are not high; and (5) a shallow zone near the bay that has high ammonia, iron, and manganese concentration, with the presence of methane, but not hydrogen sulfide.

The distribution of unstable constituents in ground water can be used to delineate zones of contamination in an aquifer and to identify where different chemical processes are occurring. The contaminant plumes have high concentrations of organic compounds (chapters E and G), particularly phenols and polyaromatic hydrocarbons. However, the concentrations of these constituents generally decrease rapidly downgradient. The plume extends greater than 30 m below land surface and more than 300 m beyond the disposal ponds toward the bay (sampling site 7). Near the bay (sampling site 8) chloride concentrations are 3,200 mg/L, which is about 1/6 the concentration of chloride in seawater. Thus, the tidal movement of saltwater is an important process and the interface between the contaminant plume and the saltwater-freshwater mixing zone should be investigated.



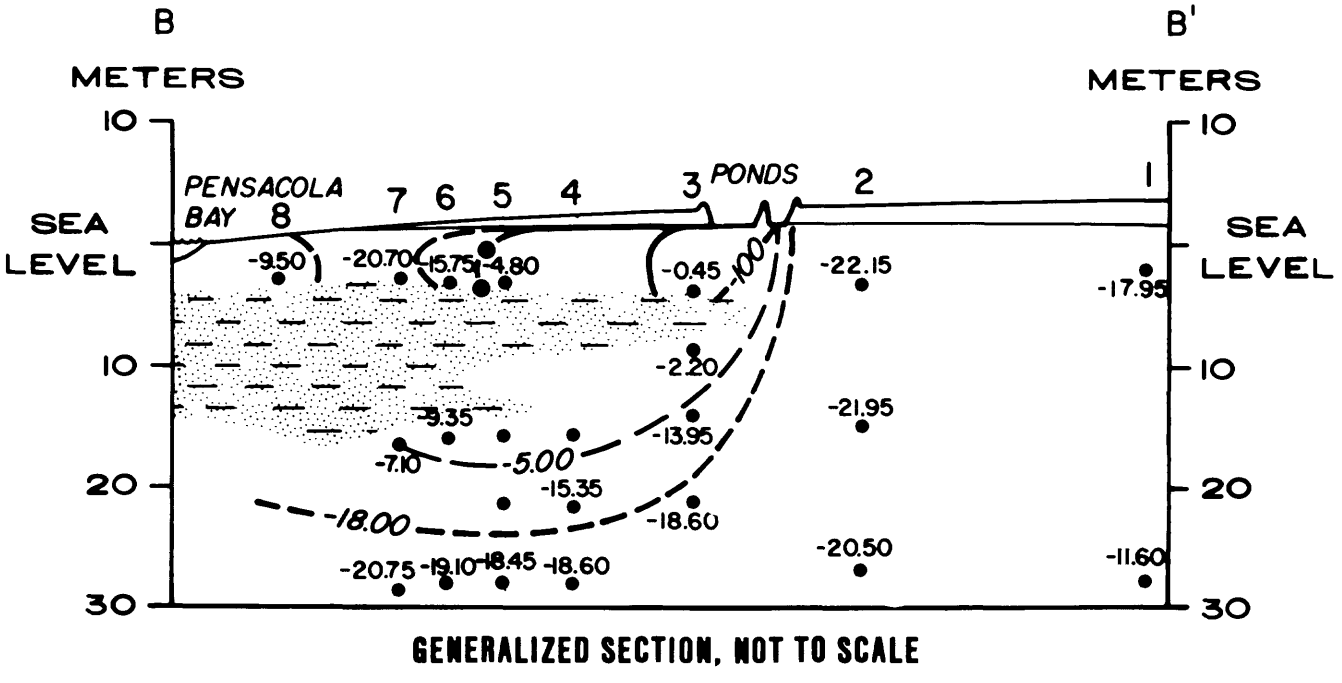
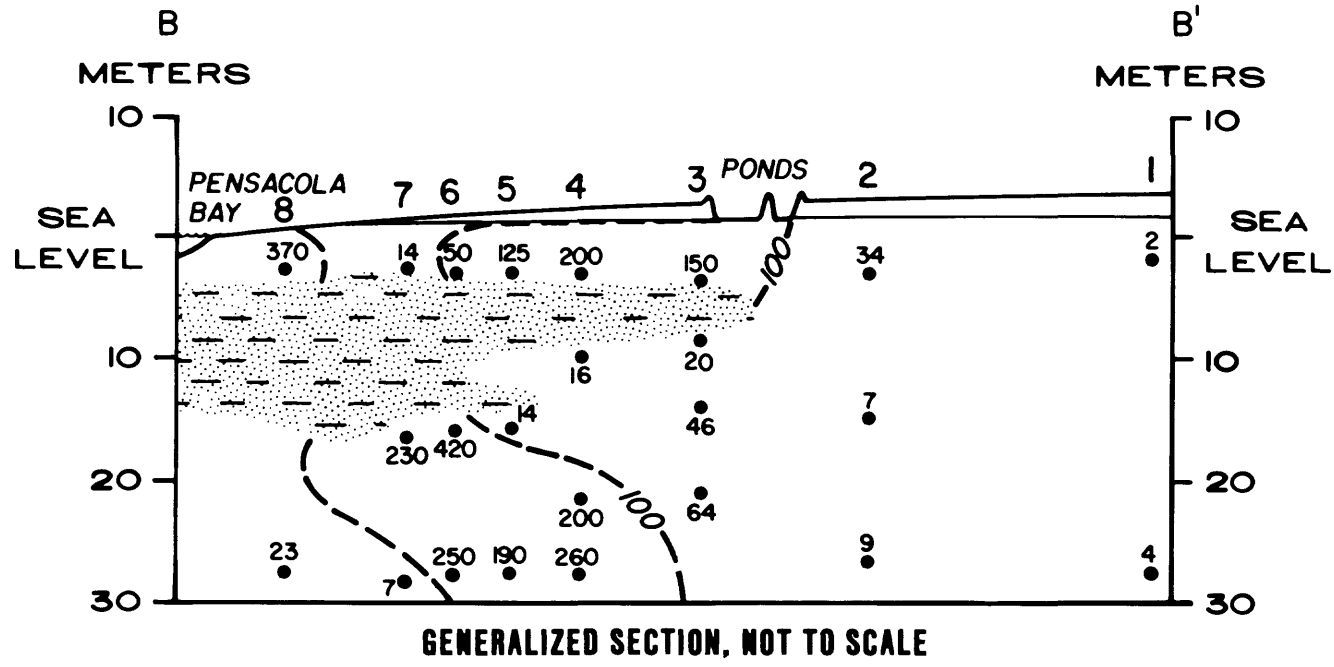


Figure 7. Distribution of methane dissolved in ground water and carbon 13 values of dissolved organic carbon, generalized section B–B'.



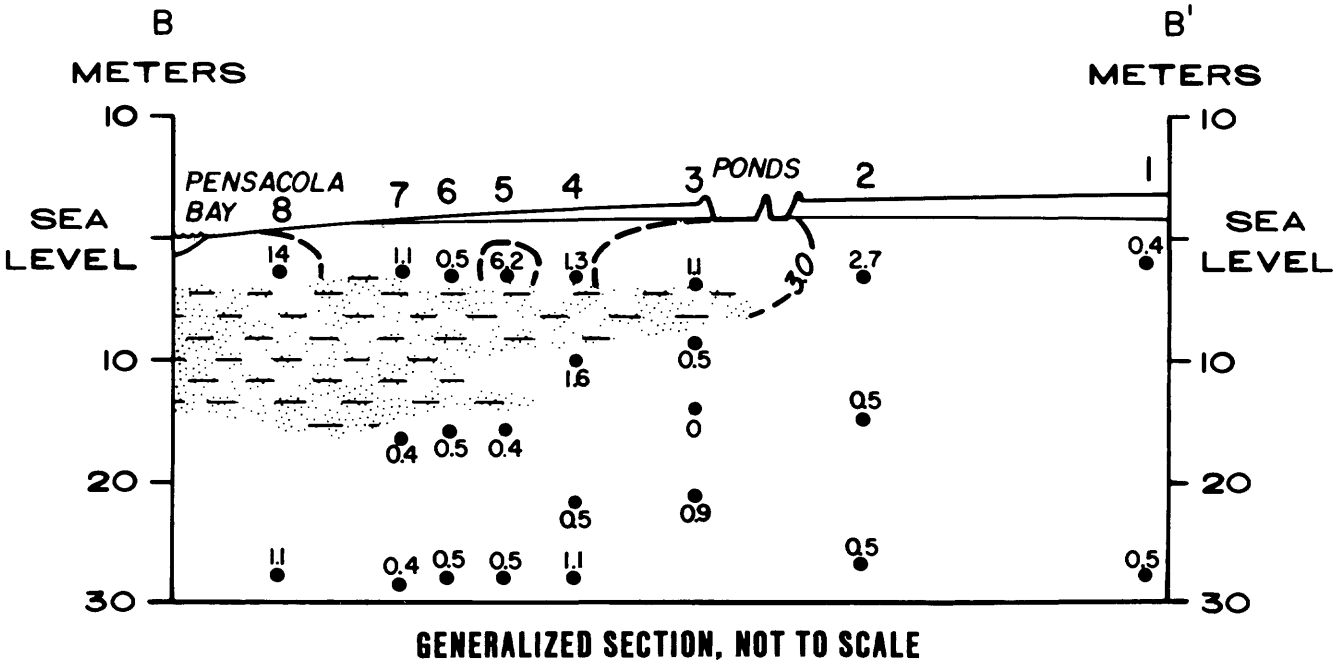


Figure 8. Distribution of iron and manganese dissolved in ground water, generalized section B–B'.

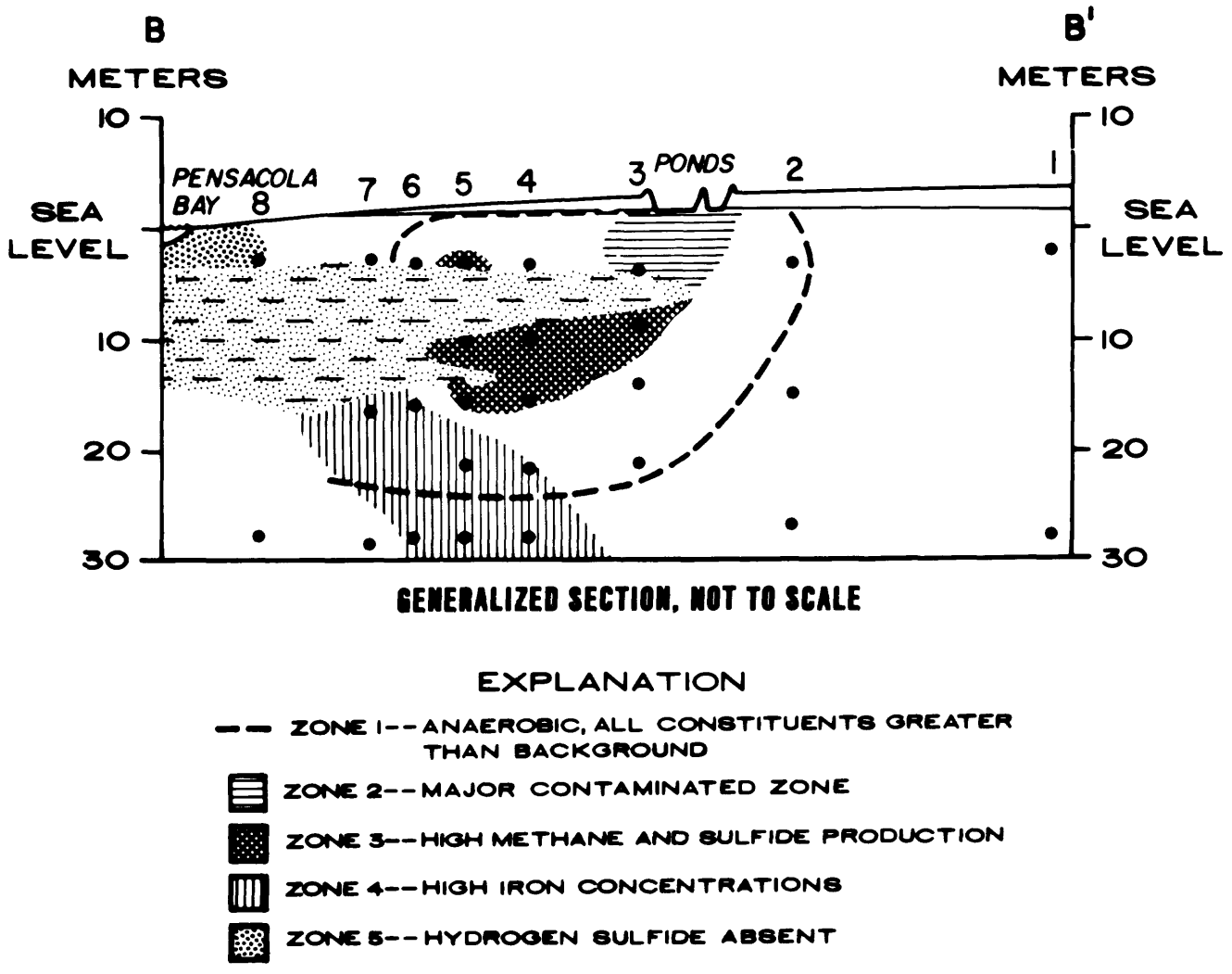


Figure 9. Location of zones based on the concentrations of unstable chemical constituents dissolved in ground water, generalized section B–B'.

REFERENCES CITED

Baedecker, M.J., and Back, W., 1979, Hydrogeological processes and chemical reactions at a landfill: Ground Water, v. 17, no. 5, p. 429–437.

Cline, J.D., 1969, Spectrophotometric determination of hydrogen sulfide in natural waters: Limnology and Oceanography 14, p. 454–458.

Golwer, A., Matthess, G., and Schneider, W., 1977, Groundwater contamination by waste deposits and the implications for methods of refuse disposal, *in* Effects of urbanization and industrialization on the hydrological regime and on water quality: Proceedings of the Amsterdam Symposium, October 1977, IAHS–AISH Publication no. 123, p. 365–369.

Chapter C. Analysis of Sand Grain Coatings and Major-Oxide Composition of Samples from a Creosote Works, Pensacola, Florida

By P. P. Hearn, Z. A. Brown, *and* K. O. Dennen

Abstract

This paper is a preliminary report on the inorganic geochemistry and mineralogy of contaminated aquifer sediments at a creosote works in Pensacola, Florida. The chemical environment of the aquifer and possible chemical reactions with contaminant phases are assessed.

Samples from the permeable zone underlying the creosote works test site are predominantly quartz sand and minor amounts of clay. The estimated clay content, on the basis of analyses of grain coatings and bulk samples, ranges from less than 1 percent to 3 percent.

Because of the proximity of the sandy permeable sediments and the impermeable clay lens, it would seem that the clay coatings on sand grains could have been derived from the same source as the clay lens. Available major-oxide data do not indicate any significant differences between grain coatings in the sandy permeable zone and the impermeable clay lens; both the grain coatings and the clays from the impermeable lens appear to have been derived from a common source.

INTRODUCTION

The leakage of pentachlorophenol and creosote wastes from holding ponds at a creosote works facility in Pensacola, Fla., has resulted in the contamination of ground water in the underlying sand aquifer. As part of a study being coordinated by the U.S. Geological Survey, Water Resources Division, the inorganic geochemistry and mineralogy of the aquifer sediments are being studied in order to evaluate their chemical environment and assess possible reactions with contaminant phases. This paper is a preliminary report of the results of this study; it briefly describes the techniques used and summarizes initial findings.

To date, 13 samples from seven sites in the vicinity of the facility (fig. 10) have been examined to determine bulk composition and to evaluate the nature and distribution of clay and iron-manganese oxide coatings on sand grains. Since the permeable zone is composed chiefly of clean quartz sand, clay and oxide grain coatings are the most likely participants in reactions with contaminants in the ground water. Seven samples were taken from the sandy permeable zone of the aquifer, and six from an impermeable clay lens that is intercalated with the sandy sediments (fig. 11). Samples were examined by a combination of scanning electron microscopy (SEM), X-ray fluorescence spectroscopy (XRF), and inductively coupled plasma spectroscopy (ICP). Splits of these samples currently are being analyzed for mineralogy by X-ray diffractometry.

METHODS

Analysis by Scanning Electron Microscopy

Only samples from the permeable sand zone were analyzed by SEM. Samples were dried in an oven at 100°C for 1 hour to remove volatiles, impregnated with epoxy, polished to expose grain cross sections, and coated with a thin layer of carbon. Analysis was carried out on an ETEC Autoscan SEM; "backscattered" electron imaging was the primary mode used during visual examination of sample by SEM. This technique detects electrons that are backscattered after penetrating the sample surface. Simply speaking, the yield of backscattered electrons is proportional to the atomic number of the sample. Because of this, areas of different average atomic number can be resolved in a backscatter image, with zones of higher average atomic number appearing as lighter shades of gray. Phases such as clays, iron-manganese oxides, and quartz can be easily distinguished from each other.

The major-oxide composition of grain coatings was determined by using an EDAX 9100 energy-dispersive X-ray analyzer (EDS). The accuracy obtainable on a polished sample normally exceeds 5 percent

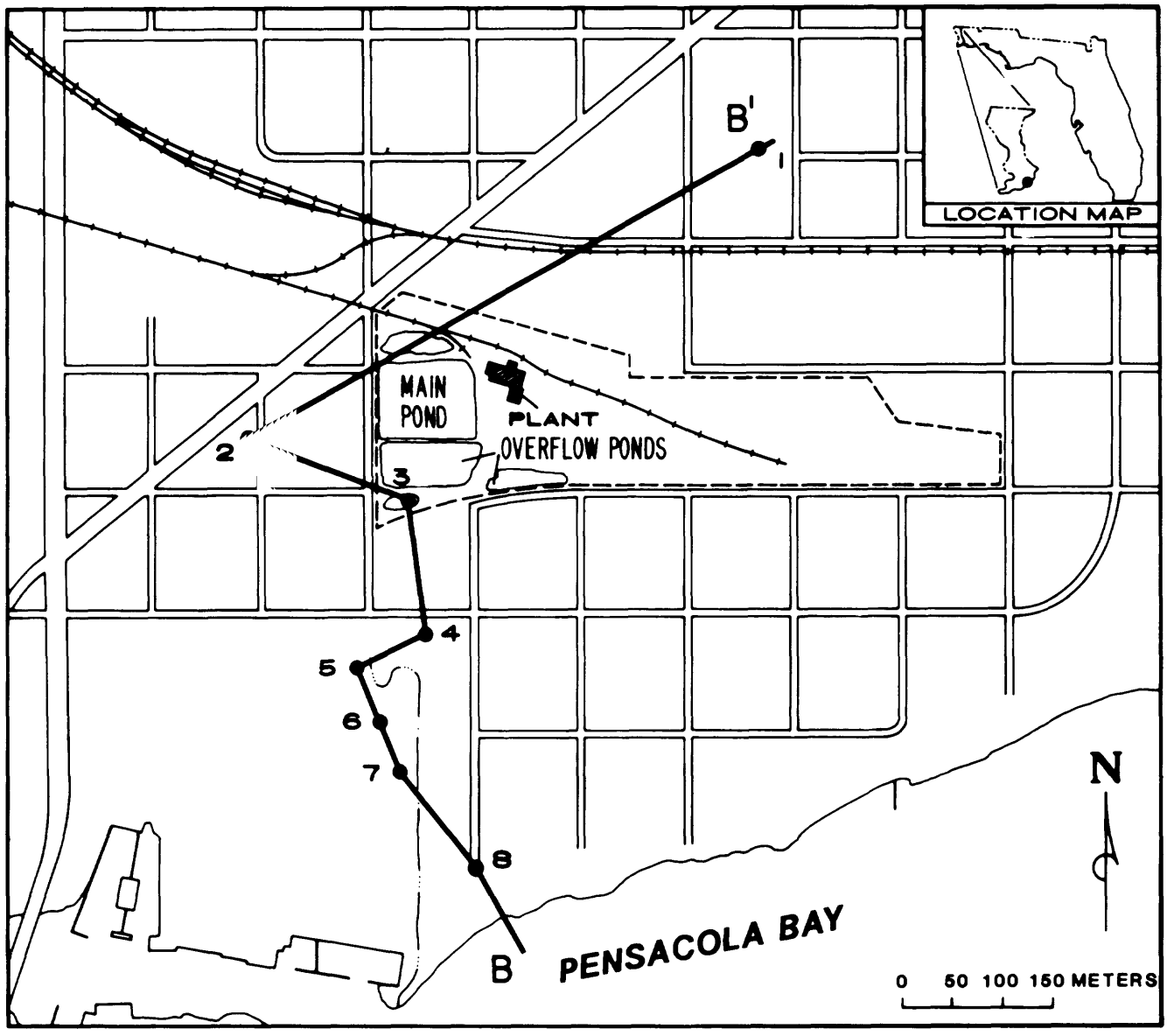


Figure 10. Location of sample well sites.

(relative); detection limits are normally a few tenths of one weight-percent. All analyses are normalized to total 100 percent; structural or adsorbed water (or any element lighter than sodium) cannot be detected.

Discrete phases in samples can be tentatively identified by using chemical analyses from the X-ray analyzer. For minerals containing only one or two elements (quartz, pyrite, gypsum, etc.) the identification is trivial. For more complex compositions the identifications are obviously more speculative. A more definitive evaluation of grain-coating mineralogy will be possible when the results of X-ray diffraction analyses are available.

Analysis by Inductively Coupled Plasma Spectroscopy and X-Ray Fluorescence Spectroscopy

Each of the samples of unconsolidated sand contained in excess of 90 percent SiO_2. To remove

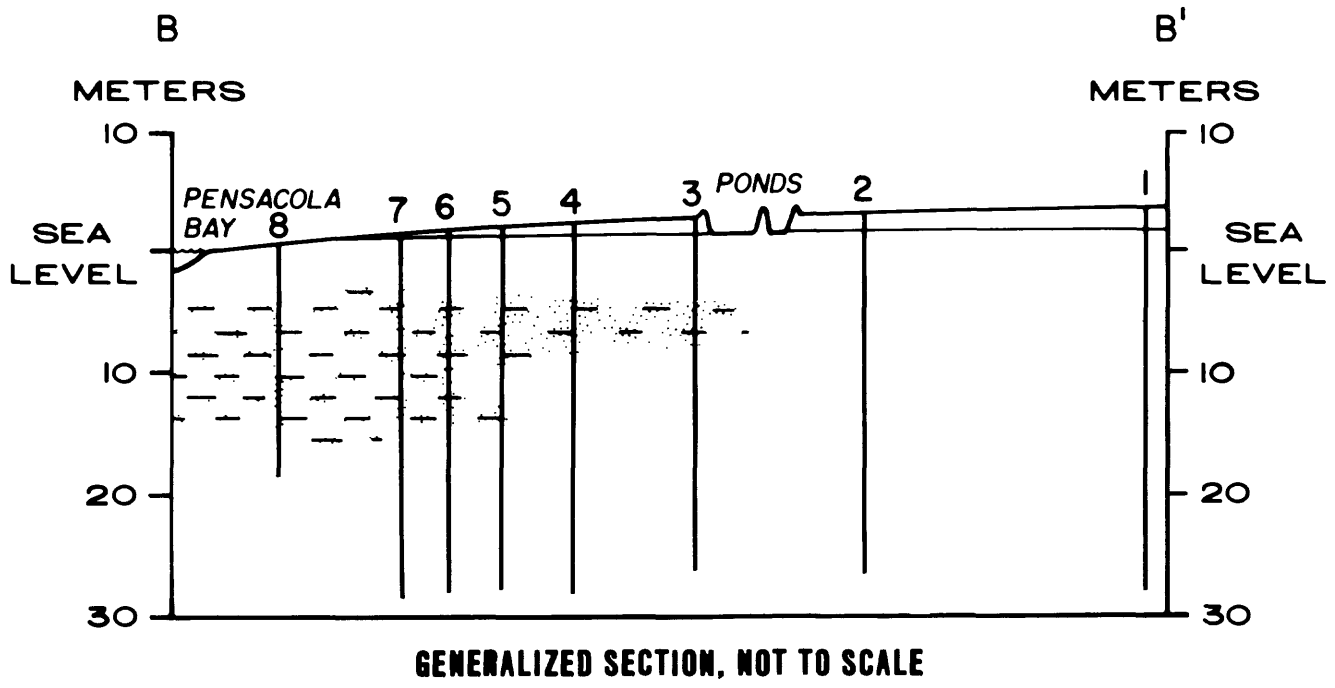


Figure 11. Geologic cross section showing position of wells and location of clay lens. Position of silt-and-clay lens is diagrammatic.

excess silica, samples were digested in hydrofluoric acid overnight and then evaporated to dryness. This procedure volatilizes silica and raises the relative concentration of other elements so they can be analyzed with more accuracy. The residue remaining after the digestion was dissolved in 5 percent hydrochloric acid and analyzed for aluminum, iron, magnesium, calcium, titanium, manganese, and potassium on a Jarrell Ash model 1160 ICP. Relative accuracy of determination exceeded 4 percent for all elements. Silica was determined separately by colorimetric techniques.

