

MOVEMENT AND FATE OF SOLUTES IN A PLUME OF SEWAGE-CONTAMINATED GROUND WATER, CAPE COD, MASSACHUSETTS: U.S. GEOLOGICAL SURVEY TOXIC WASTE GROUND-WATER CONTAMINATION PROGRAM

U.S. GEOLOGICAL SURVEY

Open-File Report 84-475



Papers presented at the Toxic Waste Technical Meeting
Tucson, Arizona, March 20-22, 1984

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Denis R. LeBlanc, Editor

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P R E F A C E

Over the past decade, the need for understanding the mechanisms of contamination of ground water by toxic wastes has become exceedingly important. Many private and government studies of contaminated aquifers have described the movement, chemical alteration, and dispersal of toxic chemicals in ground-water systems. These studies have also shown, however, that transport of contaminants in aquifers is a very complex process. Many technical questions are yet to be answered about the behavior of specific chemicals under different hydrologic and geologic conditions. Answers to these questions are needed to guide the evaluation and cleanup of contaminated ground-water supplies and to ensure safe use and disposal of toxic chemicals.

The U.S. Geological Survey has begun a nationwide program to study the fate of toxic wastes in ground water. Several sites where ground water is known to be contaminated are being studied by interdisciplinary teams of geohydrologists, chemists, and microbiologists. The objective of these studies is to obtain a thorough quantitative understanding of the physical, chemical, and biological processes of contaminant generation, migration, and attenuation in aquifers. The knowledge obtained from these site-specific studies will contribute greatly to successful evaluation, monitoring, and remedial action at similar sites where contamination by toxic chemicals occurs.

One of the sites being studied by the U.S. Geological Survey under this program is a plume of sewage-contaminated ground water on Cape Cod, Massachusetts. The plume was formed by land disposal of treated sewage to a glacial outwash aquifer since 1936. Although sewage generally is not considered a hazardous waste, even relatively "clean" domestic sewage contains many inorganic and organic chemicals such as sodium, nitrate, detergents, and volatile organic compounds which can be toxic and render a ground-water supply unfit for use. Research on how these sewage-derived contaminants move in the Cape Cod aquifer will add to the understanding of the complex interactions of geohydrologic, chemical, and microbiological processes that affect contaminant migration.

This report summarizes results obtained during the first year of research at the Cape Cod site under the U.S. Geological Survey Toxic-Waste Ground-Water Contamination Program. The seven papers included in this volume were presented at the Toxic Waste Technical Meeting, Tucson, Arizona, in March 1984. They provide an integrated view of the subsurface distribution of contaminants based on the first year of research and discuss hypotheses concerning the transport processes that affect the movement of contaminants in the plume.

- A mathematical model of solute transport is used to simulate and evaluate the movement of dissolved constituents within the ground-water-flow system.
- The distributions of inorganic and organic chemicals in the plume are described and preliminary conclusions are presented about the behavior of selected contaminants in the aquifer.
- A special technique to determine concentrations of semi-volatile organic compounds in the plume at the nanogram per liter level is evaluated and used to identify possible organic tracers of the contaminated ground water.
- The distributions of inorganic nitrogen, organic carbon, and bacterial populations in the aquifer are used to show that microbial activity significantly affects the fate of some contaminants.
- The abundance and nature of the bacterial population in sediment and water samples are described and preliminary conclusions are presented about the reaction of ground-water bacteria to the subsurface sewage contamination.
- Measurements of the denitrification potential of sediment and water samples are used to show that a zone of bacterially mediated denitrification probably has been established in the aquifer in response to the increased quantities of nitrate and organic carbon in the plume.

The authors thank the many persons who have kindly given time, information, and guidance to the project team. Particular thanks are given to Richard Quadri, Stephen Garabedian, Virginia de Lima, Albert Augustine, John Organek, Peter Haeni, Joseph Newell, and other persons in the Geological Survey who assisted with data collection and project logistics. The authors also gratefully acknowledge Col. Philip McNamara and George Sundstrom of Otis Air National Guard Base for their help and cooperation.

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ABBREVIATIONS AND CONVERSION FACTORS

The inch-pound units used in this report may be converted to metric (International System) units by the following factors.

<u>Multiply inch-pound unit</u>	<u>By</u>	<u>To obtain metric unit</u>
inch (in.)	2.540	centimeter (cm)
foot (ft)	0.3048	meter (m)
foot per second per foot [(ft/s)/ft]	0.3048	meter per second per meter [(m/s)/m]
mile (mi)	1.609	kilometer (km)
square mile (mi ²)	2.590	square kilometer (km ²)
acre	4,047	square meter (m ²)
ounce, fluid (oz)	0.02957	liter (L)
gallon (gal)	3.785	liter (L)
million gallons (Mgal)	3,785	cubic meter (m ³)
billion gallons (Bgal)	3,785,000	cubic meter (m ³)
ounce, avoirdupois (oz)	28.35	gram (g)
inch per year (in/yr)	25.4	millimeter per year (mm/a)
foot per day (ft/d)	0.3048	meter per day (m/d)
foot per mile (ft/mi)	0.1894	meter per kilometer (m/km)
million gallons per day (Mgal/d)	3,785	cubic meters per day (m ³ /d)
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
foot squared per day (ft ² /d)	0.09290	meter squared per day (m ² /d)

Temperature, in degrees Fahrenheit (°F), can be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{F} = 1.8 \text{ } ^{\circ}\text{C} + 32$$

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

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

CHAPTER A

Many sites where ground water has been contaminated by toxic wastes are located on sandy, permeable, water-table aquifers. This introductory paper describes the source and hydrogeologic setting of a plume of sewage-contaminated ground water which is located in a sandy aquifer. Research on how sewage contaminants have moved in the aquifer on Cape Cod will help scientists and engineers to understand the fate of toxic wastes in ground water. This research is described in subsequent chapters of this volume.

DESCRIPTION OF THE HAZARDOUS-WASTE RESEARCH SITE

By Denis R. LeBlanc

ABSTRACT

Disposal of treated sewage since 1936 to a sand and gravel aquifer at Otis Air Base, Cape Cod, Massachusetts, has formed a plume of contaminated ground water that is more than 11,000 feet long. The plume is being studied by the U.S. Geological Survey as part of a nationwide program to understand the fate of toxic wastes in ground water.

More than 8 billion gallons of secondarily treated sewage have been discharged to the aquifer at the Otis Air Base sewage plant since 1936. Disposal is by rapid infiltration through sand beds. The aquifer that receives the treated sewage is composed of 90 to 140 feet of stratified sand and gravel outwash underlain by silty sand and by till. Ground water in the outwash is unconfined and moves southward toward Nantucket Sound at a rate of about 1 foot per day.

INTRODUCTION

Disposal of treated sewage since 1936 through infiltration beds to a sand and gravel aquifer at Otis Air Base, Cape Cod, Massachusetts (fig. 1), has formed a plume of contaminated ground water that is 3,000 feet wide, 75 feet thick, and more than 11,000 feet long. Water in the plume contains elevated concentrations of chloride, sodium, boron, nitrogen, detergents, and other constituents of the treated sewage. The plume was previously mapped and described in a study by the U.S. Geological Survey, in cooperation with the DWPC (Massachusetts Department of Environmental Quality Engineering, Division of Water Pollution Control), to determine the impacts on ground-water quality of land disposal of sewage (LeBlanc, 1982; 1984). The sewage-disposal method used at Otis Air Base is used at more than 350 sites in the United States and has been proposed for use at other sites in Massachusetts.

DESCRIPTION OF STUDY AREA

The Otis Air Base sewage-treatment facility is located 6 miles north of Nantucket Sound on a broad glacial outwash plain of Pleistocene age (fig. 1). The study area includes 20 mi² of the outwash plain in the towns of Falmouth, Sandwich, and Mashpee, and is generally bounded by Otis Air Base to the north, the heads of several saltwater bays to the south, Coonamessett Pond to the west, and Johns Pond to the east.

The study area south of Otis Air Base is mostly rural, although many homes have been built since the plume was first mapped in 1978-79. Otis Air Base has been a military reservation since at least 1936. During World War II, the reservation housed as many as 70,000 troops, and between 1948 and 1973 the base was a major installation of the U.S. Air Force. Since 1973, the base has been used by the Massachusetts National Guard and the U.S. Coast Guard.

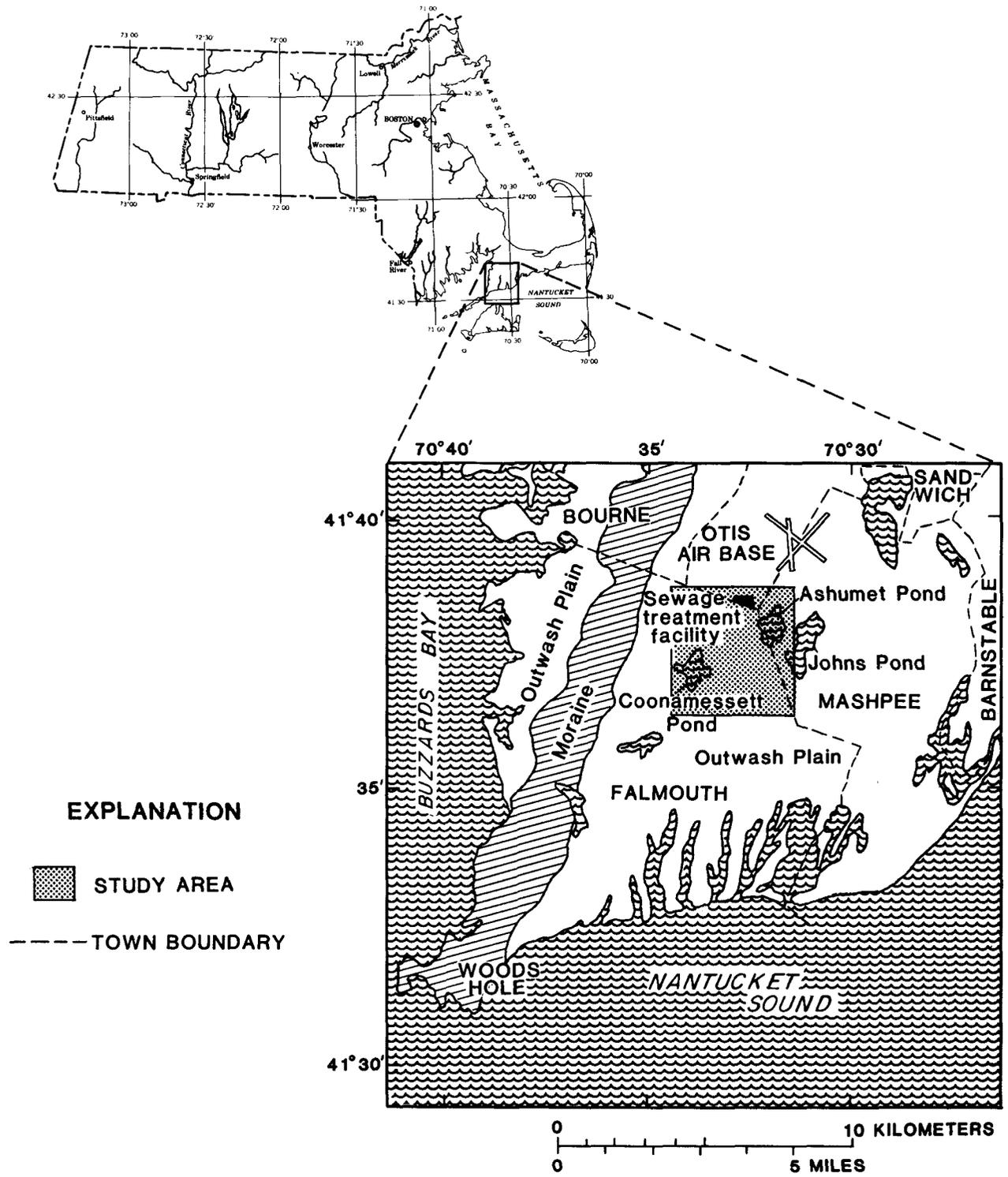


Figure 1.--Study area.

DISPOSAL OF TREATED SEWAGE

The Otis Air Base sewage-treatment facility provides secondary treatment to sewage from the base. A small treatment plant with 4 acres of sand beds served the base between 1936 and 1941. The present treatment plant was constructed in 1941 at the site of the original plant and is designed to treat an average flow of 3 Mgal/d.

The treated sewage can be discharged to 24 one-half acre sand beds (fig. 2) which are rectangular and have flat sandy surfaces. The treated sewage infiltrates into the ground at the beds and percolates to the water table 20 feet below the bed surfaces. The 24 beds have not all been actively used because actual sewage flows during 1936-80 have been much less than design rates, but historical data on bed usage are not available. Since 1977, the treated sewage has been applied exclusively to two beds at the northeast corner of the bed area. Eight other beds are being renovated and will be used for sewage disposal starting in mid-1984 (George Sundstrom, Otis Air National Guard, oral commun., 1983).

The estimated average daily volume of sewage treated at the base from 1936 to 1980 is 0.46 Mgal/d. Average flows have varied from 0.15 Mgal/d prior to World War II to 1.4 Mgal/d during 1941-44 (fig. 3). Records of sewage flows were available for only part of this period and are of questionable accuracy (George Sundstrom, Otis Air National Guard, oral commun., 1983). Sewage flows for the remainder of the period were estimated from records of pumpage for drinking water and from estimates of historical base population.

Analyses of the treated sewage in 1979-80 showed that it contains 150-180 mg/L dissolved solids, about four times the dissolved solids content of uncontaminated ground water in the study area (LeBlanc, 1982, p. 13). Few data are available on the chemical quality of the treated sewage prior to 1974. The estimated average concentrations of boron, chloride, and detergents in the treated sewage, based on analyses of the treated sewage during 1974-80 and analyses reported for earlier periods at similar treatment facilities, are given in table 1. The chemistry of the treated sewage is discussed by Thurman and others (1984).

Table 1.—Estimated average concentrations of boron, chloride, and detergents in the treated sewage and in the uncontaminated ground water

[Concentrations in milligrams per liter unless otherwise noted.]

Constituent	Treated sewage		Uncontaminated ground water Concentration
	Period	Concentration	
Boron (micrograms per liter)	1936-79	500	<50
Chloride	1936-79	30	9
Detergents (MBAS)	1936-47	.0	.0
	1948-64	3	.0
	1965-79	.3	.0

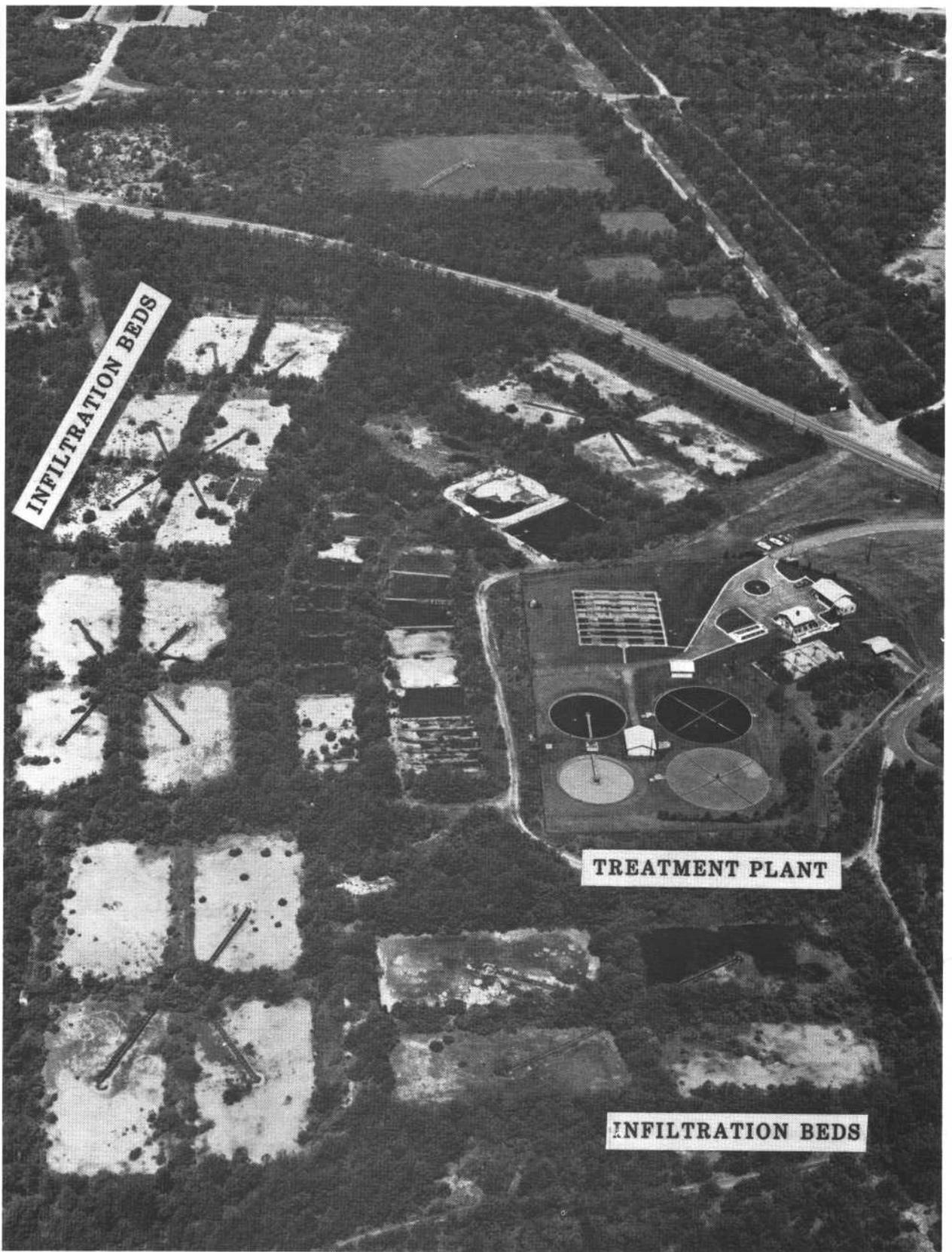


Figure 2.--View west of the Otis Air Base sewage-treatment plant.
Photograph courtesy of the U.S. Air National Guard.