Samples from the clay lens were analyzed by energy dispersive XRF. This procedure is less time consuming but somewhat less accurate (<10 percent relative) than ICP analysis. Samples were fused into glass discs by using a flux of lithium tetraborate and were analyzed for silicon, aluminum iron, magnesium, potassium, calcium, titanium, and manganese on a Kevex model 0700 energy dispersive XRF spectrometer.

RESULTS

Bulk Composition

Major-element analyses reflect the quartz-rich nature of the samples from the permeable zone and the higher concentrations of aluminosilicates in samples from the clay lens (table 3). Three of the samples from the clay lens, 420, 560, and 620, are in fact largely quartz sand with minor amounts of clay (88–90 percent SiO_2).

Analysis by Scanning Electron Microscopy

All samples from the permeable zone were predominantly quartz sand; grain size measurements of bulk samples were not made, but visual examination of polished samples suggests a mean grain diameter of 200–300 μm.

Clay was found in all samples, with the exception of 160. Clay occurs primarily as grain coatings but is also present as discrete particles. Coatings are irregular in shape, ranging from 5 to 50 μm in thickness (figs. 12–16). When coatings were present, they almost never surrounded the entire grain; in most cases, coatings covered less than 25 percent of the exposed perimeter.

Representative EDS analyses of grain coatings are given for each sample in table 4. Coatings appear to be primarily aluminosilicates; other phases found (tentative identification based on chemistry) include pyrite and zircon. A single grain of what is believed to be weathered biotite was found as an inclusion in a quartz grain (see 160 for composition). The relatively high aluminum content in most of the coatings suggests that kaolinite may be a major component, but concentrations of other elements indicate that additional phases are also present.

Table 3. Major-oxide composition of samples from clay lens and permeable zone

[Last two digits of sample number indicate depth of well, in feet; –, not detected]

Sample No.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO
Samples from clay lens (values in weight percent)									
420	88	8.8	2.7	0.3	0.8	–	0.3	0.5	0.0
560	91	6.6	2.0	.3	.8	–	.2	.4	.0
620	92	3.1	.7	.3	.0	–	.1	.3	.0
640	60	20	7.5	2.0	1.0	–	.7	.8	.1
720	63	22	4.2	.3	.2	–	.6	.9	.1
760	62	24	7.8	.3	.6	–	.9	1.0	.1
Samples from permeable zone (SiO_2, Al_2O_3, and Fe_2O_3 values in weight percent; all other values in parts per million)									
160	95	.10	.01	35	44	21	4	180	3
240	93	.67	.09	190	91	75	280	980	8
350	95	.33	.05	150	220	100	150	610	7
440	93	.58	.22	310	260	58	270	750	17
520	94	.30	.08	190	110	57	93	320	7
660	92	1.70	.15	320	100	81	800	1,300	7
750	92	.77	.44	900	440	76	610	1,000	30

Table 4. Major-oxide, chloride, and sulfur composition of grain coatings (water free)

Sample No.	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	CaO	K_2O	TiO_2	MnO	Cl	S
160–1	33.7	14.8	30.6	5.0	0.3	0.0	11.	4.3	0.2	0.0	0.0
240–1	58.1	33.5	2.6	1.1	.4	.4	1.8	2.0	.0	.1	.0
240–2	54.9	37.2	3.3	.5	.1	.4	1.7	1.4	.1	.4	.0
240–3	52.4	36.9	4.3	1.0	.3	.5	1.6	1.5	.0	.3	.0
350–1	53.1	34.7	4.2	1.4	.4	2.8	1.2	1.6	.0	.6	.0
350–2	53.9	35.4	3.2	1.6	1.0	2.0	1.3	1.3	.0	.4	.0
350–3	53.3	34.9	3.8	1.4	.6	2.5	1.4	1.4	.1	.6	.0
440–1	54.0	25.3	8.7	2.8	1.0	.8	.8	5.5	.0	.7	.4
440–2	53.3	27.0	10.9	1.1	.0	1.2	2.4	2.9	.0	.0	1.2
440–3	26.9	13.9	52.5	.0	.2	.6	.1	.9	.1	.1	4.6
520–1	51.1	32.4	6.8	2.2	.2	2.9	1.7	2.2	.2	.0	.4
520–2	61.2	25.6	4.4	2.5	.5	1.5	2.6	1.1	.0	.2	.6
520–3	56.0	29.8	5.9	1.9	.5	2.0	1.4	1.6	.0	.2	.6
750–1	57.5	24.7	10.3	1.9	.5	.6	1.3	1.2	.3	.4	1.4
750–2	64.5	18.9	10.8	1.7	.0	.7	1.4	.7	.1	.0	1.1
750–3	55.3	25.9	12.1	2.1	.1	.4	1.6	.8	.1	.0	1.6

No discrete iron or manganese was found, but elevated concentrations of iron in grain coatings in three samples (350, 520, and 750 in table 4) suggest that some iron phase is admixed with clays. Grain coatings in all of these samples contain particles of iron sulfide, probably pyrite or marcasite (see fig. 14). Analyses of zones showing no discrete particles exhibit significant concentrations of both iron and sulfur, yet more iron is present than could be coordinated as a sulfide. Even after adjusting iron values downward to account for silicate-bound iron, molar iron to sulfur ratios are much higher than expected for iron monosulfides or disulfides (fig. 17). Since these samples are located in a zone depleted in oxy-

Figure 12. Scanning electron micrograph of grain coatings from sample 240 taken from the permeable zone (back-scattered electron image). Bar indicates scale in micrometers.

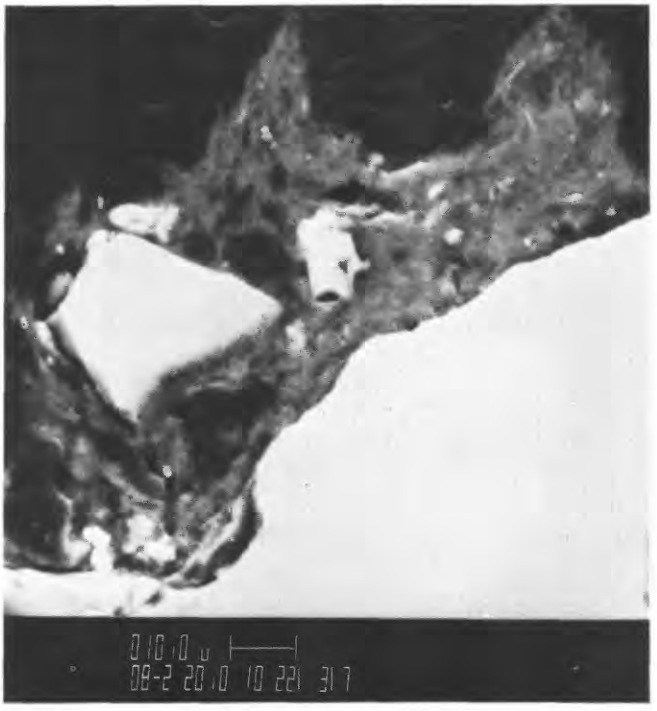


Figure 13. Scanning electron micrograph of grain coatings from sample 350 taken from the permeable zone (back-scattered electron image). Bar indicates scale in micrometers.

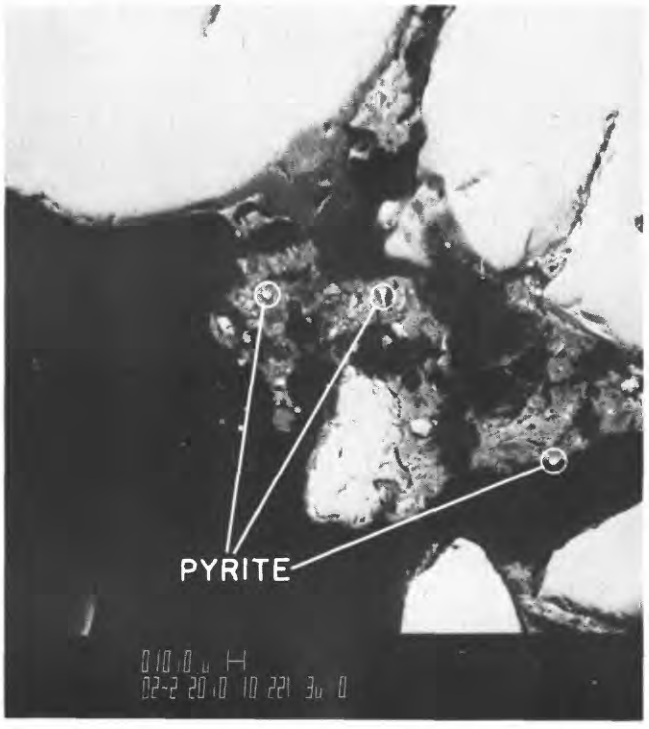


Figure 14. Scanning electron micrograph of grain coatings from sample 440 taken from the permeable zone (back-scattered electron image). Bar indicates scale in micrometers.

Figure 15. Scanning electron micrograph of grain coatings from sample 520 taken from the permeable zone (back-scattered electron image). Bar indicates scale in micrometers.

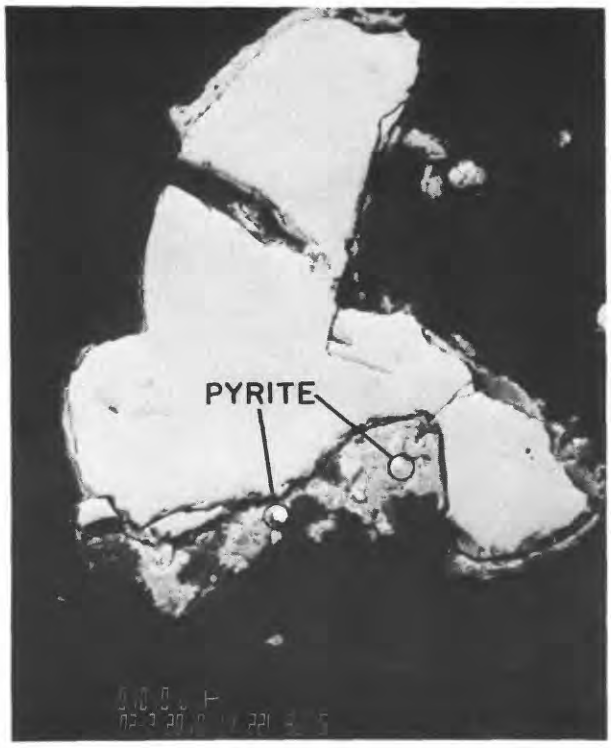


Figure 16. Scanning electron micrograph of grain coatings from sample 750 taken from the permeable zone (backscattered electron image). Bar indicates scale in micrometers.

gen (see chapter B, Baedecker and Lindsay), the excess iron is probably not present as a ferric oxide or hydroxide. It is more likely to be present as the ferrous carbonate, siderite. While the presence of siderite has not been confirmed directly, thermochemical calculations using the solubility-equilibrium computer model WATEQF show ground water at these sites to be saturated with respect to this mineral (M. Baedecker, oral commun., 1984).

Measurement of Total Mass of Grain Coatings

An estimate of clay content was made by point counting 100 grains from backscattered SEM photos of each sample. The percentage of grains having clay coatings ranged from 0 (sample number 160) to 36 percent (sample 750). The other sample numbers and percentages are as follows: 240, 25 percent; 350, 9 percent; 440, 26 percent; and 520, 7 percent.

In spite of the problems that one might expect to encounter with this technique (such as variable grain size, coating geometry, and thickness), there is very good agreement between these measurements and the results of aluminum analyses (fig. 18). Using the EDS values for aluminum in the coatings and the bulk aluminum values, we estimated the total mass of coatings to range from less than 1 percent to slightly greater than 3 percent. The "background" of 0.10 percent aluminum (sample 160) probably does not represent grain coatings but rather aluminosilicate inclusions in the quartz grains.

Source of Grain Coatings

Because of the proximity of the sandy permeable sediments and the impermeable clay lens, it would seem that the clay coatings on sand grains could have been derived from the same source as the clay lens. Until the results of X-ray diffraction work are available, major-oxide data are the only means of evaluating this possibility. Data for samples from the permeable zone and the clay lens are shown on a molar plot of aluminum, potassium, and titanium in figure 19. These elements were chosen because (1) they were consistently detected in all samples and (2) they are not affected by the precipitation of secondary minerals such as pyrite and calcite.

Data from the two sample groups fall into two clusters, which are very close together but nonetheless distinct. It is quite possible that this difference is analytical; this question will be resolved when more accurate ICP analyses of the clay lens samples are available. The data for grain coatings show more scatter than the data for the clay lens samples; this is not surprising since the clay lens data are bulk analyses. In any case, these data do not suggest different sources for the coatings on sand grains and the clays in the impermeable lens. The simplest explanation would involve a common source for both the coatings and the clay lens.

CONCLUSIONS

Samples from the permeable zone underlying the creosote works test site are predominantly quartz sand (>90 percent SiO_2); minor amounts of clay are present primarily as grain coatings. The estimated clay content, on the basis of aluminum analyses of grain coatings and bulk samples, ranges from less than 1 percent to 3 percent. The good agreement of bulk aluminum analyses and point counting measurements indicates that point counting is a reasonably accurate technique for measuring relative differences in the amount of grain coatings between samples.

Molar Fe/S ratios of some samples indicate an excess of iron over what could be precipitated as sulfides. The oxygen-depleted environment common to these samples suggests that the excess iron is not

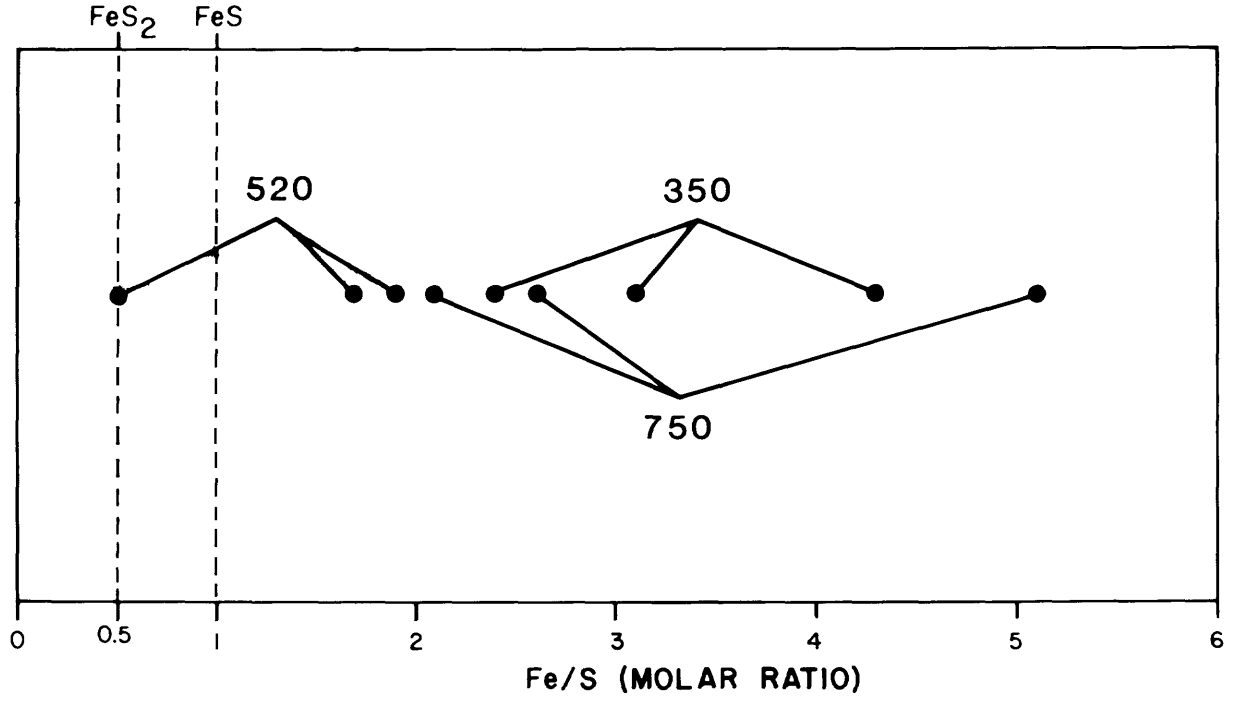


Figure 17. Iron to sulfide ratios for grain coatings in samples 350, 520, and 750. All values obtained from zones free of discrete iron-sulfide particles. To correct for silicate iron, iron values are adjusted downward by the average of analyses from other nonpyritic samples.

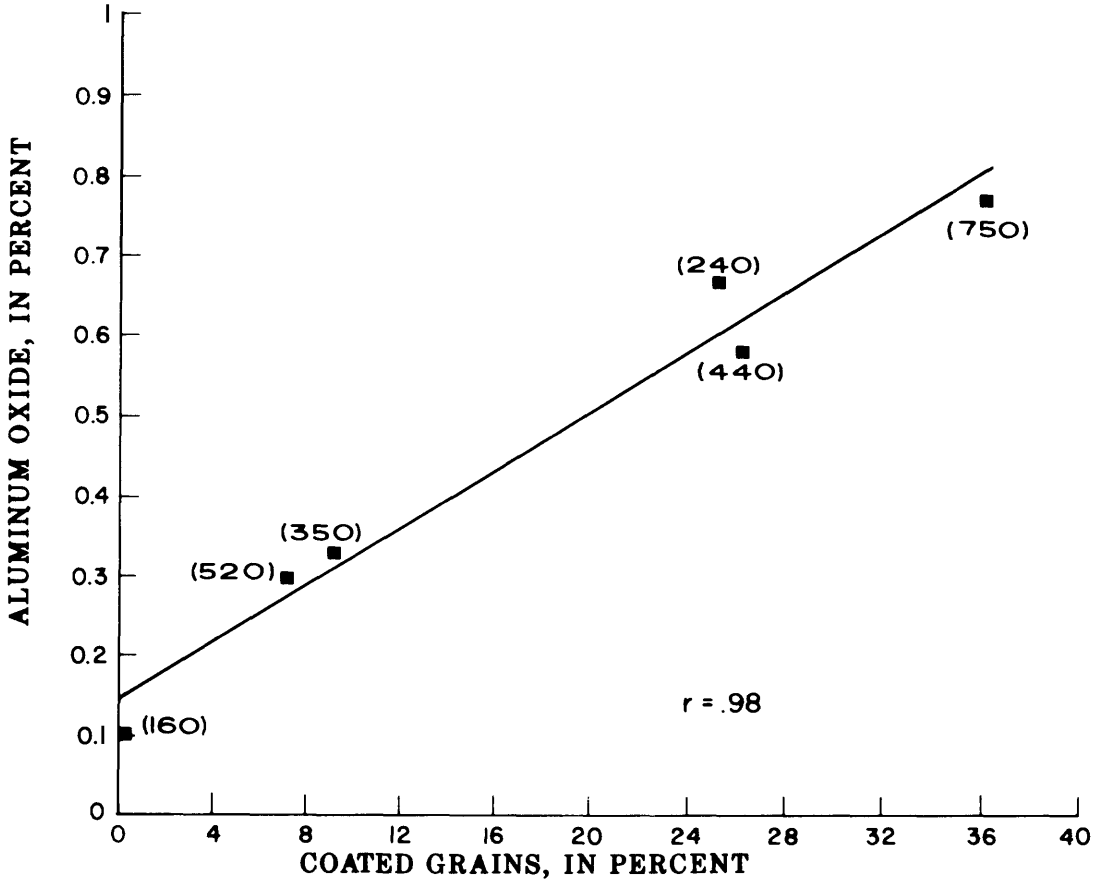


Figure 18. Percent coated grains (by point count) versus bulk percent aluminum oxide in samples from permeable zone.

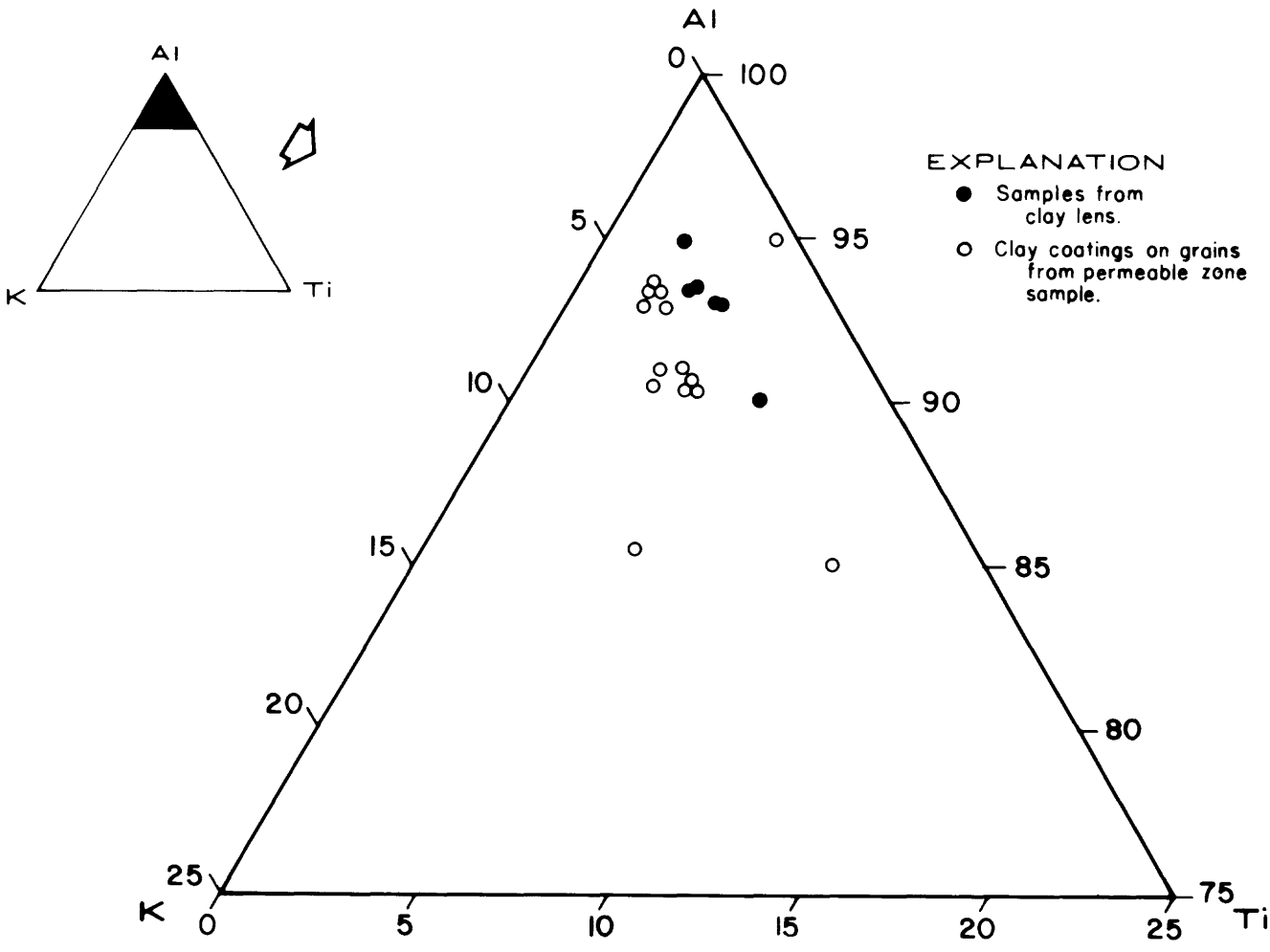


Figure 19. Molar plot of aluminum, potassium, and titanium for bulk analyses of clay lens samples and analyses of grain coatings in permeable zone samples.

present as a ferric oxide or hydroxide, but rather as siderite.

Available major-oxide data do not indicate any significant differences between grain coatings in the sandy permeable zone and the impermeable clay lens; both the grain coatings and the clays from the impermeable lens appear to have been derived from a common source.

Chapter D. Microbial Transformations of Quinoline in Soil at a Hazardous-Waste Site Near Pensacola, Florida

By Jon L. Bennett, David M. Updegraff, Wilfred E. Pereira, *and* Colleen E. Rostad

Abstract

Chemical and microbiological studies on groundwater, soil, and sediment samples collected from the site of a creosote works in Pensacola, Florida, showed heavy contamination with chemicals derived from creosote. The most abundant heterocyclic nitrogen compound in creosote is quinoline, and chemical studies indicated the presence of large amounts of 2-quinolinone in the water samples. Studies to isolate quinoline-degrading microorganisms were conducted to explore the hypothesis that quinoline and other heterocyclic compounds in the contaminated zone may be converted by bacterial action into oxygenated derivatives that generally have enhanced both solubility in water and mobility in hydrogeologic environments. Soil samples and both surface- and groundwater samples contained large numbers of bacteria capable of oxidizing quinoline to 2-quinolinone. All were aerobic, and all identified, to date, were members of the genus *Pseudomonas*, including *P. pseudoalcaligenes, P. putida, P. fluorescens,* and *P. chloraphis.* Evidence was found for at least one alternative pathway of aerobic quinoline degradation.

INTRODUCTION

Many organic compounds that infiltrate the soil zone are subject to degradation by soil microorganisms. Compounds that are not readily degraded by microorganisms are considered to be refractory. One class of compounds that is considered potentially hazardous to health is heterocyclic nitrogenous bases, many of which exhibit mutagenic activity (Rubin and others, 1976; Nagao and others, 1977). These compounds are relatively water soluble and generally considered refractory (Cooper and Catchpole, 1973; Bark and others, 1972). Among these nitrogenous bases is quinoline, a heterocyclic nitrogen compound. Little is known of the fate of the compound in soil or water environments, although Funchess (1917) reported that quinoline was degraded in acid soils to form nitrate as one degradation product; the addition of 1 percent of lime to the soil prevented the degradation of quinoline to nitrate. Grant and Al-Najjar (1976) isolated a bacterium, believed to be a species of *Moraxella*, that oxidized quinoline to 2-hydroxyquinoline under aerobic conditions. Subsequently, 2-hydroxyquinoline disappeared and a sequential oxidation was proposed in which the 2-hydroxyquinoline was oxidized to 2,6-dihydroxyquinoline, then to 2,5,6-trihydroxyquinoline, and finally to a yellow meta-cleavage product that was not further degraded.

Pereira and Rostad (chapter E) isolated 2-quinolinone from several wells at the site of a creosote works near Pensacola, Fla., and identified the compound by gas-chromatography mass-spectrometry. The origin of 2-quinolinone in ground water suggested that this compound might be derived from quinoline. Quinoline makes up about 20 percent of the nitrogen bases in coal tar and possibly even a larger percentage in creosote. Because of the abundance of this compound, its solubility in ground water, and its refractory nature, quinoline has the potential for being extremely mobile in hydrogeologic environments and, therefore, will migrate considerable distances from the point of origin in the aquifer.

The basic hypothesis of this research is that polynuclear aromatic compounds, including quinoline, are transformed in the unsaturated zone by microbially-mediated processes, such as enzymatic hydroxylation, yielding oxygenated derivatives that generally have enhanced both solubility in water and mobility in hydrologic environments. The work of Pereira and Rostad identified 2-quinolinone as an oxygenated derivative of this type in the contaminated zone. At the pH of ground water in the contaminated zone (pH 5 to 6 units) 2-hydroxyquinoline, reported to be formed from quinoline by bacterial action (Grant and Al-Najjar, 1976), will be transformed into its tautomer, 2-quinolinone. There are large numbers of bacteria in the contaminated soil and water at the site that are able to convert quinoline to 2-quinolinone.

SITE AND SAMPLING VISITS

The creosote works in Pensacola, Fla., operated from 1902 to 1981, treating utility poles with creosote and pentachlorophenol. Wastewaters were discharged into two unlined surface impoundments. These impoundments were in direct contact with an unconsolidated, highly permeable sand-and-gravel aquifer. Samples were collected on July 22, 1983, October 25, 1983, and January 9 through 13, 1984. The last two samplings occurred after massive cleanup efforts had modified the site.

MATERIALS AND METHODS

Samples of soil and water were collected aseptically in heat-sterilized 1-L glass bottles and kept refrigerated for approximately 3 months until analyzed.

Quinoline-degrading microorganisms were isolated from soil or water by adding 5 g of inoculum and 0.02 g of quinoline (not sterilized) to 100 mL of autoclaved Stainier's mineral medium containing per 1 L of deionized water: NH_4Cl, 1 g; K_2HPO_4, 1 g; $MgSO_4 \cdot 7H_2O$, 200 mg; $FeSO_4 \cdot 7H_2O$, 10 mg; $CaCl_2$, 10 mg; and trace-elements solution, 1 mL. The trace-elements solution contained, per 1 L of deionized water: $Na_2MoO_4 \cdot 2H_2O$, 0.1 g; $MnCl_2 \cdot 4H_2O$, 0.1 g; $CuSO_4$, 0.1 g; $CoCl_2$, 0.1 g; and $ZnSO_4 \cdot 7H_2O$, 0.1 g. Uninoculated control tubes showed no sign of bacterial growth. An agar medium was prepared for the isolation of quinoline-degrading bacteria by adding 0.1 g of yeast extract and 15 g of Oxoid purified agar to 1 L of the above quinoline medium. Nutrient agar plate counts were carried out on tenfold dilutions from 1-g portions of soil or water by the pour-plate method.

Most probable number (MPN) determinations also were carried out on the soil and water samples, using the liquid quinoline medium. Three tubes were inoculated from each of three or more tenfold dilutions of the sample, and the MPN values were read from the table in the American Public Health Association's Standard Methods for the Examination of Water and Wastewater, 14th ed. (1976). Pure cultures were isolated by streaking from these cultures to nutrient agar plates.

Quinoline degradation was followed by recording the ultraviolet absorption spectrum of the clear supernatant of a centrifuged culture from 210 to 400 nm. All cultures were incubated at 28°C to 30°C. Bacteria were identified by the usual battery of tests, including cultural, morphological, and biochemical observations, as described in the ASM Manual of Methods for General Bacteriology (Gerhart, 1981) and Starr and others (1981).

RESULTS AND DISCUSSION

Despite the heavy amount of creosote contamination in some of the samples, the bacterial counts were surprisingly high, although the bacterial diversity was lower than the number found in less contaminated areas.

In keeping with the hypothesis that compounds from creosote formerly considered refractory are solubilized by bacterial enzymatic action, it was decided to concentrate on aerobic microbial processes at the plant site. Through the use of the data from the plate counts, certain areas were identified where both heavy contamination as well as high bacterial counts were present. These were generally areas that apparently had been periodically submerged and then dried, as in shallow pools near a series of storage tanks. Several sites were selected in this storage tank area where, in the October 1983 trip, sampling in large volume was planned. Sampling of the soil at specific depth intervals to determine the extent and type of bacterial activity was to be of prime importance.

The unexpected cleanup of the site by the time of the October trip precluded much of the proposed sampling. The area where the tanks had been was bulldozed and covered with clay. A small amount of uncovered, bulldozed material remained near the overflow pond. Because of the disruption, the soil was unstratified and ranged from slightly contaminated sand in one pile to highly contaminated sand in another pile to creosote-coated wood chips in a third pile. Since this was the last area from which the type of material of interest could be obtained, samples were taken from these various piles. Several other sites that had not been disrupted were chosen, and stratified samples were obtained. However, these sites were removed from the areas of heaviest contamination.

To date (April 1984), tests have centered on quinoline degradation by bacteria from two locations at the plant site. The first site, sampled in July, is in an area near a small pool located just south of the overflow pond. The soil from this area supported grasses and other small plants and could be considered relatively free of creosote. However, it was underlain by a caliche-type, hard, tarry layer that was underlain by grayish sand having a strong naphthalene odor. In comparison to the soil from the plant site, this soil was determined to be less contaminated. The other soil was from the bulldozed area, mentioned previously, and was considered contaminated.

Five grams inocula from both the contaminated and less contaminated sites were placed in flasks that were incubated aerobically at 30°C and frequently

agitated. Ultraviolet (UV) spectra of centrifuged aliquots from the flasks, scanning from 400 to 210 nm, showed an alteration of quinoline to 2-quinolinone, followed by degradation of the quinolinone itself. The ultraviolet spectrum of quinoline is shown in figure 20, and that of 2-quinolinone is shown in figure

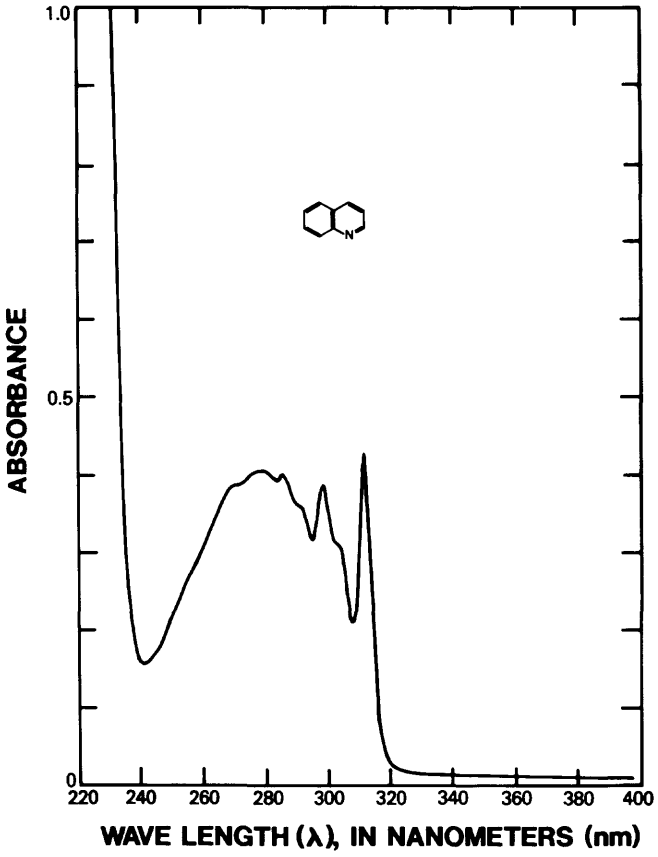


Figure 20. Ultraviolet spectrum of quinoline.

21. This alteration was apparent in samples taken from both flasks; however, it required approximately 4 days for this to occur for the less contaminated soil and only 1 day for the contaminated soil. This time differential indicates that a greater number of quinoline-degrading organisms were present or were more adapted in the contaminated soil than in the less contaminated soil, thereby causing faster degradation.

At frequent intervals, 1-mL aliquots from these flasks were serially transferred to fresh flasks containing Stainier's medium and quinoline. This had two effects: (1) it reduced the amount of extraneous organic material carried over from the soil inoculum, which gave a clearer UV spectrum of quinoline; and (2) the rate of growth of quinoline-degrading bacteria increased with each subculture, the bacteria being better adapted to degrade quinoline. A positive iden-

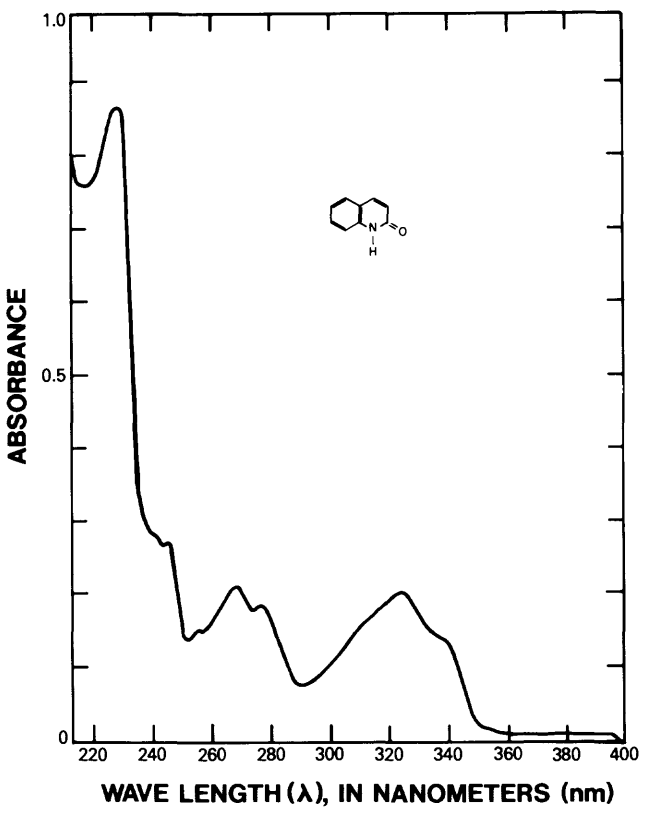


Figure 21. Ultraviolet spectrum of 2-quinolinone.

tification of 2-quinolinone, produced by the bacterial oxidation of quinoline, was made by mass spectrometry (fig. 22).

To isolate these organisms, aliquots from subcultured flasks were streaked onto nutrient agar plates. Colonies were picked to obtain pure cultures. Eight pure cultures (as shown by repeated streaking onto nutrient agar) of quinoline-degrading organisms were isolated from these cultures: two from less contaminated soil and six from contaminated soil. All were subjected to the usual sequence of tests for the classification of bacteria, as described by Starr and others (1981); results are shown in table 5. All eight cultures were small, gram-negative, rod-shaped bacteria, actively mobile by one or a few polar flagella. All grew rapidly on nutrient agar, on King's agars A and B, on glucose mineral salts agar, and on nitrate broth; and five of the eight cultures produced fluorescent-yellow pigment on King's agar B. None produced pyocyanin. All grew well from 28°C to 42°C, but none grew at 4°C. Colonies on nutrient agar after 24 hours incubation at 30°C were described as follows: all were cream-colored; 1 was rough-circular, translucent, 1 to 2 mm in diameter; 2, 3, and 5 were slightly rough, circular, translucent, 2 to 3 mm in diameter; 4 and 8 were smooth-circular, entire, 1 to 2 mm in diameter; and 6 and 7 were rough, irregular,

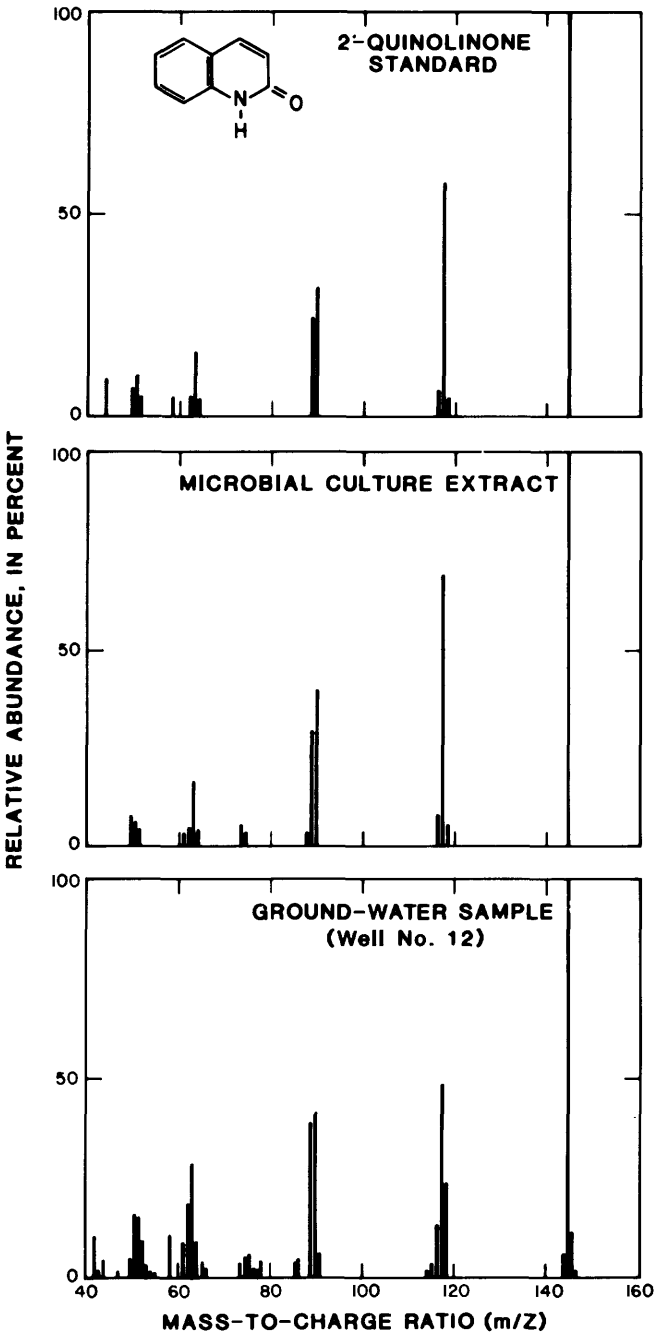


Figure 22. Mass spectra of 2-quinolinone standard; microbial culture extract; and ground-water sample.

spreading, 1 to 2 mm in diameter. Colonies on YDC agar (Starr and others, 1981) were cream-colored for all cultures. All cultures grew well, producing typical red circular colonies on the highly selective plating medium developed for the isolation of *Pseudomonas* by Levesque and Nogrady (1981). All were aerobic. On the basis of these tests, all eight cultures are species of *Pseudomonas* as listed: cultures 1, 2, and 8, *Pseudomonas pseudoalcaligenes*; cultures 3 and 5, *Pseudomonas putida*; cultures 4 and 6, *Pseudomonas fluorescens*; and culture 7, *Pseudomonas chloraphis*.

Table 5. Identification tests on quinoline-degrading bacteria

[Source: C, contaminated soil; L, less contaminated soil; + = positive test; 0 = negative test; – = test not completed]

Test	Culture number							
	1	2	3	4	5	6	7	8
Source	C	L	C	C	C	C	C	L
Cytochrome C oxidase	+	+	+	+	+	+	+	+
Gelatin liquid	0	0	0	+	0	+	+	0
Nitrate reduced to nitrite	0	+	0	0	0	+	+	+
Simmons citrate	+	+	+	+	+	+	–	–
Arginine dihydrolase	+	+	+	+	+	+	+	+
[1]Sucrose	0	0	0	0	0	0	0	0
[2]Hydrogen	0	0	0	0	0	0	0	0

[1]Sucrose utilization in mineral salts medium.
[2]Autotrophic growth on H_2 in mineral salts medium.

So far, only pseudomonads have been isolated from the contaminated soil. Attempts to isolate fungi from contaminated soil on both nutrient agar and potato dextrose agar have failed. It would appear, therefore, that pseudomonads were the predominant organisms in the soil that were capable of using quinoline. Since they are known to possess multiple metabolic pathways and have high resistance levels to many toxic chemicals, this was not unexpected. However, this result cannot be interpreted to mean that these are the only organisms that are active in this process or other degradative processes at the site.

To determine the distribution of microorganisms at the site, both nutrient agar pour plates and quinoline MPN tests were performed. This was done most extensively on surface- and ground-water samples taken during the January trip.

Nutrient agar pour plates showed zero, or very low counts, in areas where the water was most contaminated. This is evident both from the horizontal distance from the plant area and from vertical stratification at each well site. Although the count is expected to decrease with depth, even in an uncontaminated well, the effect was more pronounced in wells having high levels of contamination. As a result, these bacterial counts may be useful in delineating the extent of the plume.

MPN data indicate large numbers of quinoline-degrading organisms from contaminated soils. However, these tests are not complete. By combining data from the pour plates and the quinoline MPN tests, not only the number of organisms present can be determined but a ratio can be established as to how many of these organisms possess quinoline-degrading capability.

Quinoline-degrading pathways also are being studied. Grant and Al-Najjar (1976) mentioned the formation of a pink-colored substance by bacterial oxidation of 4-hydroxyquinoline. Although the majority of the organisms we have isolated do not produce this color during the degradation process, we have recently isolated one organism that does, although it is unidentified. Production of a pink substance may be an indication of an alternative pathway being followed by this organism.

CONCLUSIONS

Ground-water samples collected from a creosote-contaminated aquifer contain large amounts of 2-quinolinone. Soil samples and surface and ground water from the area contain large numbers of aerobic bacteria that convert quinoline into 2-quinolinone. Quinoline, the principal nitrogen-heterocyclic compound in creosote, is thus transformed by microbial oxidation into an oxygenated derivative that probably has enhanced solubility in water and mobility in hydrologic environments.

SELECTED REFERENCES

Al-Najjar, T.R., Grout, R.J., and Grant, D.J.W., 1976, Degradation of 4-hydroxyquinoline (kynurine) by a soil pseudomonad: Microbios Letters, v. 1, no. 3–4, p. 157–163.

American Public Health Association, 1976, Standard methods for the examination of water and wastewater, 14th ed.: Washington, D.C., APHA, 193 p.

Bark, L.S., Cooper, R.L., and Wheatstone, K.C., 1972, The determination of organic bases in carbonization effluents: Water Research, v. 6, no. 1, p. 117–126.

Cooper, R.L., and Catchpole, J.R., 1973, The biological treatment of carbonization effluents, IV. The nitrification of coke-oven liquors and other trade wastes and the enhancement of biological oxidation of resistant organic compounds by the addition of growth factors to activated sludge: Water Research, v. 7, p. 1137–1153.

Environmental Science and Technology, 1983, v. 17, October, p. 461A.

Freeze, R.A., and Cherry J.A., 1979, Groundwater: Englewood Cliffs, N.J., Prentice Hall, Inc., 604 p.