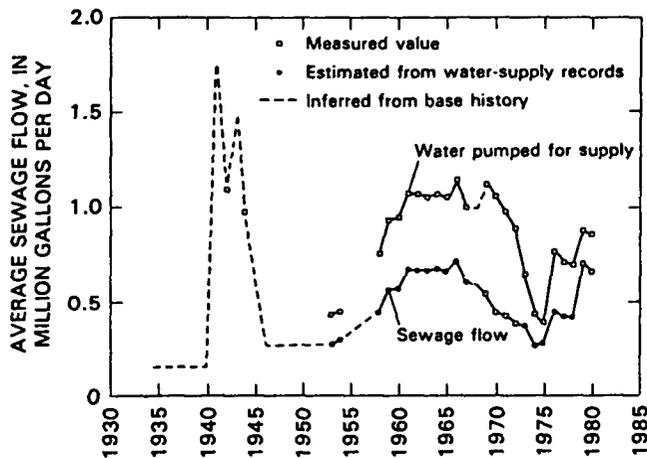


Figure 3.--Volume of sewage treated at the Otis Air Base sewage-treatment plant between 1936 and 1980 (from LeBlanc, 1982).

HYDROLOGIC SYSTEM

Hydrogeology

The aquifer that receives the treated sewage is composed of Pleistocene glacial deposits of sand, gravel, silt, and clay that overlie crystalline bedrock (fig. 4). The top 90 to 140 feet of the aquifer is composed of stratified sand and gravel outwash. These sands and gravels contain only trace quantities of silt and clay sized particles and are composed predominantly of quartz and feldspar. The saturated thickness of the outwash decreases to the south, based on examination of logs of seven boreholes that penetrate into the underlying sediments.

In the northern half of the study area, outwash overlies fine to very fine sand and silt. In the southern half, outwash overlies fine to very fine sand and silt, and dense sandy till. The till contains lenses of silt and clay and lenses of sand and gravel. The bedrock surface slopes gently from west to east across the study area (Oldale, 1969). Bedrock has been mapped as granodiorite, a gray crystalline igneous rock (Oldale and Tuttle, 1964, p. D121).

Hydrology

Ground water in the aquifer is unconfined, and the water table slopes uniformly to the south except where it is distorted by ponds (fig. 5). The water-table contour map was prepared from water levels measured in November 1979. Water levels in November 1979 were near average for the period 1963-76 (Guswa and LeBlanc, 1985) at 10 long-term monitoring sites on Cape Cod.

The hydrograph for well FSW 167 (fig. 6) is typical of water-level fluctuations in the study area. The water table fluctuates 1 to 3 feet each year due to seasonal variations in recharge from precipitation. No long-term rise or decline of average annual water levels has been observed since monitoring began in the study area in 1975. The hydrograph of well A1W 230 (fig. 6), located in a geohydrologically similar outwash deposit 14 miles east of the study area, shows no long-term rise or decline of water levels since 1960. Water levels in the study area correlate well with levels measured in well A1W 230 (Frimpter, 1980, p. 6 and plate 1). Therefore, the water-table map shown in figure 5 represents a steady-flow system.

The only natural source of water to the aquifer is recharge from precipitation. The estimated average annual recharge rate is 21 in/yr (LeBlanc, 1982, p. 10). Recharge occurs over most of the study area. Direct surface runoff is negligible because the sandy soils are very permeable.

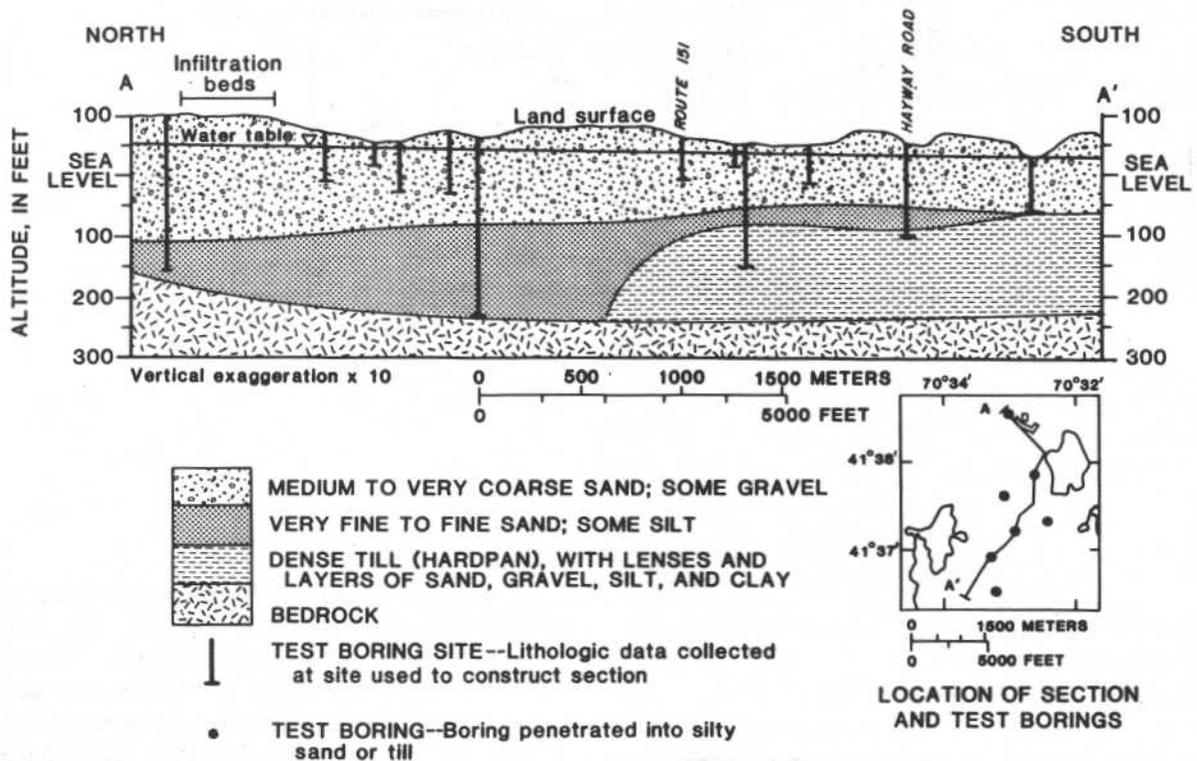


Figure 4.--Geologic section showing hydrogeologic units in the study area (from LeBlanc, 1982).

Ground water in the study area generally flows south as inferred from the water-table map and from the path of the plume. LeBlanc (1982, p. 10) estimated that ground water moves through the sand and gravel at 0.8 to 2.3 ft/d. Ground-water flow is nearly horizontal except near the ponds and presumably near the infiltration beds. Vertical variations in hydraulic head within the outwash are very small (table 2) at the five sites (fig. 5) where water levels were measured in well clusters. The observed vertical differences in head are not significantly larger than the accuracy of the measurements. There may be larger transient vertical head gradients during recharge events, but continuous water-level records at the well clusters are needed to detect these gradients.

Most ground water flowing through the study area discharges to streams, ponds, and wetlands in southern Falmouth and to Nantucket Sound. The net discharge from the aquifer by pumping wells is small because most water is returned to the aquifer through irrigation and septic systems. Water also flows between the aquifer and the three large kettle-hole ponds. Ashumet Pond, which is located 1,700 feet southeast of the infiltration beds (fig. 5), has no surface inlet or outlet. Johns Pond and Coonamessett Pond are drained by streams. Ground-water levels south of the Otis treatment plant are controlled, in part, by the relatively constant water levels along Johns and Coonamessett Ponds and the streams that flow from the ponds.

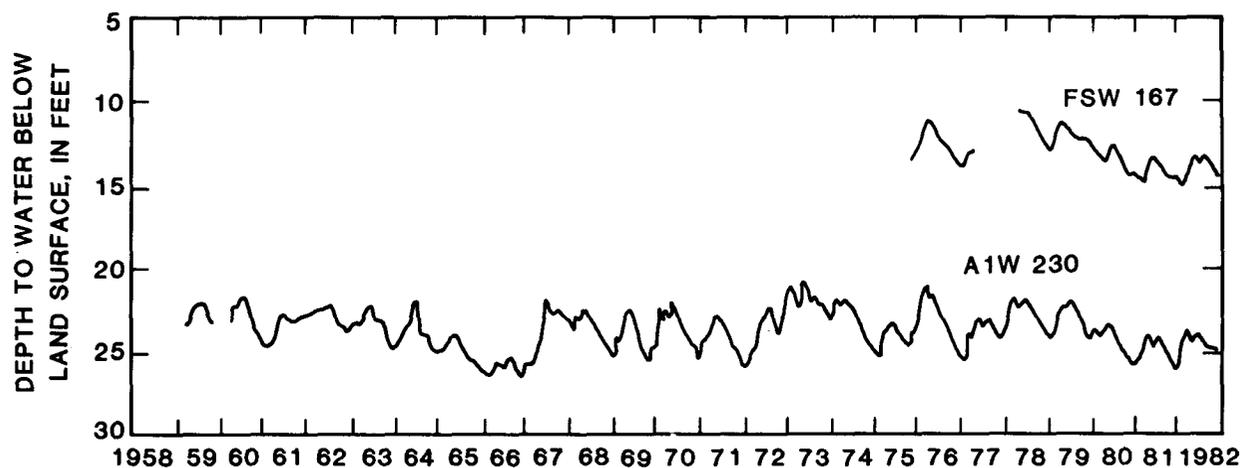


Figure 6.--Hydrograph of observed water levels in wells FSW 167 and A1W 230 for the period 1959-82.

Table 2.—Observed hydraulic head in clusters of observation wells, November 1979

[Well sites are shown in figure 5.]

Well cluster	Well depth, in feet below land surface	Hydraulic head, in feet above sea level	Well cluster	Well depth, in feet below land surface	Hydraulic head, in feet above sea level
FSW 254	26	43.84	FSW 167, 267	55	41.33
	54	43.88		88	41.33
	72	43.89		¹ 111	41.30
	107	43.88		¹ 136	41.32
	¹ 140	43.93		¹ 155	41.26
	¹ 168	43.91			
	¹ 216	43.91	FSW 271	41	30.45
				¹ 85	30.45
				¹ 141	30.49
FSW 262	41	37.69		¹ 165	30.49
	69	37.69			
	85	37.68	FSW 282	49	33.67
	¹ 109	37.72		70	33.68
¹ 159	37.53	94		33.70	
			¹ 123	33.69	

¹ Well screened below the bottom of the sand and gravel outwash.

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CHAPTER B

Contaminants in aquifers move primarily by advection with flowing ground water. Consequently, a key to understanding the fate of contaminants in ground water is a good description of the physical transport system. This paper describes the use of a two-dimensional solute-transport model of the plume to determine the geohydrologic factors that affect movement of solutes in the aquifer. This model will be used as a tool to guide data collection and to test and revise hypotheses about contaminant transport developed from these data.

DIGITAL MODELING OF SOLUTE TRANSPORT IN A PLUME OF SEWAGE-CONTAMINATED GROUND WATER

By Denis R. LeBlanc

ABSTRACT

Conservative solute transport of boron in a sewage plume in a sand and gravel aquifer was simulated with a ground-water flow and solute-transport model. The plume was formed by disposal of treated sewage through infiltration beds to an unconsolidated water-table aquifer at Otis Air Base, Cape Cod, Massachusetts, since 1936. The two-dimensional, method-of-characteristics model was used to study the hydrologic and geologic factors that affect movement of contaminants in the aquifer.

Flow was assumed to be independent of solute concentration and was simulated separately from solute transport. During calibration of the steady-state flow model, the best match between observed and computed water levels was obtained with a hydraulic conductivity of about 190 feet per day. Ground-water velocities, which averaged about 1 foot per day, were computed from the flow model results and an estimated effective porosity of 0.35.

The areal location of the simulated boron plume agreed reasonably well with the location of the plume observed in 1978-79 after 40 years of disposal. Differences between the observed and simulated locations of the plume were due, in part, to inaccurate preliminary delineation of the plume from analyses of water samples from wells. A subsequent drilling program verified the predicted location of the eastern boundary of the plume. The two-dimensional model computes average concentrations for the aquifer's entire thickness, whereas the plume occupies only part of the saturated thickness. Consequently, the model was unable to simulate the observed concentrations accurately. In these simulations, as much as 65 percent of the treated sewage discharges to a pond located near the infiltration beds. The beds cover an area that extends from 1,500 to 2,500 feet from the pond, and the rate of mass discharge to the pond is very sensitive to the distance between the pond and the active beds.

INTRODUCTION

The U.S. Geological Survey is studying the geologic, hydrologic, and chemical processes that affect the movement of contaminants in the sewage plume at Otis Air Base¹ as part of a nationwide program to describe the fate of contaminants in the subsurface. Because ground water is the sole source of drinking water on Cape Cod (U.S.

¹A description of the site, including its geologic and hydrologic setting, is given in chapter A of this volume.

Environmental Protection Agency, 1982), there is concern that land disposal of treated sewage at the base and at other sites may adversely affect ground-water quality on the Cape. An understanding of the processes that affect solute transport is needed to evaluate and predict the movement of contaminants in the plume. The understanding of these processes that will be gained by detailed study at this site will also be useful for evaluation of contamination by similar wastes in other sandy aquifers. In this report, a mathematical model of solute transport in the plume, prepared in cooperation with the Massachusetts Division of Water Pollution Control, is presented as a first step in the quantitative description of these transport processes.

In this study, a mathematical model was used to examine the relationship of the plume to its geologic and hydrologic setting. The objectives of the study were to: (1) Investigate the feasibility of simulating the plume with a mathematical model, (2) develop a predictive tool for describing and evaluating the behavior and movement of solutes in the plume, and (3) examine the geologic and hydrologic processes that affect solute transport in sand and gravel outwash.

The initial description of the plume (LeBlanc, 1982) was used as input for the modeling effort, and a documented computer code (Konikow and Bredehoeft, 1978) was used for the simulations. The study included: (1) Evaluation of hydrologic, geologic, and chemical data for its applicability to modeling; (2) estimation of aquifer properties that affect solute transport; and (3) simulation of transport in the plume with a two-dimensional model.

DESCRIPTION OF THE SEWAGE PLUME

The location and chemical composition of the plume were determined by collection and chemical analysis of water samples from 66 wells in 1978-79. The chemical composition of the plume is described by LeBlanc (1982) and Thurman and others (1984). Three constituents were identified by LeBlanc (1982) as possible tracers for modeling solute transport: Chloride, detergents, and boron.

Chloride generally is a good indicator of the contaminated zone. The conservative behavior of chloride has been described by Hem (1970, p. 172). However, chloride concentrations in the treated sewage are only 3 times greater than concentrations in uncontaminated ground water (table 1). Also, other chloride sources, especially road salts, have locally increased chloride concentrations and obscured the boundaries of the plume.

Detergents clearly delineate the plume because they are absent in uncontaminated ground water. Nonbiodegradable detergents used between 1946 and 1964 move conservatively in ground water and do not degrade chemically in most ground-water environments (Wayman and others, 1965, p. 49-96). The biodegradable detergents used since 1964 are more likely to degrade chemically (Wayman and others, 1965) or to be adsorbed (Freeze and Cherry, 1979, p. 440), but the rate of biodegradation may be insignificant in ground-water environments similar to the plume (Wayman and others, 1965, p. 56). The concentration of detergents in the sewage entering the aquifer has varied with time, however, and the pattern of variations could be only roughly estimated (table 1) from historical detergent concentrations reported for treated sewage from similar facilities.

Boron also is a good indicator of the contaminated zone. Boron concentrations in the treated sewage between 1974 and 1980 were 10 to 50 times greater than boron concentrations in the uncontaminated ground water. The major sources of boron in the sewage are cleaning agents and detergents. The concentrations of boron in the sewage prior to 1974 are unknown, but concentrations of boron in treated sewage from a similar plant (Kardos and Sopper, 1973, p. 150-151) remained constant from 1964 to at least 1973.

Boron probably moves conservatively through the outwash. Because boron forms a weak acid in ground water, it can be sorbed on weakly basic sites such as aluminum-oxide coatings or perhaps clay minerals. However, the sediments may contain few sorption sites for boron because (1) the aquifer contains less than 1 percent clay, (2) quartz and

feldspar are the principal minerals, and (3) available sites may be used by other contaminants that exist at much higher concentrations (Thurman and others, 1984). Conservative movement of boron through sand and gravel aquifers was also reported by Kimmel and Braids (1980, p. 20), Koerner and Haws (1979, p. 80), and Bouwer (1973, p. 172).

The ratio of chloride to boron in water samples of the treated sewage and ground water collected in 1978-79 also suggests that boron behaves conservatively. A plot of boron versus chloride concentrations in these samples is shown in figure 7. A theoretical dilution line connects points that represent uncontaminated ground water and the point that represents the treated sewage. Points that represent samples collected from the plume generally fall along the dilution line. This trend suggests that boron concentrations are attenuated primarily by mixing of contaminated and uncontaminated water. The scatter of points along the line is caused partly by measurement inaccuracy. Past variations of boron and chloride concentrations in the treated sewage, and chloride contamination from other sources could also cause deviations from the dilution line. Several analyses plotted in the lower right part of figure 7 contain high chloride concentrations without corresponding high boron concentrations. These samples were collected from wells located south of Route 151 that are affected by road salting (LeBlanc, 1982, p. 18-21).