Funchess, M.J., 1917, The nitrification of pyridine, quinoline, guanidine, carbonate, etc. in soils: Alabama Agricultural Experiment Station, Alabama Polytechnic Institute, Auburn, Alabama, Bulletin 191, 1 v.

Gerhardt, P., ed., 1981, Manual of methods for general bacteriology: Washington, D.C., American Society for Microbiology, 524 p.

Grant, D.J.W., and Al-Najjar, T.R., 1976, Degradation of quinoline by a soil bacterium: Microbios, v. 15, no. 61–62, p. 177–189.

Levesque, M., and Nogrady, G.L., 1981, Selective and high recovery medium for the isolation of *Pseudomonas aeruginosa*: Abstracts of the 81st annual meeting of the American Society for Microbiology, v. 21, p. 215.

Nagao, M., Yahegi, T., Senino, Y., Sugimura, T., and Ito, N., 1977, Mutagenicities of quinoline and its derivatives: Mutation Research, v. 42, no. 3, p. 335–342.

Rubin, I.B., Guerin, M.R., Hardigree, A.A., and Epler, J.L., 1976, Fractionation of synthetic crude oils from coal for biological testing: Environmental Research, v. 12, no. 3, p. 358–365.

Starr, M.P., and others, eds., 1981, The prokaryotes: New York, Springer Verlag, 2 v.

Chapter E. Geochemical Investigations of Organic Contaminants in the Subsurface at a Creosote Works, Pensacola, Florida

By Wilfred E. Pereira *and* Colleen E. Rostad

Abstract

Discharge of effluent wastes containing creosote and pentachlorophenol into surface impoundments at a wood-treatment facility has resulted in contamination of a sand-and-gravel aquifer near Pensacola, Florida. Six sites, consisting of three to five wells clustered per site, were sampled to study changes in ground-water chemistry downgradient of the impoundments and to define background concentrations of organic contaminants. Vertical and horizontal distributions of concentrations of dissolved organic carbon indicated the presence of a contaminant plume that had moved a considerable distance from the source of contamination.

Analysis of ground water by gas-chromatography mass-spectrometry near the source of contamination revealed the presence of approximately 80 organic contaminants. Classes of compounds identified included phenols, polycyclic aromatic hydrocarbons, and heterocycles containing oxygen, nitrogen, and sulfur. A selected number of compounds from each chemical class were quantitatively determined in ground-water samples. Vertical and horizontal distributions of phenols, polycyclic aromatic hydrocarbons, and heterocycles indicated the presence of an "oil-zone," a main contaminant plume, and a secondary contaminant plume.

Results of this study indicated that processes such as sorption are relatively insignificant in aquifer materials of low organic-carbon content (<0.1 percent), permitting the migration of different classes of organic compounds en masse through the porous medium. It was determined that interaction of nitrogen heterocycles with surface silanol groups and sorption by the mineral fraction of the porous media are relatively insignificant factors in the migration of these compounds through the porous medium. Solubilization of organic contaminants by high concentrations of native dissolved organic carbon or through formation of intermolecular hydrogen-bonded complexes may play an important role in their transport through the sand-and-gravel aquifer.

INTRODUCTION

Discharge of effluent wastes containing creosote, pentachlorophenol, and diesel fuel into surface impoundments at a wood-treatment facility near Pensacola, Fla., has resulted in contamination of the sand-and-gravel aquifer. This aquifer discharges into a perennial stream and Pensacola Bay; therefore, potential for contamination of the bay and possible harmful effects on the marine ecology exists.

These wastes contain polycyclic aromatic compounds (PAC), many of which are suspected carcinogens and mutagens. Seepage of these chemical wastes from surface impoundments also has resulted in vertical migration of an oil phase through the unsaturated zone to the ground-water table. This oil phase evidently has migrated within the capillary fringe in a horizontal direction parallel to the ground-water table, in the direction of the ground-water gradient, towards a perennial stream and Pensacola Bay. This stream is being contaminated by pools of black oily material that are denser than water. It is possible that many organic contaminants in the capillary fringe partition between the oil and water phases, resulting in ground-water contamination. The oil phase is thereby enriched in PAC and higher-molecular-weight polymers during its passage through the capillary fringe towards the stream and Pensacola Bay. This study is designed to expand our understanding of processes controlling the fate and movement of PAC in the subsurface environment.

HYPOTHESES

1. Partitioning of organic contaminants between the oil and aqueous phases is an important factor in the migration of PAC in the aquifer. Octanol-water or heptane-water partition coefficients of selected organic contaminants can be used to predict the distribution of these compounds between the oil and aqueous phases.
2. Chlorinated dioxin isomers present in the wastes undergo selective chemical or microbial transformation reactions in the unsaturated zone, resulting in alteration of dioxin isomer distributions.

3. PAC are transformed in the unsaturated zone by microbially mediated processes, such as enzymatic hydroxylation, yielding oxygenated derivatives that generally have enhanced solubility in water and mobility in hydrogeologic environments.

APPROACH

1. Characterize oil and water phases and determine the chemical composition of organic compounds associated with the porous media and soil samples. Ground-water and core samples from the unsaturated zone and saturated zones will be analyzed to determine (1) the nature of the organic contaminants; (2) the vertical and horizontal migration of organic contaminants; (3) the changes in ground-water chemistry downgradient of the impoundments; and (4) the background concentrations.
2. Determine the octanol-water and heptane-water partition coefficients of selected organic contaminants and their distributions in oil and water phases.
3. Study chemical and microbial transformation reactions of chlorinated dioxins in soil samples. Determine distributions of chlorinated dioxin isomers in oil and core samples from the saturated and unsaturated zones.

RESEARCH SUMMARY

In July 1983, six sites were selected for well installation in order to sample along the contaminant plume (fig. 23). A cluster of three to five wells was emplaced at each site. Location of these sites and depths of the individual wells were selected to study vertical and horizontal distributions of organic contaminants, obtain information concerning changes in ground-water chemistry downgradient of the impoundments, and define background concentrations. Details of the sampling and analysis protocol have been reported (chapter F, Rostad and others). Two approaches were used to study the contaminant plume: the group-parameter approach, using dissolved organic carbon (DOC), and the specific-compound analysis approach, using gas-chromatography mass-spectrometry (GCMS).

Dissolved Organic Carbon

Dissolved organic carbon (DOC) concentrations in ground-water samples collected from wells from sites 1 and 3 through 7, as a function of well depth, are shown in table 6. Background DOC concentrations in ground water (site 1) ranged between 10 to 13 mg/L. At each depth within the plume the general horizontal distribution of DOC concentrations indicated a decrease in DOC values with increasing distance from the contamination source. However, at site 6, DOC concentrations were greater at depths of 18.3 and 24.4 m. These high DOC values indicated the presence of a secondary contaminant plume moving through the aquifer at a considerable distance from the source of contamination. As expected, vertical distributions of DOC concentrations at each site indicated a general decrease in DOC values with increasing depth.

Analysis for Specific Compounds

Organic compounds in ground water near the source of contamination were isolated and characterized to evaluate vertical and horizontal distributions of organic contaminants in the porous medium of the saturated zone. A ground-water sample from site 3, at a depth of 6.1 m, was analyzed by gas-chromatography mass-spectrometry. Approximately 80 different organic contaminants were present in ground water. Major classes of compounds in ground water included phenols, polycyclic aromatic hydrocarbons (PAH), and heterocycles containing nitrogen, oxygen, and sulfur. PAC, with up to a maximum of four rings, were identified in ground water. Higher-molecular-weight PAC, which are known to occur in creosote and coal tar (Pereira and others, 1983), were not detected in ground water. These larger, annulated PAC probably are associated with the oil phase and sediments in the surface impoundments.

Because of the compositional complexity of the contaminants in ground water, the study was limited to a selected number of representative compounds from each chemical class. These compounds were selected to study (1) vertical and horizontal distribution of organic contaminants in ground water downgradient from the impoundments; (2) distribution of organic contaminants on the porous media; (3) possible mechanisms that might influence the distribution of organic contaminants in the aquifer, such as partitioning of organic contaminants between oil-water phases, sorption/desorption on aquifer material, complexation, ion exchange, or organic compound-mineral interactions. Any of these processes conceivably could influence the migration of organic contaminants in the porous media, resulting in a "chromatographic effect." A typical example of chemical analyses for selected organic contaminants in ground water in wells at sites 1 and 3 through 7, at a depth of 18.3 m, is shown in table 7.

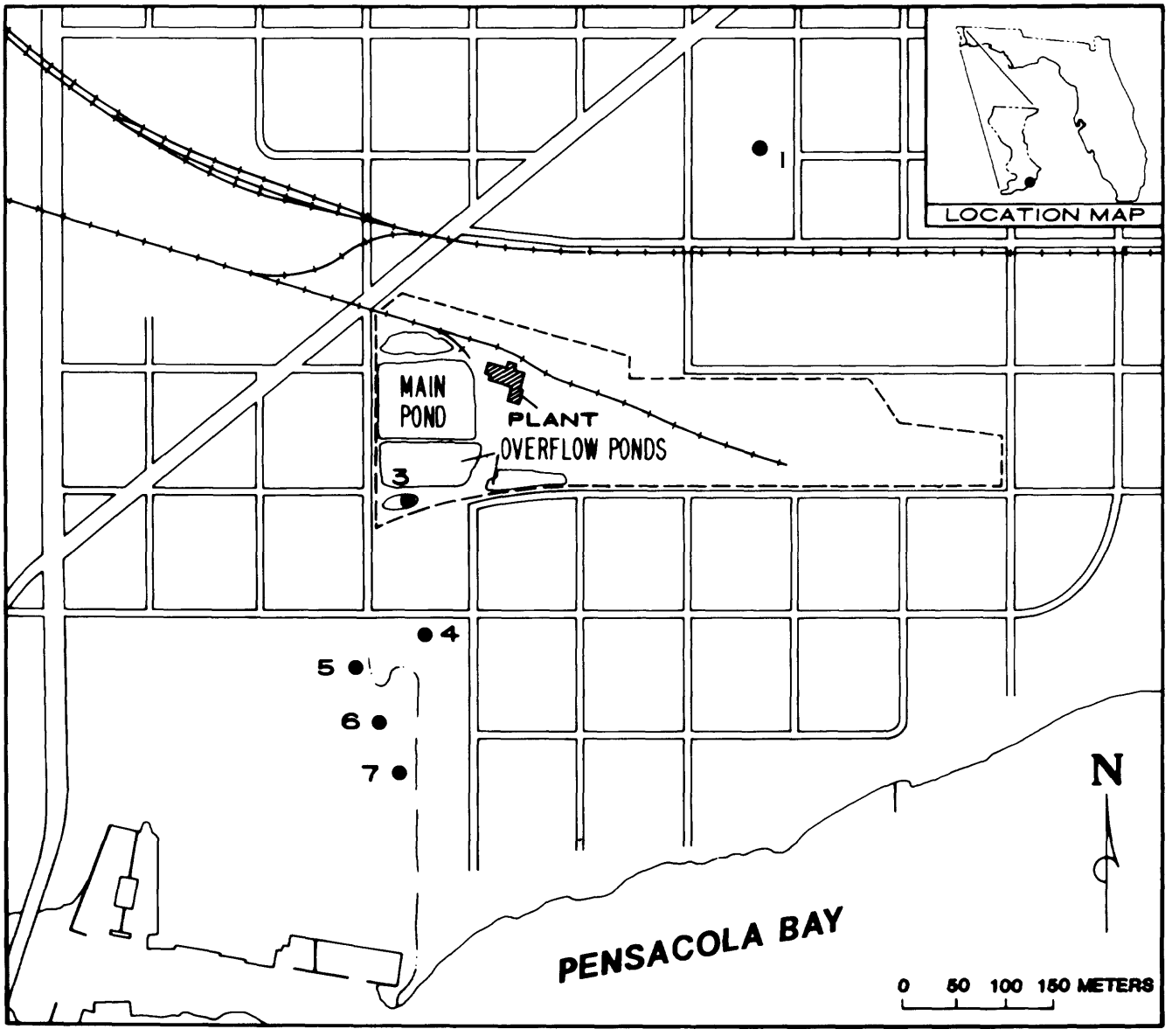


Figure 23. Location of sites at the creosote works study area.

Table 6. Dissolved organic carbon concentrations in ground-water samples from well sites 1 and 3 through 7
[Concentrations in milligrams per liter; – = not analyzed]

Sampling depth, in meters	Well site numbers					
	1	3	4	5	6	7
3	–	–	50	–	–	–
6.1	13	200	–	40	10	18
12.2	–	40	40	30	–	–
18.3	10	50	20	13	21	12
24.4	–	6	6	4.8	15	9.6
30.5	12	3	5.1	3.2	4.3	5.8

Vertical Distributions of Organic Contaminants in Ground Water

No organic contaminants were detected in any of the wells at site 1, indicating that the ground water from this site was not contaminated by wood-treatment chemicals. Having established backgroud concentrations in the ground water, vertical distributions of the contaminants were studied in wells at sites 3 through 7. These results are illustrated in figure 24, which shows the concentrations of total phenols,

Table 7. Chemical analyses for selected organic contaminants in ground water at a depth of 18.3 m at sites 1 and 3 through 7

[Concentrations in micrograms per liter; ND, not detected; –,not analyzed]

Compound	Well number					
	160	360	460	560	660	760
Phenols						
Phenol	ND	13.3	ND	ND	ND	ND
2-Methylphenol	ND	456	7.8	15.9	44.7	2.3
2,4-Dimethylphenol	ND	1,835	623	83	178	405
3,5-Dimethylphenol	ND	1,666	548	13.5	999	6.6
2,3,5-Trimethylphenol	ND	317	36.5	35.9	218.8	60.9
1-Naphthol	ND	360	ND	111	316	138
2-Naphthol	ND	317	ND	2.4	13.3	81.1
Pentachlorophenol	ND	11.6	ND	ND	ND	ND
Total phenols	ND	4,976	1,215	262	1,770	694
Polycyclic aromatic hydrocarbons						
Indane	ND	19.0	ND	54.7	435	186
Naphthalene	ND	1,976	27.3	1,038	271	1,072
2-Methylnaphthalene	ND	159	1.1	87.3	437	156
1-Methylnaphthalene	ND	91.1	0.5	44.7	260	81.3
Biphenyl	ND	22.0	–	7.8	53.2	15.4
Acenaphthene	ND	157	1.2	44.9	246	75.9
Fluorene	ND	82.1	1.2	17.3	103.4	34.5
Phenanthrene	ND	57.2	1.6	2.9	49.4	12.5
Anthracene	ND	3.2	ND	ND	3.0	ND
Fluoranthene	ND	2.8	0.2	ND	ND	ND
Pyrene	ND	1.6	0.2	ND	ND	ND
Benzo(a)pyrene	ND	ND	ND	ND	ND	ND
Total polycyclic aromatic hydrocarbons	ND	2,571	33	1,298	1,858	1,634
Nitrogen heterocycles						
2,4-Dimethylpyridine	ND	ND	ND	ND	ND	ND
Quinoline	ND	3.5	ND	ND	ND	ND
2-Methylquinoline	ND	ND	ND	ND	2.7	ND
2-Quinolinone	ND	1,217	125	214	517	94
Acridine	ND	1.0	ND	ND	ND	ND
Carbazole	ND	339	13.5	52.5	299	104
Acridinone	ND	12.4	ND	2.2	11.4	2.4
Total nitrogen heterocycles	ND	1,573	139	269	830	200
Sulfur heterocycles						
Benzo(b)thiophene	ND	268	6.0	82.7	442	157
Dibenzothiophene	ND	3.6	0.5	4.9	4.4	1.1
Total sulfur heterocycles	ND	272	7	88	446	158
Oxygen heterocycles						
Dibenzofuran	ND	89.3	0.5	15.1	101.1	31.1
Total oxygen heterocycles	ND	89	1	15	101	31

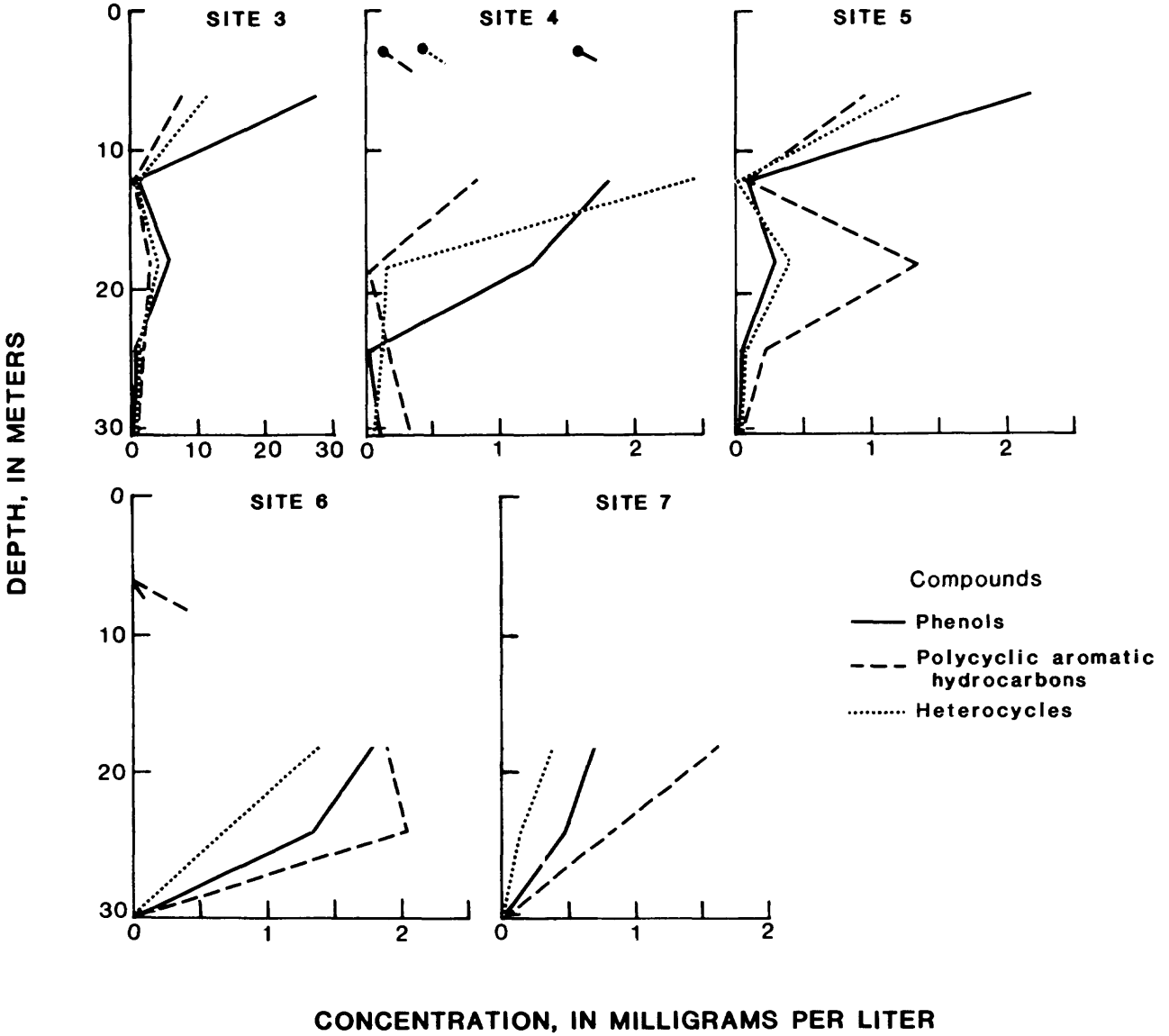


Figure 24. Vertical distribution of total phenols, polycyclic aromatic hydrocarbons, and heterocycles in ground-water samples collected from wells at sites 3 through 7.

PAH's, and heterocycles, as a function of depth. Each total is the sum of the concentrations of individual compounds in each class. Depth profiles at sites 3 and 5 showed two zones of contamination: one highly concentrated (oil zone), extending down to a depth of 12.2 m, and a less concentrated zone extending to a depth of 24.4 m (main plume). Concentrations of contaminants in this latter zone were greatest at a depth of 18.3 m. The main plume contained lower concentrations of contaminants, which were leached from the oil zone by percolating ground water. Vertical distributions of contaminants in wells at sites 3 and 5 indicated all three classes of contaminants migrated down the column of aquifer material at the same rate, resulting in no apparent chromatographic effect. The porous media was not capable of resolving classes of compounds of different polarities, such as phenols, heterocycles, and PAH's. These observations led to the conclusion that sorption to the porous media or organic mineral interactions are not important processes in governing the vertical migration of organic contaminants in this system.

Wells at site 4, in figure 24, showed a different pattern of vertical migration of contaminants than wells at sites 3 and 5. This anomalous behavior was explained as follows: (1) site 4 was offset from the vertical cross section between site 3 and 5 and (2) a clay lens at a depth of 6.1 m at site 4 impeded the flow of ground water and vertical migration of organic contaminants. This lens was also present (and was thicker) at sites 5, 6, and 7. Except for the presence of small amounts of 2,4-dimethylphenol and napthalene

at a depth of 6.1 m at site 6, wells at sites 6 and 7 did not show any evidence of contamination to a depth of approximately 18.3 m. Lack of contamination above 18 m in wells at sites 6 and 7 was related to the presence of this clay lens (affecting the flow system), plus the possible stream interactions with the upper 3 to 6.1 m of the aquifer. The main plume is located at a depth of approximately 18.3 to 30.5 m in wells at sites 6 and 7.

Horizontal Distributions of Organic Contaminants in Ground Water

Horizontal distributions of organic contaminants in wells of different depths at sites 3 through 7 are shown in figure 25. In general, at each depth, concentrations of organic contaminants decreased with increasing distance from the contamination source. At a depth of 6.1 m, all three classes of compounds migrated a distance of 215.5 m to wells at site 6. At depths of 18.3 to 30.5 m, all three classes of compounds migrated 273.4 m to wells at site 7. The presence of two contaminant plumes, at depths of 18.3 to 30.5 m, is evident in figure 25. The main, or primary, contaminant plume extended from the discharge point to site 5, a distance of 161.5 m. A secondary contaminant plume with maximum contaminant concentrations at depths of 18.3 to 30.5 m in wells at site 6, extends between sites 5 and 7, and possibly Pensacola Bay. All three classes of contaminants migrated at the same rate in the aquifer, without any apparent "chromatographic effect." Sorption to aquifer materials or organic compound-mineral interactions were not significant processes in the resolution of organic compounds in the saturated porous media.

Organic Compound–Mineral Interactions

Hydrogen Bonding of Nitrogen Heterocycles to Silica

The porous medium is composed of fine-grained quartz sand or silica. The surface chemistry of silica indicates that it contains free silanol groups that are slightly acidic. Subsurface migration of weak bases, such as nitrogen heterocycles, may result in retention of these compounds by the porous media through a hydrogen-bonding mechanism. If these compounds were retained on the porous media by weak hydrogen bonds, then elution with a stronger base, such as ammonia, would result in release of nitrogen heterocycles. A sediment-core sample was obtained from a depth of 24.4 m at site 5. This sample was in equilibrium with ground water containing organic contaminants at the time of collection. The sample was dried at ambient temperature and eluted with methylene chloride saturated with ammonia; then the eluate was evaporated to small volume. Analysis of the concentrated extract by GCMS indicated that no detectable levels of nitrogen heterocycles were present. Therefore, interaction of nitrogen heterocycles with the surface silanol groups of the porous media is a relatively insignificant process. Interactions of nitrogen heterocycles with more acidic compounds, such as phenols and carboxylic acids, which are known to be present in ground water, are more likely to occur in the contaminated aquifer.