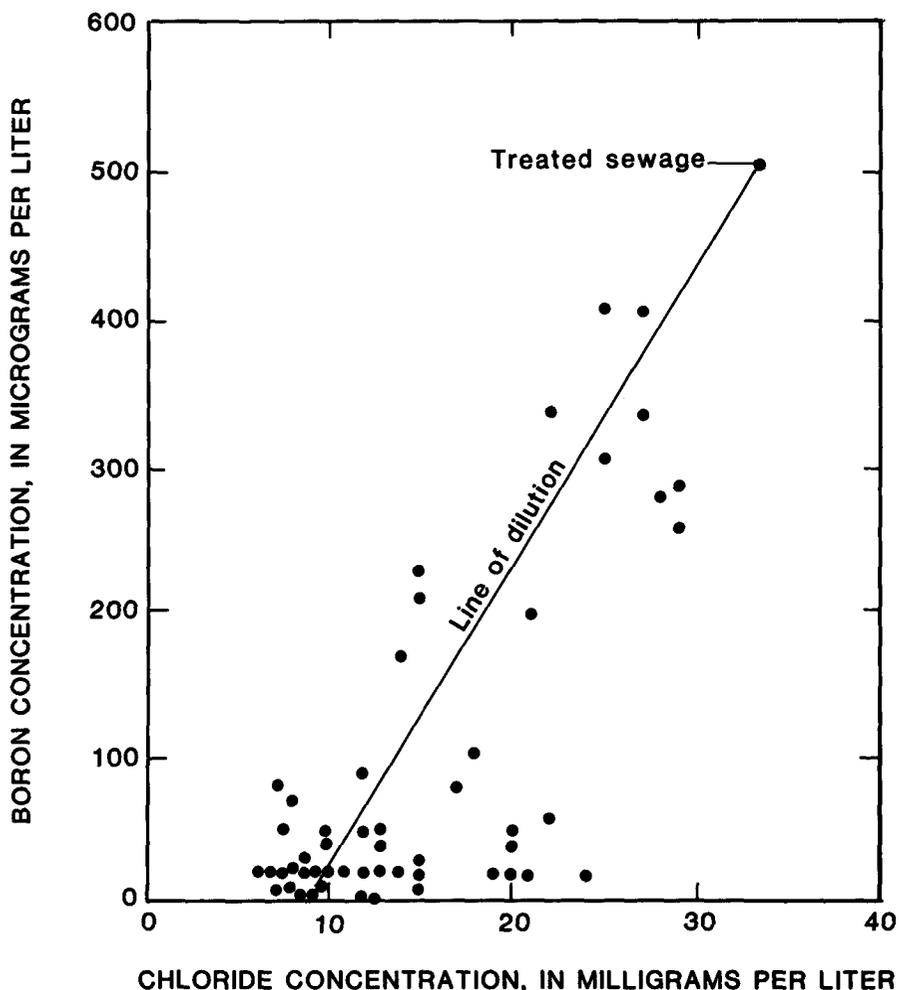


Figure 7.--Concentrations of boron and chloride in samples of ground water and the treated sewage collected in 1978-79.

The observed areal and vertical distributions of boron, chloride, and detergents are shown in figures 8 and 9. The vertical distributions of these contaminants were determined from clusters of wells screened at various depths in the aquifer. The map views were prepared only with data from wells screened at or near the depth of the center of the contaminated zone.

The plume delineated by the elevated concentrations of these contaminants is 3,000 feet wide and more than 11,000 feet long (fig. 8). Contaminants from the disposal site may have moved farther than 11,000 feet downgradient of the infiltration beds, but water samples were not collected beyond this distance in 1978-79. The large extent of the contaminated zone shows that advection of solutes with the flowing ground water is very effective in moving contaminants through the aquifer. The longitudinal axis of the plume is oriented in the direction of ground-water flow shown in figure 5. Spreading and dilution by hydrodynamic dispersion is evident along the toe and sides of the plume, but the contaminant concentrations in the center remain high as far as 8,000 feet downgradient of the sand beds. The amount of spreading could not be determined precisely because the observation wells were spaced several thousand feet apart.

The apparent limits of the plume shown in figure 8 differ for each constituent. This difference is due partly to the relation between source concentrations and concentrations above which the plume was identifiable. As illustrated in table 3, the chloride plume was delineated to a dilution ratio of 1:1.5; whereas, the detergents plume was delineated to a dilution ratio of 1:30. Consequently, the detergents plume seems to be more extensive than the chloride plume.

Table 3.—Lower limit of dilution of treated sewage used to map the plume

[Concentrations in milligrams per liter unless otherwise noted.]

Constituent	Concentration in treated sewage	Lower limit of concentration used to map plume	Lower limit of dilution used to map plume
Chloride	30	20	1.5
Detergents (MBAS)	3	.1	30
Boron (micrograms per liter)	500	100	5

Although the plume is areally extensive, it is only about 75 feet thick (fig. 9) and is contained almost entirely in the sand and gravel outwash. Its bottom boundary generally coincides with the contact between the permeable sand and gravel and the less permeable silty sand and till. A zone of uncontaminated ground water that is 20 to 50 feet thick overlies the plume (fig. 9). The source of water is areal recharge from precipitation (LeBlanc, 1982, p. 28). In the southern part of the study area, it is believed that road salting has increased chloride concentrations in the zone above the plume (fig. 9).

The treated sewage moves downward through the sand and gravel near the infiltration beds, then it moves laterally with little vertical mixing. Vertical movement of the contaminated water near the beds is probably due to vertical head gradients caused by recharge of treated sewage to the aquifer at the disposal site. Because the concentrations of total dissolved solids in the treated sewage (155 to 178 mg/L) and in uncontaminated ground water (39 mg/L) are not significantly different, vertical movement of contaminated ground water probably is not due to density contrasts.

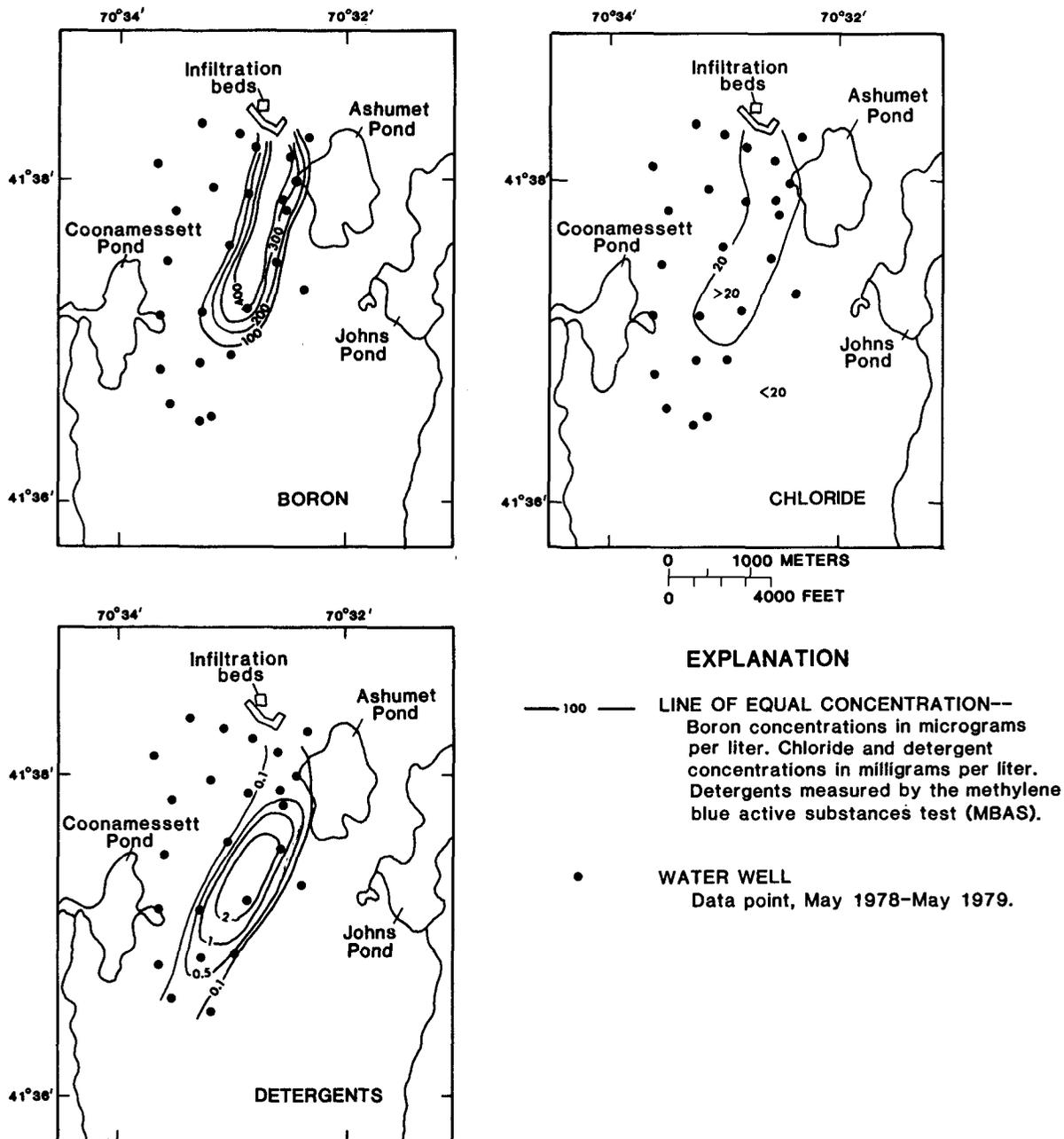


Figure 8.--Observed areal distributions of boron, chloride, and detergents in ground water, May 1978 through May 1979 (from LeBlanc, 1982).

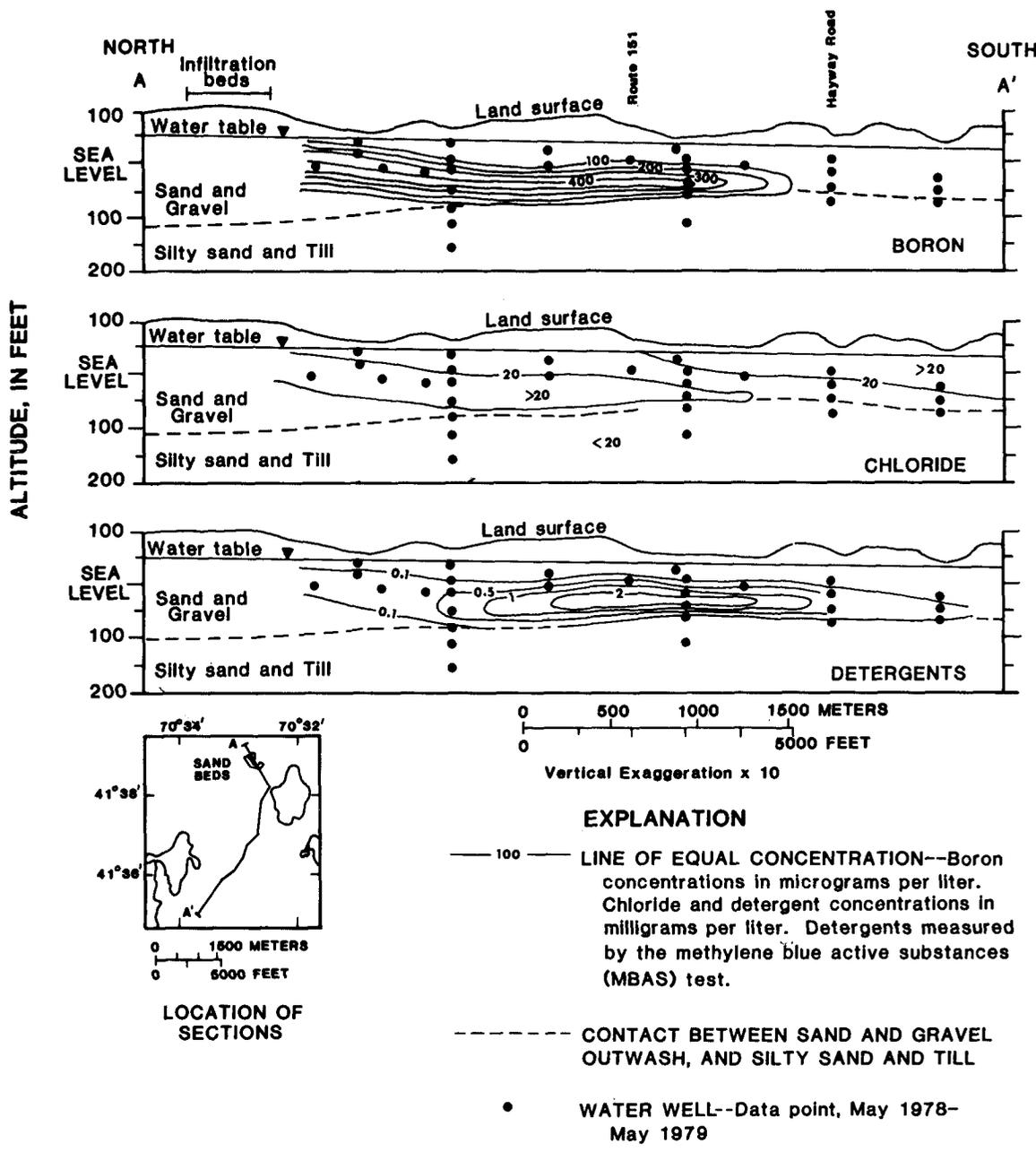


Figure 9.--Observed vertical distributions of boron, chloride, and detergents in ground water, May 1978 through May 1979 (from LeBlanc, 1982).

DIGITAL MODEL OF THE PLUME

A mathematical model was used to simulate solute transport in the aquifer to better understand the hydrologic and geologic influences on the movement of contaminants in the plume. The solute-transport model is a computer program that calculates ground-water flow and water-quality conditions in the aquifer based on the (1) hydraulic properties of the aquifer (transmissivity, porosity), (2) quantity and quality of water entering and leaving the aquifer (recharge and discharge), and (3) potential of the aquifer to disperse contaminants (dispersivity). A digital model was chosen which can simulate the complex aquifer boundaries, spatially variable hydraulic properties, variable flow, and complex hydraulic stresses that characterize the flow and transport system.

Description

The digital model that was selected was developed by Konikow and Bredehoeft (1978) and simulates both flow and transport in a two-dimensional aquifer. Differential equations describing ground-water flow and solute transport are solved numerically with a digital computer code. The flow and transport equations are solved separately because fluid properties are assumed to be independent of concentration.

The flow portion of the model solves the partial differential equation that describes two-dimensional flow through a heterogeneous, anisotropic aquifer (Konikow and Bredehoeft, 1978, p. 2). The equation, written in Cartesian tensor notation, is

$$\frac{\delta}{\delta x_i} \left(T_{ij} \frac{\delta h}{\delta x_j} \right) = S \frac{\delta h}{\delta t} + W \quad i, j = 1, 2$$

where

- T_{ij} = the transmissivity tensor, L^2/T ;
- h = the hydraulic head, L ;
- S = the storage coefficient (dimensionless);
- t = the time, T ;
- $W = W(x,y,t)$ = is the volumetric flux per unit area (source term), L/T ; and
- x_i and x_j = are the Cartesian coordinates, L .

In the model, $W(x,y,t)$ is expressed as

$$W(x,y,t) = Q(x,y,t) - \frac{K_z}{m} (H_s - h)$$

where

- Q = the rate of withdrawal or recharge per unit area, L/T ;
- K_z = the vertical hydraulic conductivity of the streambed or pond bottom, L/T ;
- m = the thickness of the streambed or pond bottom, L ; and
- H_s = the hydraulic head in the stream or pond, L .

The area of interest is subdivided into a grid, and a system of finite-difference equations that approximate the differential equation is solved to obtain the hydraulic head at each node in the grid (Konikow and Bredehoeft, 1978, p. 4-5). Darcy's law is then used to calculate the ground-water velocity distribution for input into the solute-transport model (Konikow and Bredehoeft, 1978, p. 2). This expression can be written in Cartesian tensor notation as

$$V_i = - \frac{K_{ij}}{n} \frac{\delta h}{\delta x_j} \quad i, j = 1, 2$$

where

- V_i = the seepage velocity in the direction of x_i , L/T ;
- K_{ij} = the hydraulic conductivity tensor, L/T ; and
- n = the effective porosity (dimensionless).

The solute-transport portion of the model solves the partial differential equation that describes two-dimensional transport of a nonreactive dissolved contaminant in flowing ground water (Konikow and Bredehoeft, 1978, p. 3).

The equation may be written as

$$\frac{\delta(C b)}{\delta t} = \frac{\delta}{\delta x_i} \left(b D_{ij} \frac{\delta C}{\delta x_j} \right) - \frac{\delta}{\delta x_i} \left(b C V_i \right) - \frac{C' W}{n} \quad i, j = 1, 2$$

where

- C = the concentration of the dissolved chemical species, M/L³;
- D_{ij} = the coefficient of hydrodynamic dispersion related to aquifer dispersivity and seepage velocity, L²/T;
- b = the saturated thickness of the aquifer, L; and
- C' = the concentration of dissolved chemical in a fluid source or sink, M/L³.

The first term on the right side of this equation represents the change in concentration due to hydrodynamic dispersion. The second term describes the effects of advective transport, while the third term represents a fluid source or sink.

The method of characteristics is used to solve the differential equation. In this method, reference particles are distributed throughout the modeled area and are tracked over time as they move with the flowing ground water to simulate advective transport. Concentrations assigned to each particle are used to calculate the concentrations in each block of the finite-difference grid. Concentrations are adjusted by a finite-difference method to reflect the effects of hydrodynamic dispersion and mixing due to fluid inflow and outflow (Konikow and Bredehoeft, 1978, p. 5-11).

Simplifying Assumptions

Application of the model requires some simplification of the real system. The simulations must be interpreted with consideration of the assumptions made in the modeling procedure. Four major assumptions are discussed below.

1. The aquifer is formed only by the sand and gravel outwash: The underlying silty sand and till are at least 10 to 20 times less permeable than the outwash (table 4), and vertical hydraulic-head gradients across the contact between the outwash and fine-grained sediments are small (table 2). Also, the plume remains mostly in the sand and gravel, although contaminants penetrate 10 to 15 feet into the silty sand near the toe of the plume. Therefore, it is reasonable to assume that the silty sand and till approximate an impermeable bottom boundary to the aquifer.

2. The aquifer can be represented by a single, two-dimensional layer in which vertical variations in hydraulic head and solute concentration are negligible: The assumption of two-dimensional flow is reasonable because ground-water flow in the outwash is nearly horizontal. Vertical flow occurs at the infiltration beds, kettle-hole ponds, and streams, but the hydraulic influence of recharge and discharge at these sites is roughly equivalent to uniform, vertically distributed inflow and outflow because these areas are small or are located at the flow-system boundaries. The assumption of complete vertical mixing of contaminants does not agree with observations that the plume occupies only part of the thickness of the aquifer. The effect on the simulations of this difference between assumed and actual conditions is discussed later in this report.

3. The density and viscosity of the contaminated and uncontaminated ground water are essentially identical, so only hydraulic-head gradients affect the velocity distribution: The difference in total dissolved solids concentration between the treated sewage (155 to 178 mg/L) and uncontaminated ground water (39 mg/L) is small, and ground-water temperatures vary only slightly. Therefore, density differences due to solute-concentration and temperature variations are negligible.

4. Ground-water levels and the velocity distribution do not change with time and represent a steady-flow system: Although water levels fluctuate 1 to 3 feet seasonally, no long-term rise or decline of water levels has been observed since observations began in 1975. The short-term fluctuations are relatively uniform throughout the area and have little effect on the hydraulic gradient. Therefore, the flow model is solved only once to obtain hydraulic heads for a given set of aquifer properties, inflow and outflow rates, and aquifer boundaries.