Sorption to Mineral Surfaces

Sorption of neutral organic molecules such as PAH to the surface of the porous media involves electrostatic interactions between the silica surface and an electron-rich, π-electron system of the aromatic nucleus. In the aquifer, the porous media is saturated with water, resulting in deactivation of mineral surfaces. Therefore, sorption by the mineral fraction of the porous media is relatively unimportant in the saturated zone, presumably because of strong dipole interactions between the mineral surface and water, resulting in exclusion of neutral organic contaminants from the mineral surfaces of the porous media (Chiou and others, 1983). Analysis of the porous media from site 6 at a depth of 24.4 m in the vicinity of the secondary contaminant plume showed no detectable amounts of neutral organic contaminants.

Organic-Organic Interactions

Sorption to Organic Coatings on the Porous Media

One of the major factors controlling the migration of organic contaminants in the porous media is the organic carbon content of the porous media. The distribution coefficient (K_d) for a given solute is proportional to the organic carbon content of a soil or sediment; the larger the organic carbon content, the greater the value of K_d (Karickhoff and others, 1979). It has been stated that transfer of nonionic organic compounds from water to the soil or sediment organic phase is essentially a process of partitioning rather than physical adsorption (Chiou and others, 1979; 1983). Analysis of the porous media in the vicinity of the secondary contaminant plume showed no detectable amounts of organic contaminants, such as PAH, associated with the sediments. The organic carbon content of the porous media in the sand-and-gravel aquifer at Pensacola, Fla., is less than 0.07 percent; hence, processes such as sorption to the organic coat-

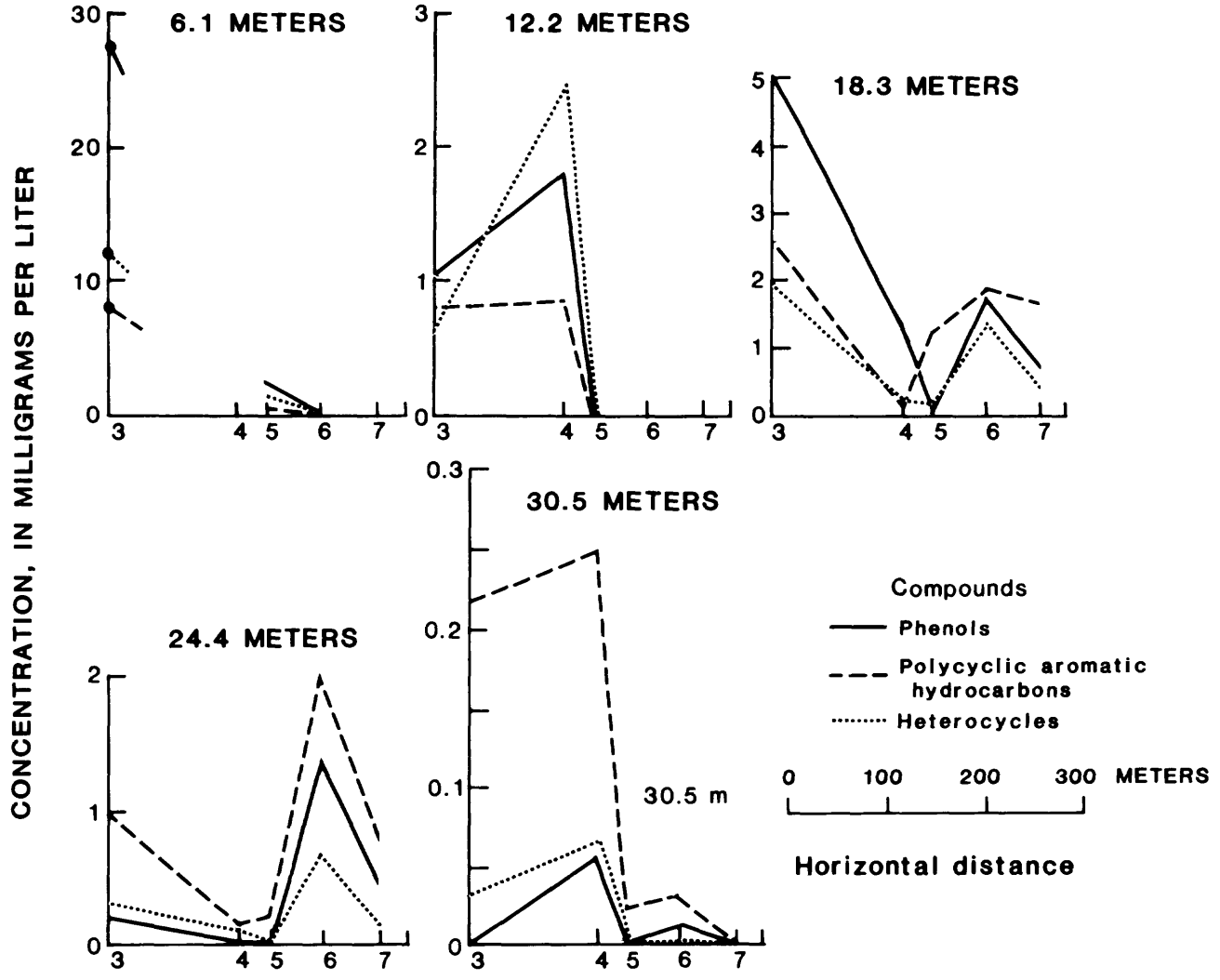


Figure 25. Horizontal distributions of total phenols, polycyclic aromatic hydrocarbons, and heterocycles in ground-water samples collected from wells at sites 3 through 7.

ings of the porous media are minimized. It has been reported that retention of highly lipophilic compounds is rather small in aquifers composed of materials of organic carbon content less than 0.1 percent (Schwarzenbach and others, 1983).

Solubilization of Organic Contaminants by Dissolved Organic Carbon

The presence of elevated amounts of dissolved organic carbon (DOC) can reduce sorption of organic contaminants to surface coatings on sediments. This may be due to increased solubility of the organic contaminants in ground water containing high levels of DOC or to competitive adsorption (Wershaw and others, 1969). DOC concentrations in natural ground-water samples collected from various parts of the United States ranged from less than 0.1 to 15 mg/L, with a median value of 0.7 mg/L (Leenheer and others, 1974). DOC concentrations in uncontaminated ground water from the sand-and-gravel aquifer at Pensacola ranged between 10 to 13 mg/L. These high DOC concentrations in ground water probably minimize processes such as sorption to the porous media.

Intermolecular Association Complexes

Migration of organic compounds, such as phenols and polycyclic aromatic hydrocarbons, en masse through the porous media suggests that these compounds may be solubilized in ground water by processes such as hydrogen bonding, micelle formation, and so forth. Solubilization of organic compounds, such as benzo[a]pyrene, by phenols has been reported (Futoma and others, 1981). Preliminary studies by infrared spectroscopy on a contaminated groundwater sample suggested a strong hydrogen-bonded as-

sociation between 2-quinolinone and aliphatic carboxylic acids. A similar association between 2-quinolinone and carboxylic acids in asphalt has been reported (Petersen and others, 1971). These molecular complexes can be in the form of cyclic mixed-dimers with carboxylic acids via a carboxylic acid carbonyl oxygen-hydrogen bond (fig. 26*A*), cyclic dimers via a π-hydrogen bond (fig. 26*B*), or self-association dimers (fig. 26*C*) (Petersen, 1971). Molecular-association complexes of this kind may play an important role in the transport of organic contaminants through the porous media.

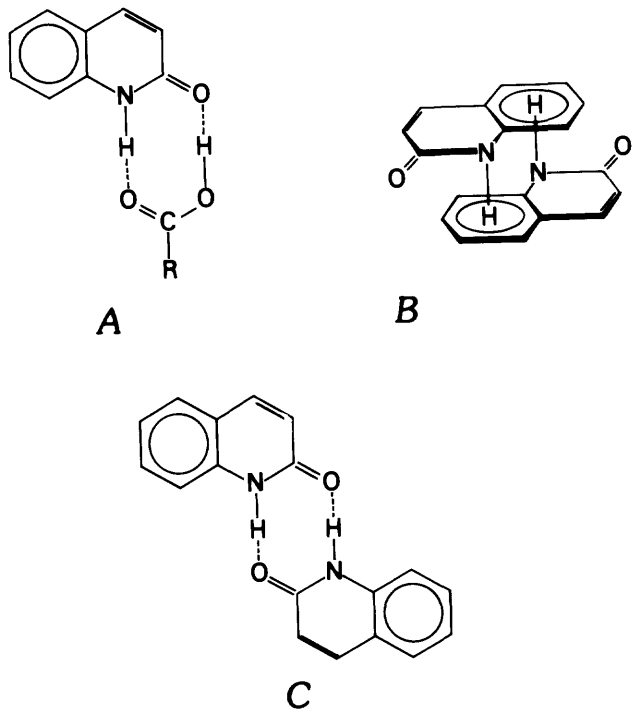


Figure 26. Intermolecular association of hydrogen-bonded complexes: *A*, cyclic mixed-dimer with carboxylic acid via a carboxylic acid carbonyl oxygen-hydrogen bond; *B*, cyclic dimer via a π-hydrogen bond; and *C*, self-association hydrogen-bonded dimer.

CONCLUSIONS

Results presented in this report clearly demonstrate that the sand-and-gravel aquifer at the creosote works site near Pensacola, Fla., is contaminated by hazardous organic compounds. Studies of vertical and horizontal distributions of phenols, PAH, and heterocycles indicate that all three classes of compounds migrated at the same rate in the porous media. These findings suggest that transport of organic compounds through aquifer material of low organic carbon content are relatively unaffected by sorption-controlled processes. Similarly, organic compound-mineral interactions are relatively unimportant factors. Solubilization of organic contaminants by high concentrations of native DOC or through formation of intermolecular association complexes may be an important factor in organic compound transport. Because of the presence of similar classes of organic compounds in wastes derived from coal- and oil-shale conversion processes, research findings at this site may have significant transfer value to ground-water contamination problems associated with alternate-fuel technologies.

REFERENCES CITED

Chiou, C.T., Peters, L.J., and Freed, V.H., 1979, A physical concept of soil-water equilibria for nonionic organic compounds: Science, v. 206, no. 16, p. 831–832.

Chiou, C.T., Porter, P.E., and Schmedding, D.W., 1983, Partition equilibria of nonionic compounds between soil organic matter and water: Environmental Science and Technology, v. 17, no. 4, p. 227–231.

Futoma, D.J., Smith, S.R., Smith, T.E., and Tanaka, J., 1981, Polycyclic aromatic hydrocarbons in water systems: Boca Raton, Fla., CRC Press, 190 p.

Karickhoff, S.W., Brown, D.S., and Scott, T.A., 1979, Sorption of hydrophobic pollutants on natural sediments: Water Research, v. 13, p. 241–248.

Leenheer, J.A., Malcolm, R.L., McKinley, P.W., and Eccles, L.A., 1974, Occurrence of dissolved organic carbon in selected ground-water samples in the United States: Journal of Research of the U.S. Geological Survey, v. 2, no. 3, p. 361–369.

Pereira, W.E., Rostad, C.E., Hult, M.F., and Garbarino, J.R., 1983, Ground-water contamination by organic bases derived from coal-tar wastes: Environmental Toxicology and Chemistry, v. 2, no. 3, p. 283–294.

Petersen, J.C., 1971, Thermodynamic study by infrared spectroscopy of the association of 2-quinolone, some carboxylic acids, and the corresponding 2-quinolone-acid mixed dimers: Journal of Physical Chemistry, v. 75, no. 8, p. 1129–1135.

Petersen, J.C., Barbour, R.V., Dorrence, S.M., Barbour, F.A., and Helm, R.V., 1971, Molecular interactions of asphalt-tentative identification of 2-quinolones in asphalt and their interaction with carboxylic acids present: Analytical Chemistry, v. 43, no. 11, p. 1491–1496.

Schwarzenbach, R.P., Giger, W., Hoehn, E., and Schneider, J.E., 1983, Behavior of organic compounds during infiltration of river water to ground water: Environmental Science and Technology, v. 17, no. 8, 1983, p. 472–479.

Wershaw, R.L., Bucar, P.J., and Goldberg, M.C., 1969, Interaction of pesticides with natural organic material: Environmental Science and Technology, v. 3, p. 271–273.

Chapter F. Isolation of Organic Compounds from Ground Water by Using Bonded-Phase Extraction Columns

By C.E. Rostad, W.E. Pereira, *and* S.M. Ratcliff

Abstract

A procedure for isolation of hazardous organic compounds from water for gas-chromatography mass-spectrometry analysis is presented and applied to ground water contaminated by creosote and pentachlorophenol, resulting from wood-treatment processes near Pensacola, Florida. This simple procedure involved passing a 50- to 100-mL sample through a bonded-phase extraction column, eluting the trapped organic compounds from the column with 2 to 4 mL of solvent, and evaporating the sample to 100 µL with a stream of dry nitrogen, after which the sample was ready for gas-chromatography mass-spectrometry analysis. Representative compounds indicative of creosote contamination were used for recovery and precision studies from the cyclohexyl bonded phase. Recovery of these compounds from n-octyl, n-octadecyl, cyclohexyl, and phenyl bonded phases was compared. Recovery of neutral compounds (polycyclic aromatic hydrocarbons and sulfur and oxygen heterocycles) was comparable from all four phases. Acidic and phenolic compounds were best recovered from cyclohexyl and phenyl phases. Basic compounds (nitrogen heterocycles) were best recovered from n-octyl and n-octadecyl phases. The bonded phase that exhibited the best recovery and least bias toward acidic or basic compounds was the n-octadecyl phase. The procedure applied the cyclohexyl bonded-phase extraction column to creosote- and pentachlorophenol-contaminated ground water. A complex chromatogram is given for one of the ground-water samples from the contaminated aquifer.

INTRODUCTION

The trend in the scientific community is toward increased efficiency in apparatus, instrumentation, and methods. New analytical apparatus, such as chromatographers using fused-silica capillary columns, provide increased efficiency in separation and analysis time. New analytical instrumentation, such as the inductively coupled plasma spectrophotometer, provide increased efficiency by yielding more sample information in less analysis time. Analytical methods, too, need to become more efficient.

Traditional methods for isolation of hazardous organic compounds from water for GC or GCMS analysis are variations of the acid/base/neutral liquid-liquid extraction (Keith, 1976; Environmental Protection Agency, 1979a,b; Wershaw and others, 1983). After pH adjustment with aqueous H_2SO_4 or KOH, the water sample is extracted with an organic solvent in a separatory funnel. The pH is readjusted, and the water sample is re-extracted. The organic extracts are dried by addition of anhydrous Na_2SO_4, concentrated in a Kuderna-Danish apparatus, evaporated with dry nitrogen to final volume, and injected into the GCMS for analysis. This procedure involves large volumes of expensive solvents, and extensive labor, time, and glassware. In addition, each step in the sample preparation may introduce contamination or increase sample loss (American Chemical Society Committee on Environmental Improvement, 1983). The acid/base/neutral extraction method separates the organic compounds by functionality so that they can be analyzed on different GC columns. New, versatile Durabond (J &W Scientific) capillary columns make this separation unnecessary, so extracts are now combined for analysis. While significant advances have been made in analytical instrumentation and data management, sample preparation for organic analysis has remained virtually the same (Yago, 1984).

An alternative sample-preparation method was investigated: an application of bonded-phase extraction columns. Previously, a different bonded phase had been used for each different class of compound. In this alternative method, one bonded phase is used for isolating a variety of compounds rapidly, with no lengthy treatment of sample. This method involves passing the filtered water sample through a small column containing a solid bonded-phase sorbent that sorbs the organic compounds. Then the column is eluted with a small quantity of solvent, and the sample is ready for GCMS analysis. This method is much simpler than the acid/base/neutral extraction method. Very little glassware is needed. It does not

use much solvent, it does not take much time. Fewer steps mean less sample loss and fewer artifacts introduced. If the sample-preparation method is effective in the laboratory, it can be applied onsite. The water sample could be passed through the column as it is pumped from the sampling point. Ground-water samples for organic analysis, for example, are usually pumped into 1-L glass bottles and shipped to a laboratory for acid/base/neutral extraction. Transfer of the ground-water sample from an anaerobic aquifer to an aerobic environment may initiate oxidation or biodegradation of the organic compounds, which continues during transport until the sample is extracted for GCMS analysis. If organic compounds are isolated from ground water immediately, much of the possible sample alteration between the time of sampling and analysis would be eliminated. The lightweight column could be sealed and shipped to the laboratory for elution and GCMS analysis.

The feasibility of this onsite collection and preservation method was first tested in the laboratory. The application for this new method was the isolation of creosote compounds resulting from wood-treatment processes from contaminated ground water collected at a hazardous-waste site near Pensacola, Fla. Creosote contains a wide variety of organic compounds: polycyclic aromatic hydrocarbons, nitrogen, oxygen and sulfur heterocycles, and phenols (Lang, 1967; Pereira and others, 1983). Many of these organic compounds had entered the aquifer. The bonded-phase extraction column would have to effectively isolate all organic compounds from the ground water regardless of polarity, functionality, or solubility in water. A group of representative compounds was chosen for the recovery study, including 7 phenols, 10 polycyclic aromatic hydrocarbons, 2 sulfur heterocycles, 1 oxygen heterocycle, and 6 nitrogen heterocycles. Compounds of increasing molecular weight and hydrophobic or hydrophilic character were included to pinpoint any recovery bias from increasing solubility in water or molecular size. The compounds were spiked into ground water collected from an uncontaminated area of the aquifer under study. Matrix effects from ground water were included in the study (American Chemical Society Committee on Environmental Improvement, 1983). Recovery of these compounds from ground water was studied by using the cyclohexyl bonded-phase extraction column. After reproducibility was verified, recovery at several concentrations was investigated. Recovery of these compounds from four different bonded phases also was studied. The method was applied to a contaminated ground-water sample collected near the hazardous-waste site where ground water contains creosote and pentachlorophenol.

METHODS

Apparatus

Equipment for the extraction procedure consists of three main parts: a sample reservoir, the bonded-phase extraction column (Analytichem Internat.), and a vacuum manifold. The cylindrical sample reservoir is made of polypropylene and is available in 75- and 150-mL capacities. The reservoir has a wide opening at the top for introduction of the sample and a narrow opening at the bottom that fits into the bonded-phase extraction column. An adapter forms a water-tight seal between the sample reservoir and the extraction column below. The smaller 3-mL cylindrical polypropylene extraction column is one-third full with 500 mg of the bonded phase. A variety of functional bonded phases is available. Polyethylene frits are located above and below the bonded phase to hold minute particles in place to keep the chromatographic column intact. The extraction fits directly into the vacuum manifold below. A beaker is placed in the vacuum manifold to collect the water as it is pulled through the extraction column when vacuum is applied. A vacuum gage on the manifold ensures that consistent, reproducible vacuum is applied to each water sample.

Standards

Analytical standards for the quantitation compounds were acquired from commercial sources (Aldrich Chemical Co., Merck and Co., ChemService, Polyscience, Ultra Scientific, Fluka) and the U.S. Environmental Protection Agency. all organic solvents were high purity, distilled in glass (Burdick and Jackson). Freshly distilled water was exposed to ultraviolet (UV) radiation for 30 minutes in ORGANICpure (SYBRON/Barnstead) prior to use. Procedural blanks were verified to be clean. For each standard stock solution the compounds were individually weighed neat, except for phenols, which were weighed by weight percent in benzene into 5-mL volumetric flasks and diluted to volume with methylene chloride. A standard mixture, containing 100 ng/μL of each compound, was prepared by transferring aliquots of each standard stock solution to one 5-mL flask. Various quantities of the standard mixture were used to spike the samples to obtain various concentrations in the natural ground water for recovery studies. Spiked recovery samples and the standard mixture were spiked with the internal standard, phenanthrene-d_{10}, in iso-octane immediately prior to GCMS analysis.

A reverse-search library was built, containing mass spectra and relative retention times of the internal standard and the compounds to be quantified. The GCMS standards, solutions of the standard mixture at three concentrations (50, 100, and 150 ng/μL), were analyzed by GCMS to determine response factors for each compound relative to the internal standard, phenanthrene-d_{10}. Concentration of the internal standard was 100 ng/μL in each GCMS standard, and in all samples. A computer quantitation routine searched for each compound within an elution time window. If the library spectra matched a peak in the time window, the area of a preselected ion was quantified. This area was converted to a quantity, based on the area of the internal standard base peak, by using the response factors determined previously. Throughout the study, at least one of the GCMS standards was analyzed each day, and the new response factors were added to the response-factor lists.

Procedure

Real samples were first filtered through prebaked glass-fiber filters (binder-free, Type A-E, Gelman Sciences) to remove suspended sediment. The ground water used in the recovery studies, however, was not filtered. The bonded-phase extraction column was cleaned by the passing through of 5 mL of methylene chloride, 5 mL of methanol, and then 5 mL of distilled, organic-free water. The column was not allowed to dry before the water sample was added to the reservoir. The water sample, 50 to 100 mL, was slowly passed through the column by using 5 mm of mercury vacuum. After the sample had passed through, the vacuum was left on for 5 minutes to dry the column. The water sample was removed from the vacuum manifold and discarded. The reservoir and adapter were removed from above the column. To remove the remaining water, the column was placed in a centrifuge tube and centrifuged at 1,000 revolutions per minute. A new centrifuge tube was used for elution. The column was eluted with 1 mL of acetonitrile and two 2-mL portions of methylene chloride, by adding the solvent to the column, centrifuging to pass the solvent through, and collecting the eluent in the centrifuge tube. Residual water was eliminated by passing the eluent through a microcolumn of anhydrous Na_2SO_4. The eluent was slowly evaporated to 100 μL under a stream of dry nitrogen after the internal standard was added. Each prepared sample was analyzed within 48 hours.

Instrumentation

Analyses were performed on a Finnigan OWA 1020 computerized capillary gas-chromatography quadrupole mass-spectrometry system (GCMS). The GC was equipped with a fused-silica capillary column 30 m long by 0.26 mm inside diameter, with 0.25-μm bonded film of DB-5 (J&W Scientific). Linear velocity of helium through the column was 26 cm/s. Injections of 1 μL were made, using the splitless injection technique. The GC oven was held at 50°C for 4 minutes and increased at 6°C per minute to a maximum of 300°C. The vent valve was automatically opened at 45 seconds, and the filament and multiplier were automatically turned on at 240 seconds. Data acquisition began simultaneously with injection of the sample. The MS was operated in the electron-impact mode, using an ionizing voltage of 70 electron volts (eV) and an ionization current of 250 microamperes (μA). The instrument was repetitively scanned from 40 to 450 atomic mass units (amu) in 0.9 seconds.

RESULTS

Cyclohexyl Recovery at 100 μg/L

Ground water was spiked with 100 μg/L of each compound, passed through the cyclohexyl bonded-phase extraction column, and analyzed by GCMS. Five identical 200-mL samples were analyzed. The precision data, as percent recovery, are shown in table 8. Except for phenol, recovery of phenolic compounds was excellent, 80 to 105 percent. Recovery of neutral compounds (polycyclic aromatic hydrocarbons, sulfur and oxygen heterocycles, and carbazole) was acceptable, 51 to 111 percent. Recovery of the nitrogen heterocycles varied widely. Reproducibility of several nitrogen heterocycles was poor; specifically, 37.57 percent relative standard deviation for 2-methylquinoline and 66.24 percent relative standard deviation for acridine. Limited recovery of phenol and 2,4-dimethylpyridine will be discussed later.