Table 4.—Estimated hydraulic conductivity of sediment samples of sand and gravel, silty sand, and sandy till

Geohydrologic unit shown in figure 4	Well number (sites shown in figure 5)	Depth of sample below land surface, in feet	Grain-size diameter, in millimeters		Estimated hydraulic conductivity, ¹ in feet per day ²
			Percent finer by weight 10 percent	50 percent	
Sand and gravel	FSW 347	41	0.32	0.80	254
		42	.51	1.03	562
		72	.29	.54	182
	FSW 234	72	.30	.63	181
	FSW 237	63	.27	.58	155
	FSW 239	83	.16	.36	60
	FSW 244	98	.28	.58	172
	FSW 254	107	.26	.66	141
	FSW 262	87	.07	.34	15
		88	.29	.65	170
	FSW 279	148	.09	.21	20
	FSW 282	79	.15	.66	57
Average			.35	.59	164
Silty sand	FSW 254	138	.014	.125	1.6
		168	.092	.20	19
		198	.078	.16	13
		268	—	.155	5.8
Average			—	.16	10
Till	FSW 262	155	.115	.22	28
		160	.068	.26	13
Average		179	—	.23	14

¹ Assumes ground-water temperature of 10°C.

² From Krumbein and Monk, 1943.

Finite-Difference Grid

The limits of the modeled area were selected to include the entire area of the mapped plume and the areas downgradient into which the plume would likely spread (fig. 10). The modeled area, approximately 12.9 mi², was subdivided into a finite-difference grid of uniformly spaced rectangles arranged in 40 rows and 36 columns (fig. 11). The grid contains 1,440 rectangles, but only 957 rectangles fall in the active model area. Each rectangle, or block, has dimensions of 500 feet by 750 feet. The block size was chosen so that (1) the width of the plume was spanned by at least 7 blocks and (2) boundaries and sources could be represented in sufficient detail.

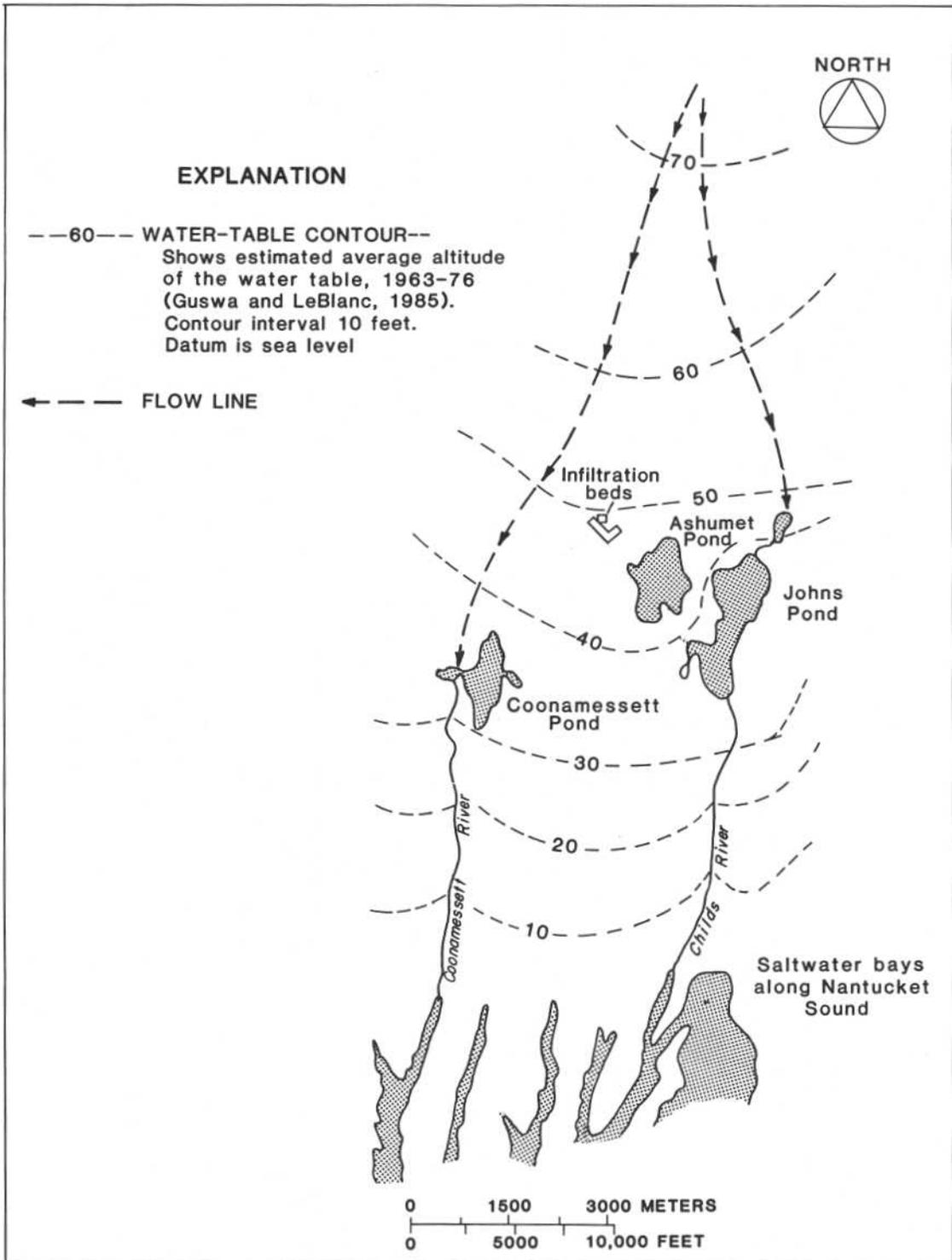


Figure 10.--Major hydrologic features and boundaries of the modeled area.

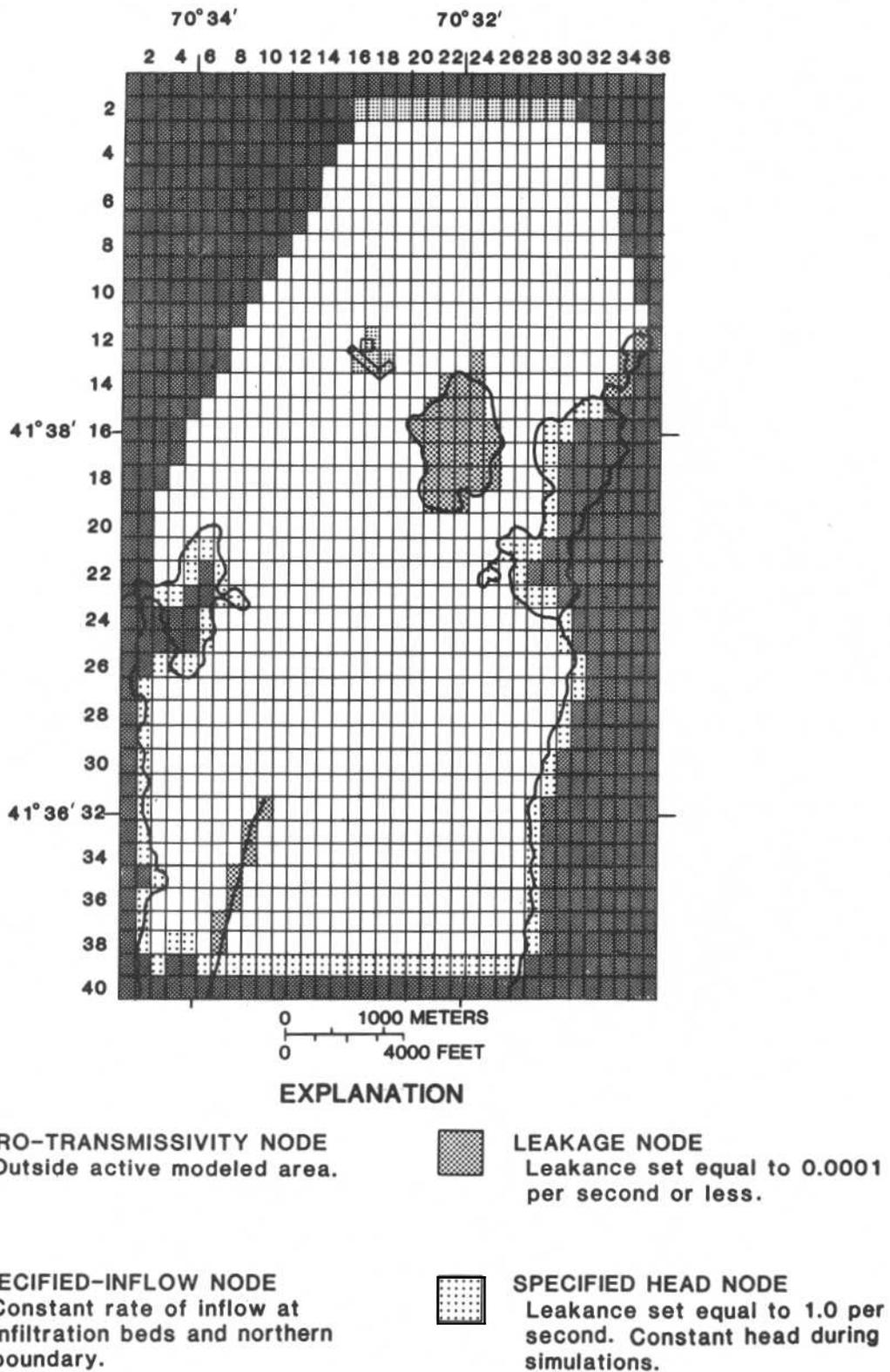


Figure 11.--Finite-difference grid used to model the study area.