Recovery of Different Concentrations

Final concentrations of 20, 50, 100, and 200 μg/L of each compound were prepared by using the ground water. Recoveries of these compounds from 50 mL (100 mL for 20 μg/L) ground water from the cyclohexyl bonded phase are shown in table 9. Limited phenol recovery was verified. Other acidic- and phenolic-compound recoveries were as expected. Pentachlorophenol recovery decreased significantly at the lowest concentration, 20 μg/L. Recovery of neutral compounds was consistent with earlier data, although recovery of fluorene, phenanthrene, anthracene, and dibenzothiophene was less at the highest concentration, 200 μg/L. Recovery of 2-quinolinone

Table 8. Precision data, as percent recovery, for 100 µg/L of each compound from cyclohexyl bonded phase

Compound	Mean (percent)	Standard deviation (micrograms per liter)	Relative standard deviation
Phenolic compounds			
Phenol	26	4.39	16.81
2-Methylphenol	80	11.06	13.85
2,4-Dimethylphenol	104	15.54	14.95
3,5-Dimethylphenol	105	14.43	13.79
2,3,5-Trimethylphenol	101	9.57	9.52
1-Naphthol	108	19.60	18.16
2-Naphthol	98	5.15	5.25
Pentachlorophenol	87	25.60	29.54
Polycyclic aromatic hydrocarbons			
Indane	51	7.25	12.66
Naphthalene	72	5.77	8.07
2-Methylnaphthalene	69	5.40	7.84
1-Methylnaphthalene	64	2.25	3.55
Biphenyl	70	6.45	9.21
Acenaphthene	80	3.20	4.01
Fluorene	70	12.10	17.30
Phenanthrene	72	13.90	19.23
Anthracene	69	15.84	23.09
Sulfur heterocycles			
Benzothiophene	74	5.38	7.22
Dibenzothiophene	72	12.71	17.71
Oxygen heterocycles			
Dibenzofuran	72	8.28	11.47
Nitrogen heterocycles			
2,4-Dimethylpyridine	0	0	0
Quinoline	70	11.29	16.21
2-Methylquinoline	12	4.44	37.57
2-Quinolinone	86	16.74	19.56
Acridine	21	13.59	66.24
Carbazole	81	12.73	15.73
Acridinone	111	32.18	28.91

and acridinone was high, significant at all concentrations. Recovery of other nitrogen heterocyclic compounds was limited, except for quinoline at higher concentrations.

Recovery from Different Bonded Phases

Identically spiked ground-water samples, each containing approximately 100 µg/L of each compound, were passed through four extraction columns, each containing a different bonded phase. The n-octyl, n-octadecyl, cyclohexyl, and phenyl bonded phases recovered the assortment of compounds differently (table 10). Recovery of neutral compounds, which are all hydrophobic, was similar from each phase. Recovery of 2-quinolinone and phenolic compounds was limited on the n-octyl phase. The other three bonded phases had similar excellent recovery. Recovery of nitrogen heterocycles was better from the n-octyl and n-octadecyl bonded phases, although no phase showed excellent recovery for these basic compounds.

Table 9. Percent recovery from cyclohexyl bonded phase at various concentrations

Compound	Percent recovery at indicated concentrations, in micrograms per liter			
	20	50	100	200
Phenolic compounds				
Phenol	0	19	8	22
2-Methylphenol	45	95	59	79
2,4-Dimethylphenol	71	98	70	98
3,5-Dimethylphenol	69	98	73	96
2,3,5-Trimethylphenol	74	96	77	95
1-Naphthol	80	104	88	101
2-Naphthol	90	103	95	102
Pentachlorophenol	35	67	81	84
Polycyclic aromatic hydrocarbons				
Indane	52	64	49	67
Naphthalene	76	102	63	88
2-Methylnaphthalene	74	99	69	78
1-Methylnaphthalene	67	87	62	76
Biphenyl	74	92	72	64
Acenaphthene	81	90	76	75
Fluorene	76	95	83	42
Phenanthrene	81	106	86	44
Anthracene	74	110	89	31
Sulfur heterocycles				
Benzothiophene	82	108	67	92
Dibenzothiophene	76	99	87	44
Oxygen heterocycles				
Dibenzofuran	75	97	77	57
Nitrogen heterocycles				
2,4-Dimethylpyridine	0	0	0	0
Quinoline	0	0	78	72
2-Methylquinoline	3	10	4	0
2-Quinolinone	76	101	89	79
Acridine	6	0	90	20
Carbazole	82	109	94	60
Acridinone	197	150	110	105

Table 10. Recovery of various compounds by using four bonded phases at 100 µg/L

Compound	Percent recovery for indicated bonded phase			
	n-Octyl	n-Octyldecyl	Cyclohexyl	Phenyl
Phenolic compounds				
Phenol	1.8	14	27	15
2-Methylphenol	10	52	88	47
2,4-Dimethylphenol	46	106	110	133
3,5-Dimethylphenol	43	102	110	135
2,3,5-Trimethylphenol	74	107	103	124
1-Naphthol	60	116	108	143
2-Naphthol	144	98	97	102
Pentachlorophenol	79	96	103	119
Polycyclic aromatic hydrocarbons				
Indane	49	58	55	75
Naphthalene	78	79	74	87
2-Methylnaphthalene	75	73	69	78
1-Methylnaphthalene	72	73	64	69
Biphenyl	75	74	69	75
Acenaphthene	89	84	80	90
Fluorene	67	68	64	68
Phenanthrene	65	71	65	66
Anthracene	54	64	52	66
Sulfur heterocycles				
Benzothiophene	75	82	77	91
Dibenzothiophene	68	71	65	69
Oxygen heterocycles				
Dibenzofuran	70	72	68	72
Nitrogen heterocycles				
2,4-Dimethylpyridine	2.7	0	0	0
Quinoline	65	87	58	61
2-Methylquinoline	36	40	9.1	8.2
2-Quinolinone	11	75	73	118
Acridine	45	55	7.9	1.5
Carbazole	67	80	71	83
Acridinone	96	128	113	170

DISCUSSION

The cyclohexyl bonded phase was very effective for recovering phenolic and neutral compounds spiked into ground water. For most compounds, the recovery did not decrease even at lower concentrations. A typical sample size of 50 mL is still recovered down to 20 µg/L. Recoveries varied for the nitrogen heterocycles that are basic (quinoline, 2-methylquinoline, acridine). The compound 2,4-dimethylpyridine was not recovered from the cyclohexyl bonded phase; it was assumed that if it were present in a sample, it would not be detected in the analysis. Only 27 percent of the phenol was recovered from the cyclohexyl bonded phase. Therefore, phenol may or may not appear in the analysis. However, the other phenolic compounds exhibited excellent recovery. Isolation of organic compounds using the cyclohexyl bonded-phase column provided an easy, rapid, and inexpensive sample preparation method that would be very useful in monitoring

water contamination. Each periodic sampling could involve 50 to 100 ground-water samples for immediate organic analysis. This method would streamline the sample preparation to an appreciable extent.

Of the various bonded phases studied, the n-octadecyl had the most uniform recovery of the different compounds. Originally, each phase was specifically used to isolate a particular chemical functional group. If one phase could isolate all organic compounds, that would be ideal. Limited recovery of phenol and 2,4-dimethylpyridine occurred with each bonded phase. Because this limited recovery was independent of the acidity or basicity of the compounds, it may have been due to their volatility or solubility. However, indane is as volatile as phenol, and its recovery was much better than that for phenol. The low capacity of the column for very water soluble, very polar compounds may cause the limited recoveries. This effect can be minimized by using a 50-mL sample size, no larger, on the 500-mg column.

APPLICATION USING AN ACTUAL GROUND-WATER SAMPLE

Methods often have been proposed that worked well in laboratory applications but failed when applied to real samples. An example of actual recovery by the cyclohexyl bonded-phase extraction column from a creosote contaminated ground-water sample is shown in figure 27. Only 25 mL of ground-water sample was used to examine ground-water quality in detail. The filtered sample was passed through the cyclohexyl bonded-phase extraction column, eluted, concentrated, and after addition of the internal standard (for quantitation purposes) analyzed by GCMS. With this method, a maximum amount of chemical information on organic contamination was determined with minimal sample-preparation effort. Of the wide range of organic compounds in creosote, many diffused into the ground water. This method isolated an enormous variety of compounds in one step.

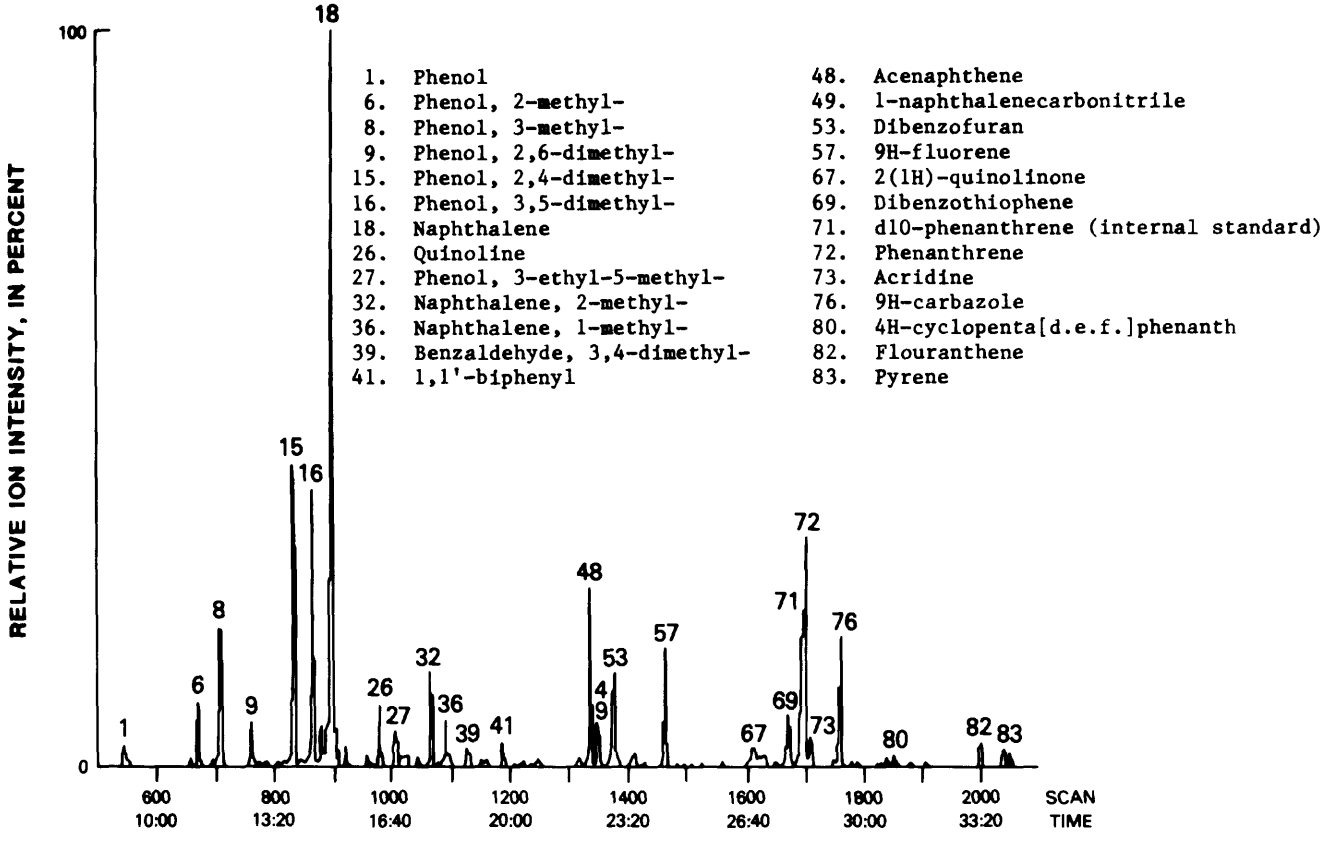


Figure 27. Reconstructed ion chromatogram of an extract of ground water from well 3 at a depth of 12.2 m.

CONCLUSIONS

The cyclohexyl bonded-phase method efficiently recovers a variety of organic compounds containing different functional groups. Very little organic solvent is required. Evaporation of large volumes of expensive solvents into the atmosphere is eliminated. The few glassware items used are general laboratory type, instead of expensive, one-use items. Fewer steps in the method reduce procedure variability from technician to technician. Less sample loss should result from fewer sample-transfer steps. Fewer steps also provide fewer opportunities for introduction of artifacts. This short method involves minimal sample exposure to possibly hazardous samples, which is important, in view of the increasing demand for analysis of hazardous-waste-related samples. This method could be a great asset onsite. Isolating organic compounds immediately would retard any sample degradation ordinarily possible during transport. Field personnel, who already do field filtrations, will find the technique for organic-compound isolation very similar. The column would be sealed and shipped to the laboratory for elution and GCMS analysis. Using this method in the field would avoid the shipment, and possible breakage in transit, of potentially hazardous water samples. Thus, in many respects, this method is much more efficient than methods used previously.

REFERENCES CITED

American Chemical Society Committee on Environmental Improvement, 1983, Principles of Environmental Analysis: Analytical Chemistry, v. 55, no. 14, p. 2210–2219.

Keith, L.H., 1976, Identification and analysis of organic pollutants in water: Ann Arbor, Mich., Ann Arbor Science Publishers, 718 p.

Lang, K.F., and Eigen, I., 1967, Im Steinkohlenteer nachgewiesene organische Verbindungen: Fortschritte der Chemischen Forschung, v. 8., p. 91–170.

Pereira, W.E., Rostad, C.E., Garbarino, J.R., and Hult, M.F., 1983, Ground-water contamination by organic bases derived from coal tar wastes: Environmental Toxicology and Chemistry, v. 2, p. 283–294.

U.S. Environmental Protection Agency, 1979a, Base/neutrals, acids, and pesticides—Method 625: Federal Register, v. 44, no. 233, p. 69540–69552.

———1979b, Polynuclear aromatic hydrocarbons—Method 610; Federal Register, v. 44, no. 233, p. 69514–69517.

Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., 1983, Methods for the determination of organic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations Open-File Report 82–1004, 173 p.

Yago, L.S., 1984, Bonded phase sample preparation technology: A growing trend: American Laboratory, v. 16, no. 1, p. 4–6.

Chapter G. Chemistry of Ground Water at a Creosote Works, Pensacola, Florida

By D. F. Goerlitz, E. M. Godsy, D. E. Troutman, *and* B. J. Franks

Abstract

Previous studies of the behavior of wood-preserving chemicals in ground water have indicated that (1) organic solutes (contaminants) are differentially altered or sorbed during ground-water transport and (2) pentachlorophenol may function as a conservative tracer.

A wood-treatment plant near Pensacola, Florida, was studied to test these hypotheses. Water samples were analyzed for dissolved organic compounds by using previously developed methodology. Techniques of high-performance liquid chromatography, gas chromatography, and mass spectrometry were used for these determinations.

Results of chemical analyses and sorption experiments that used samples from a creosote works near Pensacola, Florida, show the following:

1. Phenol, 2-methylphenol, 3-methylphenol, and 4-methylphenol are being degraded in the contaminated ground water;
2. The dimethylphenols are not sorbed or degraded and 2,4-dimethylphenol and 3,5-dimethylphenol may be useful as reference tracers;
3. Sorption of the phenols or polynuclear aromatic hydrocarbons by the aquifer sediments is insignificant; and
4. Pentachlorophenol is not present in solution in the ground water at concentrations greater than 0.01 milligram per liter.

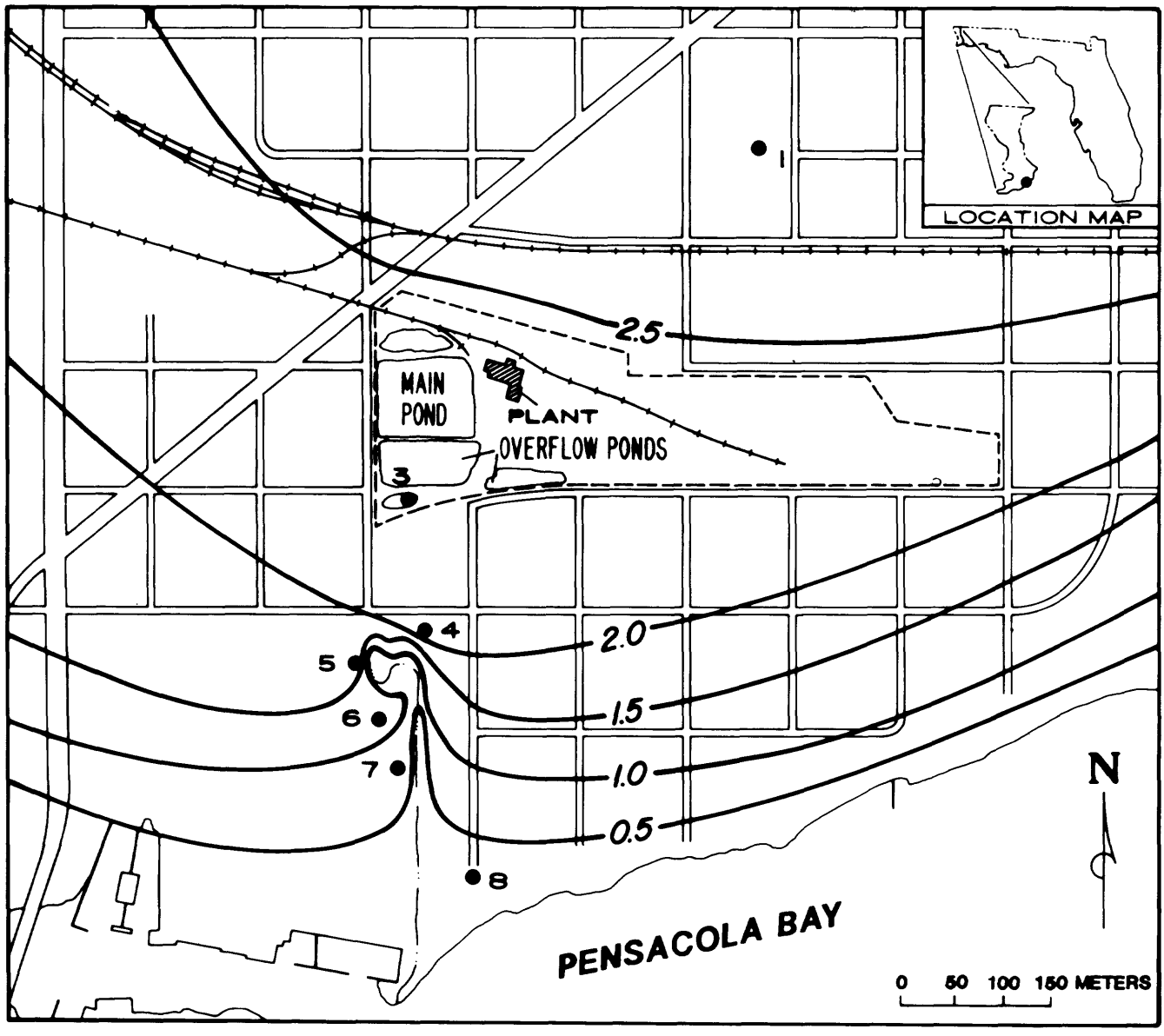
INTRODUCTION

Since 1976, the Menlo Park Organics Project has been actively studying the behavior of wood-preserving chemicals contaminating the ground water at Visalia, Calif., St. Louis Park, Minn., and, more recently, at Pensacola, Fla. At Visalia, pentachlorophenol and the soluble polynuclear aromatic hydrocarbons traveled with the ground water almost unimpeded by sorption. The polynuclear aromatic hydrocarbons appeared to undergo degradation at the surface of the water table, especially when the level was falling during drought conditions, but pentachlorophenol remained. The other phenolic components of creosote were conspicuously absent. At St. Louis Park, the ground-water contaminants consisted of polynuclear aromatic hydrocarbons and phenols (Ehrlich and others, 1982). Pentachlorophenol was not used there and was not found in the study area. The knowledge that was gained at Visalia and St. Louis Park and that set the approach for the Pensacola study indicates that (1) organic solutes (contaminants) are differentially altered or sorbed during ground-water transport and (2) pentachlorophenol may function as a conservative tracer.

In August 1981, samples from existing wells were analyzed to determine the nature and extent of the ground-water contamination (Troutman and others, 1984). This information was used to evaluate the site for suitability as a field laboratory and for placement of new test wells for a more comprehensive well drilling and sampling effort. The major well drilling and sampling was done in July and August 1983. Water samples were analyzed for dissolved organic compounds by using techniques of high-performance liquid chromatography, gas chromatography, and mass spectrometry.

WATER CHEMISTRY

Data obtained from analysis of samples taken during the 1983 sampling period presented a somewhat different condition than originally conceived. Pentachlorophenol was only found near the source of contamination and only when two liquid phases were present. None was found in aqueous solution at significant concentrations. In general, the polynuclear aromatic hydrocarbons and phenols migrated with the ground water as expected, and their concentrations were attenuated with distance. However, at a considerable distance downgradient from the source, approximately 300 m, both the phenol and polynuclear aromatic hydrocarbon concentrations increased sharply. Figure 28 is a map of the area showing the major surface features, the sampling sites, and the



EXPLANATION

6 ● SITE AND NUMBER

—1.5— ALTITUDE OF WATER TABLE. CONTOUR INTERVAL 0.5 METER. DATUM IS SEA LEVEL

Figure 28. March 1984 potentiometric surface at creosote works.

water-table gradient. The surface stream that begins adjacent to site 5 likely is influencing the migration of the organic components beyond site 5. Sites 3 and 5 were chosen as the end members of the study reach to avoid the obvious complications in the hydrology beyond.

In the study reach, the chemical data show that, in addition to dilution by normal dispersion, some of the phenols are being attenuated with distance more than the other solutes (table 11). At site 3, a less permeable "clay" layer was found at the 12.2-m depth and is likely responsible for lower solute con-

Table 11. Polycyclic aromatic hydrocarbons and phenolic compounds at site 3, site 4, and site 5
[Concentrations in milligrams per liter]

Compound	Sample depth, in meters														
	Site 3					Site 4					Site 5				
	6.1	12.2	18.3	24.4	30.5	6.1	12.2	18.3	24.4	30.5	6.1	12.2	18.3	24.4	30.5
Polycyclic aromatic hydrocarbons															
Indane	1.31	0.01	0.89	0	0	0.17	0.25	0	0	0	0.31	0	0	0	0
Naphthalene	15.60	4.39	10.71	0.60	0	1.26	2.31	1.02	0.22	0.45	2.65	0	1.86	0.22	0.05
Benzothiophene	1.36	0	1.03	0	0	0	.01	0	0	0	.26	0	0	0	0
2-Methylnaphthalene	1.40	.63	.84	0	0	0	.01	0	0	0	.17	0	0	0	0
1-Methylnaphthalene	.79	.30	.46	0	0	0	.01	0	0	0	.09	0	0	0	0
Biphenyl	.36	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Acenaphthalene	.76	0	0	0	0	0	0	0	0	0	0	0	.01	0	0
1,2-Dihydroacenaphthalene	1.09	.67	.44	0	0	0.22	0	0	0	0	0.08	0	.01	0	0
Dibenzofuran	.49	.41	0	0	0	0	0	0	0	0	.06	0	0	0	0
Fluorene	.61	.42	0	0	0	0	0	0	0	0	0	0	0	0	0
Phenanthrene	.78	.76	0	0	0	0	0	0	0	0	0	0	0	0	0
Carbazole	.57	0	.55	0	0	0	0	0	0	0	0	0	0	.07	0
Total[1]	25.12	7.59	14.92	.60	0	1.65	2.59	1.02	.22	0.45	3.69	0	1.88	.22	0.05
Phenolic compounds															
Phenol	10.40	.08	.21	0	0	0	0	0	0	0	0	0	0	0	0
2-Methylphenol	7.10	.10	1.22	0	0	0	0.04	.04	0	0	0	0	0	0	0
3-Methylphenol	13.73	.15	1.42	0	0	0	0	.05	0	0	0	0	0	0	0
4-Methylphenol	6.17	.07	.84	0	0	0	0	0	0	0	0	0	0	0	0
2,6-Dimethylphenol	.90	.06	.46	0	0	.25	.22	.16	0	0	.29	0	.17	0	0
2-Ethylphenol	.43	0	.19	0	0	0	0	0	0	0	0	0	0	0	0
2,4-Dimethylphenol	5.65	.27	3.93	.01	0	1.01	.99	.55	0	0	1.07	.03	.60	.01	0
2,5-Dimethylphenol	3.04	.42	2.55	0	0	.55	.54	.29	0	0	.57	.02	.33	0	0
3,5-Dimethylphenol	9.52	.32	3.27	.01	0	1.67	1.34	.68	0	0	1.64	.04	.89	.01	0
2,3-Dimethylphenol	1.05	.03	.45	0	0	.12	.18	0	0	0	0	0	0	0	0
3,4-Dimethylphenol	2.20	.04	.85	0	0	.23	.36	.10	0	0	.16	0	0	0	0
2,4,6-Trimethylphenol	.23	0	.17	0	0	.05	.05	0	0	0	.09	0	.04	0	0
2,3,6-Trimethylphenol	.67	0	.28	0	0	.12	.12	.08	0	0	.22	0	.06	0	0
Ethylmethylphenol	2.71	.05	.42	0	0	.33	.27	.17	0	0	.40	0	.19	0	0
2,3,5-Trimethylphenol	.46	0	.33	0	0	.13	.10	.04	0	0	.04	0	.03	0	0
2,3,5,6-Tetramethylphenol	.14	0	.03	0	0	.26	.22	.13	0	0	.07	0	.14	0	0
Naphthol (1 and 2)	1.19	.05	.08	0	0	0	0	0	0	0	0.08	0	.09	0	0
Total[1]	65.59	1.64	16.70	.02	0	4.72	4.43	2.29	0	0	4.63	0.09	2.54	0.02	0

[1]Does not include similar compounds that occur in amounts less than 0.01 mg/L each but that, on summation, represent 20 to 25 percent of total.

centrations at this level. Phenol and the methylphenols are present in high concentration in samples from site 3 but are attenuated differentially with depth and are hardly in evidence at sites 4 and 5. By contrast, significant amounts of the other solutes are present at sites 4 and 5. The dimethylphenols move with the ground water and appear to reach a constant concentration or steady state in the affected zone downgradient. Further analyses (table 12) showed the presence of methane in the ground water, amounts increasing from background concentrations of less than 1 mg/L to levels exceeding saturation in the contaminated zone. This evidence suggests that methane is being produced by microbes in the aquifer and that they are utilizing some of the phenols for maintenance (Godsy and others, 1983).

Table 12. Dissolved methane in water samples from sites 1 and 3 through 7
[Concentrations in milligrams per liter; –, not analyzed]

	Sample depth, in meters				
Site No.	6.1	12.2	18.3	24.4	30.5
Site 1 ------	0.13	–	0.19	–	0.10
Site 3 ------	19.30	21.00	6.20	0.15	.01
Site 4 ------	10.10	19.90	8.60	4.30	2.70
Site 5 ------	20.30	13.40	15.60	2.20	.01
Site 6 ------	5.60	–	39.70	51.30	.74
Site 7 ------	3.50	–	36.40	14.80	.47

Similar amounts of other organic solutes were found in the samples from site 3 and they could also be involved in methane production. The other major components include volatile fatty acids, benzoic acid, and quinolinone (table 13). Of these solutes, only acetic and small amounts of formic and benzoic acid were found at site 4. These low-molecular-weight organic acids are likely products of biotransformations occurring at site 4.

SORPTION

Although the chemical evidence and experience from previous investigations indicates that microbial degradation is reducing the amounts of certain contaminants in the aquifer, the possibility that sorption is influencing solute migration was not ruled out. To test this, column sorption studies using aquifer sediments obtained from a well drilled upgradient from the source of contamination were performed. Solutions of relevant compounds at concentrations found in the contaminated aquifer were pumped through the sediment (Goerlitz, 1984). The pH of the solution was adjusted to that of the ground water and the velocity of the solution through the column was similar to that of ground water. The results (fig. 29) show that the phenols are not sorbed by the sediments. Data for the column experiment are given in table 14.

Table 14. Experimental data for column elution

Parameter	Value
Sediment (<2 mm)	Quartz sand
Column length	20.2 cm
Column diameter	1.50 cm
Volume	35.7 cm^3
Dry weight, sediment	60.1 g
Pore volume (gravimetric)	13.80 cm^3
Pore volume (elution inflection)	13.82 cm^3
Porosity	.374
Flow rate	.000789 cm^3/s
Column-UV detector dead volume	.040 cm^3
Column-RI detector dead volume	.090 cm^3
Dispersion	.000255 cm^2/s
k PCP	.426
k Naphthalene	.521

Table 13. Ancillary compounds in water samples from sites 3 and 4
[Concentrations in milligrams per liter; –, not analyzed]

Ancillary compounds	Site 3			Site 4		
	Sample depth, in meters			Sample depth, in meters		
	6.1	12.2	18.3	6.1	12.2	18.3
Acetic acid ----------	45.14	–	0.14	4.60	0.72	0.66
Formic acid ----------	.13	–	0	.07	.97	.09
Propionic acid ----------	23.60	–	.02	0	0	0
Propionic acid, 2-methyl ----------	2.49	–	.04	0	0	0
Butanoic acid ----------	12.87	–	.17	0	0	0
Butanoic acid, 3-methyl ----------	1.32	–	.01	0	0	0
Pentanoic acid ----------	4.13	–	.22	0	0	0
Benzoic acid ----------	27.49	–	3.06	.01	0	0
2(1H)-Quinolinone ----------	14.13	–	1.12	0	0	0

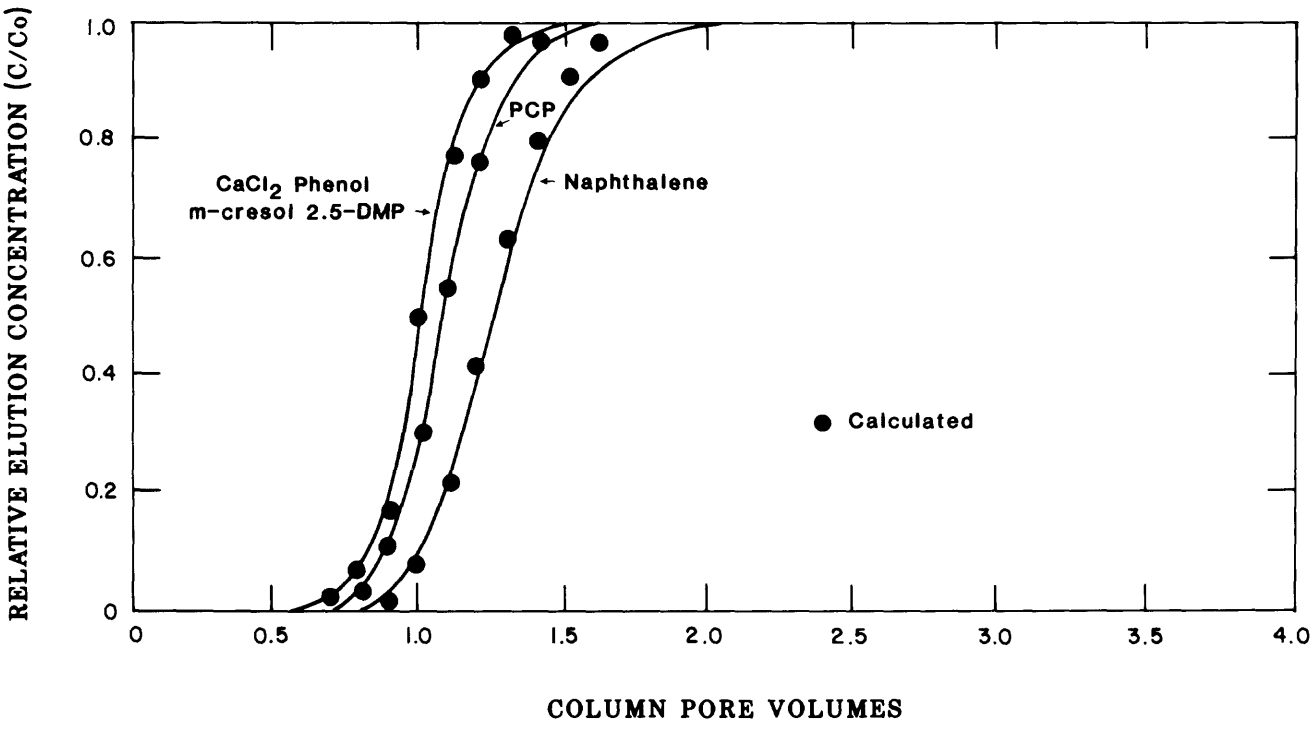


Figure 29. Comparison of elution histories of selected solutes through aquifer sediment to calculated fit.

RESULTS

Results of chemical analyses and sorption experiments that used samples from the creosote works near Pensacola, Fla., show the following:

1. Phenol, 2-methylphenol, 3-methylphenol, and 4-methylphenol are being degraded in the contaminated ground water;
2. The dimethylphenols are not sorbed or degraded and 2,4-dimethylphenol and 3,5-dimethylphenol may be useful as reference tracers;
3. Sorption of the phenols or polynuclear aromatic hydrocarbons by the aquifer sediments is insignificant; and
4. Pentachlorophenol is not present in solution in the ground water at concentrations greater than 0.01 mg/L.

REFERENCES CITED

Ehrlich, G.G., Goerlitz, D.F., Godsy, E.M., and Hult, M.F., 1982, Degradation of phenolic contaminants in ground water by anaerobic bacteria; St. Louis Park, Minnesota: Ground Water, v. 20, no. 6, p. 703–710.

Godsy, E.M., Goerlitz, D.F., and Ehrlich, G.G., 1983, Methanogenesis of phenolic compounds by a bacterial consortium from a contaminated aquifer in St. Louis Park, Minnesota: Bulletin of Environmental Contamination and Toxicology, v. 30, no. 3, p. 261–268.

Goerlitz, D.F., 1984, A column technique for determining sorption of organic solutes on the lithological structure of aquifers: Bulletin of Environmental Toxicology, v. 32, no. 3, p. 261–268

Troutman, D.E., Godsy, E.M., Goerlitz, D.F., and Ehrlich, G.G., 1984, Phenolic contamination in the sand-and-gravel aquifer from a surface impoundment of wood treatment wastes, Pensacola, Florida: U.S. Geological Survey Water-Resources Investigations Report 84-4230, 36 p.

Chapter H. Anaerobic Microbial Transformations of Phenolic and Other Selected Compounds in Contaminated Ground Water at a Creosote Works, Pensacola, Florida

By E. M. Godsy *and* D. F. Goerlitz

Abstract

It generally has been known that certain phenolic compounds present in waste plumes downgradient from ground water contaminated with coal tar derivatives are anaerobically biodegradable to methane and carbon dioxide.

In ground-water samples collected from an area contaminated by wastes from a wood-preserving plant near Pensacola, Florida, a sequential disappearance of C_3 through C_6 carboxylic acids, phenol and benzoic acid, 3- and 4-methylphenol, and finally 2-methylphenol was observed during downgradient movement in the aquifer. In laboratory digestors containing enriched bacterial cultures from contaminated ground water, the same sequential disappearance was observed with concomitant production of methane and carbon dioxide. Of the two dozen or so compounds that make up the bulk of the phenolic fraction of the pollutant load, only the aforementioned compounds have been shown to be substrates for methanogenic fermentation.

The study suggests that a single, but unique, organism is responsible for the nonmethanogenic step in the conversions of phenol to acetate and methylphenols to acetate and formate in laboratory digestors. In water from the contaminated sites, acetate and formate along with methane occur in elevated concentrations, suggesting methanogenesis may be an important process in the disappearance of these compounds in this ground-water system.

INTRODUCTION

Previous studies conducted at a tar and chemical company site in St. Louis Park, Minn., on ground water contaminated with coal tar derivatives concluded that certain phenolic compounds present in the waste plume were biodegraded to methane (CH_4) and carbon dioxide (CO_2) (Ehrlich and others, 1982; Godsy and others, 1983). Similar conclusions were reached after a preliminary study at a creosote works site near Pensacola, Fla., in 1981 (Troutman and others, 1984).

These studies demonstrated conclusively that phenol, 2-methylphenol, and 3-methlyphenol were biodegraded to CH_4 and CO_2 in the ground water and that phenol and 3-methylphenol could be degraded in laboratory digestors to CH_4 and CO_2. Of the dozen or so compounds that make up the bulk of the phenolic fraction of the pollutant load at the Pensacola site only the aforementioned phenols have been shown to be substrates for methanogenic fermentation.

The purpose of this study was threefold. The first objective was to determine which phenolic and related compounds found in the water soluble fraction of creosote from well 320 were anaerobically biodegradable to CH_4 and CO_2. The other two objectives were to determine the degradation sequence of the biodegradable compounds and to determine the reaction pathway of the biodegradable phenolic compounds.

DETERMINATION OF BIODEGRADABLE PHENOLIC COMPOUNDS

Laboratory digestors were prepared by using anaerobic mineral salts containing 200 mg/L of the single compound of interest. The digestors were inoculated with a mixed bacterial population from an anaerobic sewage sludge digestor and from sites 3 and 4, then monitored for CH_4 production and compound disappearance for 12 months. All biodegradable compounds were degraded to CH_4 and CO_2 within 150 days. Nineteen individual phenolic and related compounds were tested for biodegradability. Phenolic compounds tested were phenol; 2-, 3-, and 4-methylphenol; 2- and 4-ethylphenol; and 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dimethylphenol. The other related compounds tested were benzoic acid;

cyclohexanol; cyclohexanone; 1- and 2-naphthoic acid; and 1- and 2-naphthol. Of the compounds tested only phenol, 2-, 3-, and 4-methylphenol, and benzoic acid could serve as the sole carbon and energy source for methanogenic fermentation.

DETERMINATION OF THE BIODEGRADATION SEQUENCE OF SELECTED COMPOUNDS

The ability of bacterial cultures from the area of contamination to degrade phenolic and related compounds to CH_4 and CO_2 in the water from well 320 was tested in the laboratory. One hundred mL of well 320 water was placed in a 500-mL serum bottle filled with washed sand that passed through a 1.0-mm sieve but was retained on a 0.5-mm sieve. One mL of amorphous FeS reducing agent and 5.0 mL of an active methanogenic culture adapted for growth on well 320 water was added under an oxygen-free argon atmosphere in an anaerobic glove box.

The biodegradation of selected compounds in the digestor is shown in figure 30. The biodegradation of C_3 through C_6 carboxylic acids present in this water sample started immediately and was completed after approximately 48 hours. Benzoic acid and phenol degradation started immediately and continued for 11 days. Biodegradation of 3- and 4-methylphenol started on day 11 and continued until day 25. The concentration of 2-methylphenol remained unchanged as of day 60. A lag time of 130 days was observed in the first part of this study before the onset of 2-methylphenol biodegradation.

These results demonstrate that there is a sequential degradation of biodegradable compounds in water from well 320. The C_2 through C_6 carboxylic acids were the first compounds degraded, followed by simultaneous degradation of phenol and benzoic acid. When phenol and benzoic acid were degraded, 3- and 4-methylphenol were simultaneously degraded. This sequential degradation of phenolic compounds also was observed in water samples at the study site during downgradient movement from site 3 to sites 4 and 5 at 6.1 m and 18.3 m (figs. 31 and 32). This disappearance of the biodegradable phenols can be seen when compared to the refractory 3,5-dimethylphenol. This sequential degradation of the phenolic compounds also is evident during vertical movement from 6.1 m to 18.3 m at site 3 (fig. 33).

DETERMINATION OF THE BIODEGRADATION PATHWAY

The degradation of complex organic compounds in anaerobic environments depends on a successive, coordinated interaction of different specific

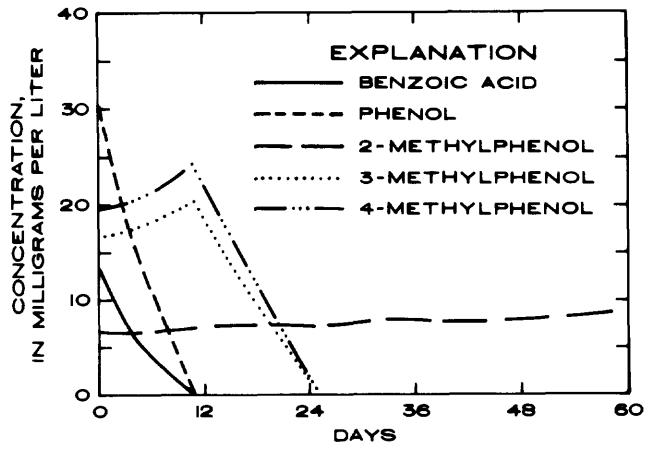


Figure 30. Degradation of compounds in digestor containing water from well 320.

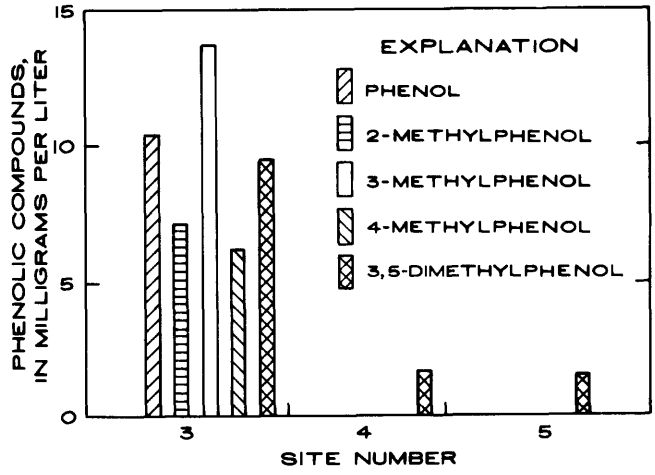


Figure 31. Concentrations of biodegradable phenolic compounds at the creosote works compared to 3,5-dimethylphenol, 6.1 m depth.

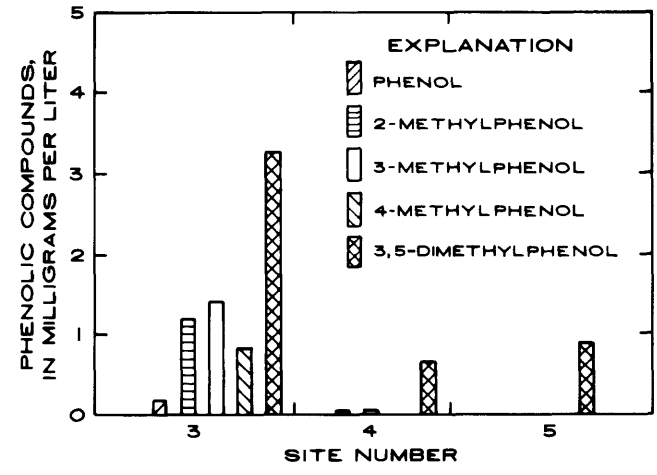


Figure 32. Concentrations of biodegradable phenolic compounds at the creosote works compared to 3,5-dimethylphenol, 18.3 m depth.

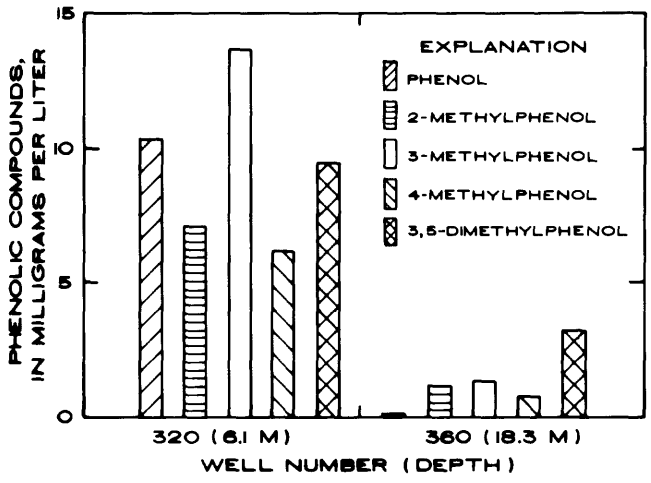


Figure 33. Concentrations of biodegradable phenolic compounds at the creosote works at site 3.

microbial populations. Anaerobic digestion is considered to have two separate and distinct phases brought about by different populations of bacteria: (1) the nonmethanogenic phase, where a variety of bacteria transform complicated substrates to a variety of soluble and gaseous fermentation products including methanol, methylamines, acetate, hydrogen (H_2), and CO_2; and (2) the methanogenic phase, where methanogenic bacteria utilize these as substrates in methanogenesis.

The reaction pathways for the biodegradable phenols can be determined by inhibiting the methanogenic phase of degradation, thereby causing an increase in intermediate products from the nonmethanogenic phase of degradation. To achieve the separation of the nonmethanogenic phase from the methanogenic phase, 5.0 mM bromoethanesulfonic acid (BESA) was added to separate cultures from sites 4 and 5 that were actively degrading phenol, 3-methylphenol, and compounds in water from well 320. Time-course studies revealed acetate as the only intermediate in the methanogenesis of phenol, while both acetate and formate were intermediates in the methanogenesis of 3-methylphenol and water from well 320. Acetate concentration increased approximately 100 times after 2 weeks growth in the presence of BESA in all three digestors (table 15). Formate also increased approximately 100 times in the 3-methylphenol and well 320 digestors. No formate was detected in the phenol digestor. The addition of BESA failed to cause accumulation of monocarboxylic acids, chain length C_3–C_6, or C_4–C_6 dicarboxylic acids.

Shown in table 16 are the concentrations of acetate and formate for selected depths at sites 3, 4, and 5. The persistence of acetate and formate in the downgradient sites of the bioreactor zone is consistent with the observations in the laboratory digestors. Acetate and formate are intermediates in the biodegradation of phenolic compounds.

Table 15. Concentrations of acetate and formate in laboratory digestors

[Concentrations in milligrams per liter; ND = not detected]

Digestor	Acetate	Formate	Inhibited with 5.0 mM of bromoethanesulfonic acid: Acetate	Inhibited with 5.0 mM of bromoethanesulfonic acid: Formate
Phenol	1.20	ND	234	ND
3-Methylphenol	1.80	2.76	186	194
Well 320	1.80	2.30	174	189

Table 16. Concentrations of acetate and formate in water from selected wells

[Concentrations in milligrams per liter; ND = not detected; –, not analyzed]

Depth, in meters	Site 3		Site 4		Site 5	
	Acetate	Formate	Acetate	Formate	Acetate	Formate
6.1	45.0	0.14	0.72	0.97	0.42	0.87
12.3	–	–	4.60	.07	–	–
18.3	0.42	ND	.66	.09	.12	ND

The following steps in the overall conversion of phenol and methylphenol to CH_4 and CO_2 are proposed:

Phenol

1. Degradation of phenol to acetate and H_2.
   $2C_6H_6O + 10\,H_2O \rightarrow 6C_2H_4O_2 + 4\,H_2$
2. Conversion of acetate to CH_4 and CO_2.
   $6C_2H_4O_2 \rightarrow 6CH_4 + 6CO_2$
3. Reduction of CO_2 with H_2.
   $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$
4. Sum.
   $2C_6H_6O + 8H_2O \rightarrow 7CH_4 + 5CO_2$

Methylphenol

1. Degradation of methylphenol to acetate, formate, and H_2.
   $4C_7H_8O + 32H_2O \rightarrow 10C_2H_4O_2 + 8CH_2O_2 + 20H_2$
2. Conversion of acetate to CH_4 and CO_2.
   $10C_2H_4O_2 \rightarrow 10CH_4 + 10CO_2$
3. Conversion of formate to CO_2 and H_2.
   $8CH_2O_2 \rightarrow 8CO_2 + 8H_2$
4. Reduction of CO_2 with H_2.
   $28H_2 + 7CO_2 \rightarrow 7CH_4 + 14H_2O$
5. Sum.
   $4C_7H_8O + 18H_2O \rightarrow 17CH_4 + 11CO_2$

These steps are consistent with both laboratory and field observations and with the stoichiometry of phenol and methylphenol conversion to CH_4 and CO_2 given by the equation of Tarvin and Buswell (1934):

$$C_nH_aO_b + [n - a/4 - b/2]H_2O \rightarrow [n/2 - a/8 + b/4]CO_2 + [n/2 + a/8 - b/4]CH_4$$

The study suggests that a single but unique organism is responsible for the nonmethanogenic step in the conversions of phenol and methylphenol to their respective intermediates. When a phenol-degrading consortium was challenged with methylphenol, a 4- to 6-week period was observed before degradation began, while the same consortium, when challenged with phenol, immediately degraded phenol. Similarly, when a methylphenol-degrading consortium was challenged with phenol, a 4- to 6-week delay was observed, while methylphenol was degraded without delay.

CONCLUSIONS

Enriched bacterial cultures from the area of contamination at the creosote works are able to sequentially convert C_3 through C_6 carboxylic acids, phenol and benzoic acid, 3- and 4-methylphenol, and finally 2-methylphenol present in water from well 320 to methane and carbon dioxide in laboratory digestors. In laboratory digestors, acetate and formate are intermediates in the methanogenesis of phenolic compounds. In water from sites 3, 4, and 5 these compounds along with methane occur in concentrations (chapter G, Goerlitz and others) that suggest methanogenesis may be an important process in the disappearance of these compounds in this ground-water system.

REFERENCES CITED

Ehrlich, G.G., Goerlitz, D.F., Godsy, E.M., and Hult, M.F., 1982, Degradation of phenolic contaminants in ground water by anaerobic bacteria, St. Louis Park, Minnesota: Ground Water, v. 20, no. 6, p. 703–710.

Godsy, E.M., Goerlitz, D.F., and Ehrlich, G.G., 1983, Methanogenesis of phenolic compounds by a bacterial consortium from a contaminated aquifer in St. Louis Park, Minnesota: Bulletin of Environmental Contamination and Toxicology, v. 30, p. 261–268.

Tarvin, D., and Buswell, A.M., 1934, The methane fermentation of organic acids and carbohydrates: Journal of American Chemical Society, v. 56, p. 1751–1755.

Troutman, D.E., Godsy, E.M., Goerlitz, D.F., and Ehrlich, G.G., 1984, Phenolic contamination in the sand-and-gravel aquifer from a surface impoundment of wood treatment wastes, Pensacola, Florida: U.S. Geological Survey Water-Resources Investigations Report 84–4230, 36 p.

Chapter I. Creosote Discharge to the Nearshore Estuarine Environment in Pensacola Bay, Florida: Preliminary Assessment of Effects

By John F. Elder *and* Paul V. Dresler

Abstract

Both ground water and surface water moving toward Pensacola Bay from a wood-treatment site are contaminated with byproducts of the creosote and pentachlorophenol treatment process. Some of these compounds may have discharged into the bay and accumulated in sediments or in tissues of estuarine biota, possibly affecting the ecological characteristics of the nearshore benthic community. The purposes of the study are to test the following hypotheses.

1. Diversity and abundance of benthic invertebrate species in Pensacola Bay are affected by organic contamination of ambient water and sediments.
2. The concentrations of organics in water, sediments, and living organisms in Pensacola Bay are correlated to each other and to distance from the plant discharge area.
3. Organic compounds have accumulated in tissues of mollusks inhabiting the area near Bayou Chico, and this accumulation is greater than that which may have occurred in the same organisms in similar habitats remote from the site.

INTRODUCTION

The creosote works site is located less than ½ km from the shore of Pensacola Bay, near Bayou Chico inlet (fig. 34). The general direction of surface- and ground-water flow is directly south, toward the bay (chapter A, Mattraw and Franks). Recent determinations (chapter A, Mattraw and Franks; chapter E, Pereira and Rostad) have shown that both ground water and surface water moving toward the bay from the site are contaminated with byproducts of the creosote treatment process. Some of these compounds may have discharged into the bay and accumulated in sediments or in tissues of estuarine biota, possibly affecting the ecological characteristics of the nearshore benthic community. Other industries in the Bayou Chico area have been sources of some pollution in the bay, but none produces all of the same kinds of organic compounds found in creosote byproducts. This chapter describes a study of the effects of creosote byproduct discharge into the bay and presents some preliminary findings of the study.

Background

Studies elsewhere in the past decade have produced numerous reports on the flux of manmade organic compounds to estuarine and lake sediments (Frank and others, 1980; Lopez-Avila and Hites, 1980; Gschwend and Hites, 1981; Eadie and others, 1982). Reports of bioaccumulation in aquatic organisms (Wyman and O'Connors, 1980; Eadie and others, 1982; Readman and others, 1982; Conner, 1984) indicate that concentrations in body tissues vary greatly, depending on location, type of compound, species, and concentrations in ambient water and sediments. Much less information is available in the literature on effects of organic pollution on benthic faunal abundance and diversity in estuaries. Tagatz and others (1981) did investigate effects of different concentrations of pentachlorophenol (PCP) on various estuarine benthic species in Santa Rosa Sound, Fla. At concentrations of 140 µg/L PCP, community structure was significantly altered and average density of most species declined. No such effect was observed at a concentration of 13 µg/L.

The study is being conducted in western Pensacola Bay, near its outlet to the Gulf of Mexico (fig. 34). Surface salinities generally fall in the range of 12–22 parts per thousand. Bottom materials are dominated by fine- and medium-grained sands. In some areas nearshore, considerable quantities of fine organic detritus lies on or near the surface of the sand. Macrophytes are nearly absent. Rock, concrete, and wood surfaces in some areas provide habitat for some gastropods and decapods. Most such habitats are artificial, resulting from installation of piers, breakwater barriers, marker pilings, and the like. All

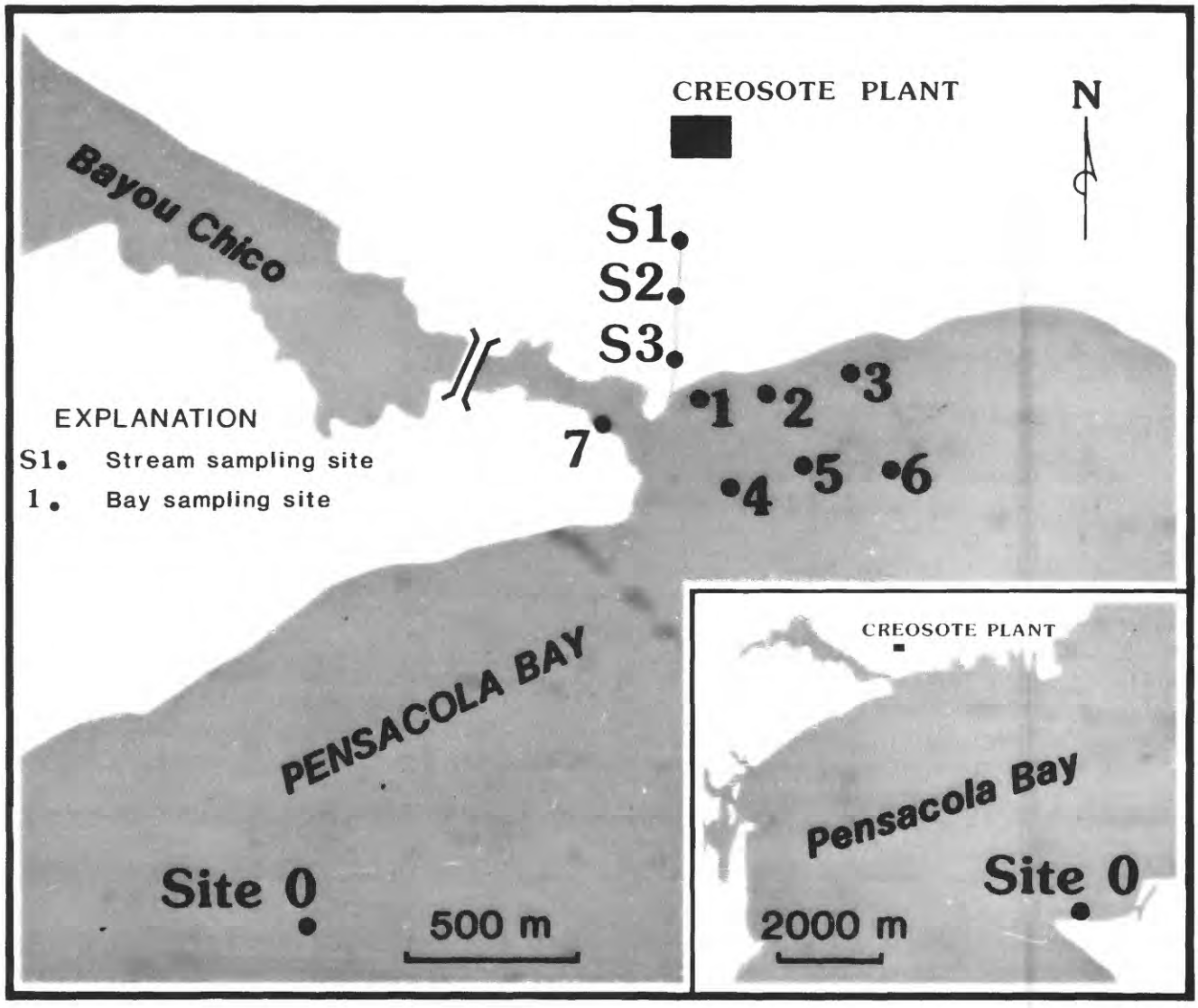


Figure 34. Sampling sites in Pensacola Bay, Bayou Chico, and stream near the creosote works plant.

of the sites where samples are collected for the current study are nearshore, with depths not exceeding 2 m at high tide.

As a coal tar distillate, creosote is a mixture of over 200 chemical compounds (U.S. Department of Agriculture, 1980). Among the most common constituents are napthalene, acenaphthene, dibenzofuran, fluoranthene, pyrene, and phenolic compounds. PCP, another common wood preservative, also was used extensively at the Pensacola site. PCP is an important inhibitor of microbial biodegradation of phenol (E.M. Godsy, written commun., 1984). All of these compounds must be considered as possible contaminants in Pensacola Bay, although they are certainly subject to dilution and, in many cases, chemical transformation upon release into aerobic estuarine waters. For the sake of simplicity, the term "creosote/PCP" will be used in this paper to refer collectively to the group of organic compounds that may be discharging into the estuary from the site.

Hypotheses

1. Diversity and abundance of benthic invertebrate species in Pensacola Bay are affected by creosote/PCP contamination of ambient water and sediments.
2. The concentrations of creosote/PCP in water, sediments, and living organisms in Pensacola Bay are correlated to each other and to distance from the creosote discharge area.
3. Creosote/PCP compounds have accumulated in tissues of mollusks inhabiting the area near Bayou Chico, and this accumulation is greater than that which may have occurred in organisms of

the same species in similar habitats remote from the site.

The purpose of the study is to test these hypotheses. Sampling was concentrated within a 700-m radius of the mouth of Bayou Chico, except for one control site across the bay. Only benthic invertebrate species underwent biological analyses; other biota are not included in the study. Chemical analyses are limited to acid-extractable and base-neutral organic compounds, those most commonly associated with wood-preserving wastes.

APPROACH

Sampling was conducted at seven sites near the creosote works in Pensacola Bay, three sites in the stream draining from the creosote works to the bay, and one control site across the bay, near Gulf Breeze Island (fig. 34). Six of the bay sites are in an approximate grid pattern bounded on the west by the creosote works stream outlet and the channel into the bay from Bayou Chico. Three sites are within 50 m of shore, and the other three are approximately 200 m offshore. The seventh site is in the mouth of Bayou Chico. All 11 sites have been sampled three times: June 1983, October 1983, and February 1984.

Samples for biological analyses of estuarine infauna were taken with the benthic corer shown in figure 35. This device extracts a core representing approximately the top 15 cm of the sediments. Ten cores from each site were taken each sampling date and analyzed separately to give adequate replication. Each core sample was sieved through a ½-mm mesh and preserved with formalin mixed with Rose Bengal stain. At the time the biological samples were collected, field measurements of pH, temperature, and salinity of the water also were taken. At sites 1 and 5, and at the control site, 1-L water samples and 200-g sediment samples were taken for analysis of organic constituents. The samples were extracted in methylene chloride at pH 2 and pH 9 to determine acid-extractable and base-neutral creosote/PCP compounds by gas-chromatography mass-spectrometry.

A large benthic mollusk species was needed for determinations of bioaccumulation of organic contaminants in organisms inhabiting the nearshore area of the bay near the creosote works discharge. The most abundant and widely distributed large mollusk species is the oyster drill snail (*Thais haemostoma*). In October 1983, *Thais* samples were taken from sites 1 and 2, each sample consisting of a composite of approximately 25 animals. The snails were shelled, frozen, and analyzed for polynuclear aromatic hydrocarbons and phenols.

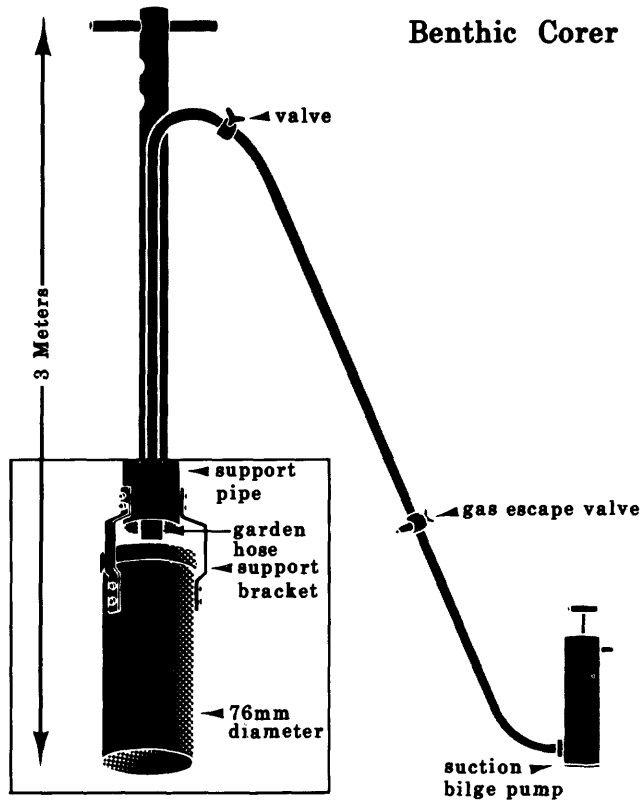


Figure 35. Corer used for replicate grabs of sediments at estuarine sampling sites.

RESULTS

Concentrations of compounds in sediments from site 4 are shown in table 17. Phenol and its derivatives were not detected. A large number of base-neutral compounds and pentachlorophenol also were undetected. Only a few of the polynuclear aromatic hydrocarbons and phthalates appeared at detectable concentrations.

Tests for bioaccumulation in *Thais* showed a number of polycyclic aromatic and heterocyclic compounds (table 18). In this analysis of the organisms, there were no samples from the control site for comparison.

Benthic invertebrate abundance data from initial counts of the June 1983 samples are shown in table 19. These data are preliminary and unquestionably subject to change; they are based on analysis of only one core sample from each site. In the stream, there does appear to be a trend of increasing abundance in a downstream direction, possibly due to dilution of wastes. This trend is likely to hold true as more data are analyzed because it appears that there is a severe limitation in the number of organisms that can survive in the heavily contaminated upstream reach. The data from the estuary are still too limited

Table 17. Concentrations of compounds in sediments at Pensacola Bay site 4, June 1983

Compound	Concentration (micrograms per kilogram)
Detected	
bis(2-Ethylhexyl)phthalate	3,400
Di-n-butyl phthalate	370
Chrysene	100
Fluoranthene	190
Benzo(k)fluoranthene	150
Pyrene	160
Benzo(a)pyrene	40
Benzo(a)anthracene	75
Not detected	
Base/neutral-extractable organics (detection limit = 10 µg/kg)	
1,2-Dichlorobenzene	
1,3-Dichlorobenzene	
1,4-Dichlorobenzene	
Hexachloroethane	
Dibenzo(a,h)anthracene	
Benzo(g,h,i)perylene	
4-Chlorophenyl phenyl ether	
3,3'-dichlorobenzidine	
Hexachlorobutadiene	
Hexachlorobenzene	
1,2,4-Trichlorobenzene	
bis(2-Chloroethoxy)methane	
Naphthalene	
2-Chloronaphthalene	
Isophorone	
Nitrobenzene	
Anthracene	
Benzo(b)fluoranthene	
Indeno(1,2,3-cd)pyrene	
Benzidine	
bis(2-Chloroethyl)ether	
Hexachlorocyclopentadiene	
N-Nitrosodiphenylamine	
N-Nitrosodimethylamine	
N-Nitrosodi-N-propylamine	
bis(2-Chloroisopropyl)ether	
2,4-Dinitrotoluene	
2,6-Dinitrotoluene	
4-Bromophenyl phenyl ether	
Di-n-octylphthalate	
Dimethyl phthalate	
Diethyl phthalate	
Acenaphthylene	
Acenaphthene	
Butylbenzyl phthalate	
Fluorene	
Phenanthrene	

Table 17. Concentrations of compounds in sediments at Pensacola Bay site 4, June 1983—Continued

Compound	Concentration (micrograms per kilogram)
Acid-extractable organics (detection limit = 20 µg/kg)	
Phenol	
2-Nitrophenol	
4-Nitrophenol	
2,4-Dinitrophenol	
Pentachlorophenol	
2-Chlorophenol	
2,4-Dichlorophenol	
2,4,6-Trichlorophenol	
2,4-Dimethylphenol	

Table 18. Results of analyses of *Thais haemostoma* snails collected at Pensacola Bay sampling sites, October 1983

[Concentrations in micrograms per kilogram, wet weight; ND = not detected; Compounds analyzed but not detected in either sample: phenol, indane, 2-methylphenol, 2,4-dimethylpyridine, 3,5-dimethylphenol, quinoline, 2,3,5-trimethylphenol, 2-methylquinoline, 1-naphthol, pentachlorophenol]

Compound	Concentration	
	Site 1	Site 2
2,4-Dimethylphenol	ND	0.5
Naphthalene	15	34
Benzothiophene	0.1	.3
2-Methylnaphthalene	2.1	7.8
1-Methylnaphthalene	2.0	10
Biphenyl	0.7	3.2
Acenaphthene	2.1	8.8
2-Naphthol	.5	ND
Dibenzofuran	.9	4.3
Fluorene	1.3	6.3
2-Quinolinone	ND	4.8
Dibenzothiophene	1.2	2.7
Phenanthrene	66	190
Anthracene	9.0	25
Acridine	.4	.6
Carbazole	ND	.7
Acridinone	7.7	9.7
Fluoranthene	26	61
Pyrene	23	40
Benzo(a)pyrene	2.5	2.8
Cyclopenta(d,e,f)phenanthrene	5.6	11

to indicate what differences, if any, exist among the sites.

Most of the organisms encountered in the stream sites were larval forms of annelids and mollusks. Larval forms were also common in the estuarine community, but a more diverse assemblage of polychaetes, isopods, nematodes, and mollusks was found.

Table 19. Abundance of benthic invertebrate species at the creosote works stream and Pensacola Bay sampling sites, June 1983

Site	Number of individuals: log number per square meter
Stream:	
1	2.7
2	3.2
3	3.5
Bay:	
0	3.3
1	3.2
2	3.5
3	3.6
4	4.5
5	4.3
6	4.0
7	4.0

CONTINUATION OF THE STUDY

It is intended that the basic sampling program will conclude in summer 1984. This will provide four sample sets, covering a 15-month period, representing different seasons and environmental conditions. In addition to the regular sampling, the oyster culturing and the artificial substrate experiment is expected to be initiated and completed by fall 1984. The resulting data should provide a basis by which the previously-stated hypotheses can be accepted or rejected.

One of the purposes of doing the work in the estuary is to identify any relation that might exist between freshwater contamination (both ground water and surface water) and estuarine pollution and community structure. Whatever information is generated about solute transport, plume migration, and microbial degradation of phenolic compounds and other creosote byproducts will be very useful in interpretation of the estuarine data.

SELECTED REFERENCES

Conner, M.S., 1984, Fish/sediment concentration ratios for organic compounds: Environmental Science and Technology, v. 18, no. 1, p. 31–35.

Eadie, B.J., Faust, W., Gardner, W.S., and Nalepa, Tom, 1982, Polycyclic aromatic hydrocarbons in the sediments and associated benthos in Lake Erie: Chemosphere, v. 11, no. 2, p. 185–191.

Frank, R., Thomas, R.L., Braun, H.E., Rasper, J., and Dawson, R., 1980, Organochlorine insecticides and PCB in the surficial sediments of Lake Superior (1973): Journal of Great Lakes Research, v. 6, no. 2, p. 113–120.

Gschwend, P.M., and Hites, R.A., 1981, Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States: Geochimica Cosmochimica Acta, v. 45, no. 12, p. 2359–2367.

Lopez-Avila, V., and Hites, R.A., 1980, Organic compounds in an industrial wastewater: their transport into sediments: Environmental Science and Technology, v. 14, no. 11, p. 1382–1390.

Readman, J.W., Mantoura, R.F.C., Rhead, M.M., and Brown, L., 1982, Aquatic distribution and heterotrophic degradation of polycyclic aromatic hydrocarbons (PAH) in the Tamar Estuary: Estuarine, Coastal, and Shelf Science, v. 14, no. 4, p. 369–389.

Tagatz, M.E., Ivey, J.M., Gregory, N.R., and Oglesby, J.L., 1981, Effects of pentachlorophenol on field and laboratory developed estuarine benthic communities: Bulletin of Environmental Contamination and Toxicology, v. 26, no. 1, p. 137–143.

U.S. Department of Agriculture, 1980, The biological and economic assessment of pentachlorophenol, inorganic arsenicals, creosote, v. 1, wood preservatives: Technical Bulletin No. 1658–1, 435 p.

Wyman, K.D., and O'Connors, H.B., 1980, Implications of short term PCB uptake by small estuarine copepods from PCB-contaminated water, inorganic sediments and phytoplankton: Estuarine, Coastal and Marine Science, v. 11, no. 2, p. 121–131.