Parameter Estimation

From the 1978-79 description of the plume and its hydrologic and geologic setting, LeBlanc (1982, p. 28) showed that solutes in the aquifer move primarily by advection with the flowing ground water and are diluted by hydrodynamic dispersion. As a first step toward digital simulation of the movement of contaminants in the plume, estimates of hydraulic conductivity, porosity, and dispersivity were obtained because these factors are fundamental aquifer properties that control advective-dispersive transport of solutes. Estimates of these factors must be reasonably accurate if mathematical modeling is to be successful.

Hydraulic Conductivity

The average hydraulic conductivity of the sediments was estimated from: (1) Flow-net analysis of the regional water-table map, (2) measured hydraulic conductivity at four aquifer-test sites near the study area (Palmer, 1977, p. 21-45) and at three sites in similar sediments elsewhere on Cape Cod (Guswa and LeBlanc, 1985, p. 6), (3) aquifer parameters used in a digital model of regional ground-water flow on Cape Cod (Guswa and LeBlanc, 1985, p. 32-36), and (4) an empirical equation relating grain-size distribution to permeability. The empirical equation (Krumbein and Monk, 1943) was applied to grain-size analyses of 12 split-spoon cores of the sand and gravel, 4 cores of the fine to very fine sand and silt, and 3 cores of the till (table 4).

The estimates of average hydraulic conductivity of the sand and gravel, obtained by all the above methods, ranged from 140 to 220 ft/d. Estimates of hydraulic conductivity from grain-size data for core samples of the sand and gravel varied over an order of magnitude (table 4) because the split-spoon cores sample individual fine-grained and coarse-grained layers that form the stratified outwash. The average hydraulic conductivity for the cores of the outwash was 164 ft/d. Although Mather and others (1942, p. 1153) reported an areal trend in the grain-size distribution of the outwash, an areal trend in hydraulic conductivity was not evident from the estimates shown in table 4. In the digital model described in this report, a hydraulic conductivity of 170 ft/d was initially assigned to the outwash. This value was modified slightly (increased 10 percent) during calibration of the flow model.

Estimates of hydraulic conductivity from grain-size data for the silty sand and till are 10 to 20 times lower than estimates for the sand and gravel. Several cores contained mostly silt and clay, and estimates of hydraulic conductivity of these cores could not be made with the empirical relations. The hydraulic conductivity of these silts and clays may be less than 1 ft/d (Todd, 1980, p. 72).

Porosity

Porosity of the sand and gravel was estimated from (1) measured porosity of the outwash near the sewage-treatment plant and (2) measured porosity of similar outwash on Long Island, New York. The average porosity of samples collected from shallow wells near the sewage-treatment plant was 0.32 (Kerfoot and Ketchum, 1974). The porosities of two core samples of outwash on Long Island were 0.34 and 0.38 (Perlmutter and Lieber, 1970, p. G12). The grain-size distributions of the Long Island samples were very similar to the grain-size distributions for outwash in the study area. Porosities of 0.36 to 0.42 were reported by Morris and Johnson (1967, p. D20-D29) for undisturbed samples of sandy stratified glacial deposits.

From these data, the average porosity of the sand and gravel was estimated to be about 0.35. Although the total pore space may not be available for flow due to dead-end pores and adhesion of water to the sediment grains (Bear, 1979, p. 63), the effective porosity available for flow is essentially equal to total porosity in coarse-grained unconsolidated media (Todd, 1980, p. 27).

Dispersivity

Hydrodynamic dispersion causes the plume to spread and mix with uncontaminated ground water in the direction of flow and, to a lesser extent, perpendicular to flow. It is a function of ground-water velocity and dispersivity, a property of the aquifer (Freeze and Cherry, 1979, p. 390). Initial estimates of dispersivity were obtained for the outwash from values determined for similar aquifers in other areas. These values, summarized in Anderson (1979, p. 127) and Pickens and Grisak (1981, p. 1192), were determined by matching observed plumes with mathematical models by trial-and-error adjustment of dispersivity and other parameters. Based on these estimates, reasonable values for the outwash at Otis Air Base are (1) 40 to 100 feet for longitudinal dispersivity, and (2) 13 to 30 feet for horizontal transverse dispersivity.

Data Requirements

Aquifer properties and stresses must be defined at all active nodes of the finite-difference grid, and boundary conditions must be specified for nodes along the edges of the grid. Initial estimates of properties, stresses, and boundary characteristics described in previous sections of this report were adjusted during the simulation procedure so the simulated system reasonably approximated the observed system. The estimates were adjusted within limits consistent with the accuracy of the data and uncertainty of the estimation procedures. Because the adjustments required were generally small, only the final input data for boundaries, aquifer properties, and inflows and outflows are described in this report.

Aquifer Boundaries

The lateral boundaries to the ground-water-flow system are shown in figure 10, and their representations in the finite-difference model grid are shown in figure 11. The northern boundary, at the 60-foot water-table contour, was specified as a constant-inflow boundary. Extension of the modeled area to the ground-water divide would have greatly increased the size of the finite-difference grid, and reasonable estimates of inflow across the boundary were obtained by several methods.

Coonamessett Pond and the Coonamessett River and Johns Pond and the Childs River (fig. 10) act as drains to the ground-water-flow system along which water levels are relatively constant. These ponds and streams were specified as constant-head boundaries in the model (fig. 11). This is accomplished by representing the boundaries as leakage nodes at which leakance is set to a high value [1.0 (ft/s)/ft]. Leakance is the vertical hydraulic conductivity of the streambed or pond bottom divided by bed thickness. The pond water levels were measured in November 1979 (fig. 5) and the stream water levels were estimated from topographic maps.

Because there are no physical boundaries to flow extending north of the two ponds, no-flow boundaries were delineated by tracing flow lines on the regional water-table map from the northern ends of the ponds to the 60-foot water-table contour (fig. 10). In the model, flow does not cross these lines, although in the real system their positions are not fixed and move in response to changes in ground-water levels.

The southern boundary to the modeled area, along the 10-foot water-table contour (figs. 10 and 11), was specified as a constant-head boundary. Because of the proximity of this boundary to sea-level saltwater bays, water levels in the aquifer remain nearly constant along the 10-foot water-table contour.

Aquifer Properties

Transmissivity, a measure of the rate at which water will flow through the aquifer under a unit hydraulic gradient, was determined from saturated thickness and hydraulic conductivity of the outwash. The transmissivity for the modeled area ranged from 24,300 ft²/d north of the infiltration beds to 16,800 ft²/d south of Coonamessett and

Johns Ponds. These values are based on an average hydraulic conductivity of 186 ft/d and a saturated thickness that decreases from 130 feet north of the infiltration beds to 90 feet at the southern boundary of the model. At the kettle-hole ponds, transmissivity was decreased to reflect lower saturated thickness of the outwash beneath the ponds. Although the simulated position of the water table differed slightly from the observed water levels used to calculate saturated thickness, transmissivities were not adjusted during the simulations because the differences between observed and computed saturated thicknesses generally were less than 2 percent.

Effective porosity was set equal to 0.35 everywhere in the modeled area. A longitudinal dispersivity of 40 feet and a transverse dispersivity of 13 feet were used in the model. These values are at the low end of the range of dispersivities reported in other modeling studies.

Inflow and Outflow

The rate of areal recharge from precipitation was estimated by application of the Thornthwaite and Mather (1957) method to climatic data for Falmouth. The original recharge estimate, 21 in/yr, was adjusted downward to 19.8 in/yr during model calibration. Recharge directly to the aquifer was assumed to be zero over Coonamessett, Ashumet, and Johns Ponds. The net gain of water to the ponds from precipitation minus evaporation was accounted for in the model by a net leakage from the ponds to the aquifer. The recharge rate was decreased slightly to 18.9 in/yr at nodes where the water table is within 5 feet of land surface. The total annual evapotranspiration in these low-lying areas where plant roots reach the water table should be higher than in upland areas where soil moisture typically becomes depleted at the end of the summer. However, the Thornthwaite estimates of potential evapotranspiration do not greatly exceed the estimates of actual evapotranspiration on Cape Cod because precipitation is evenly distributed through the year and, in most months, exceeds the evapotranspiration demand. Therefore, significant recharge probably still occurs where the water table is near land surface.

Inflow across the northern boundary of the study area was estimated by two methods. First, an inflow rate of 2.5 ft³/s was obtained from Darcy's law using estimates of aquifer properties and observed hydraulic gradient at the 60-foot water-table contour. Second, an inflow rate of 2.2 ft³/s was obtained by multiplying the area between the 60-foot contour and the water-table divide by the estimated areal recharge rate (19.8 in/yr), then decreasing the calculated rate to account for water pumped from a supply well located north of the 60-foot contour and for water that moves down into the fine-grained sediments that underlie the sand and gravel. An average of the two estimates, 2.3 ft³/s, was evenly distributed along the model's northern boundary.

The rate of recharge of treated sewage at the infiltration beds was set equal to 0.72 ft³/s, the average rate of sewage inflow at the plant for the period 1936-78. Because the pattern of distribution to the 24 beds is unknown, the recharge was distributed uniformly over four nodes that include all the beds (fig. 11).

The interaction between the ground-water-flow system and Ashumet Pond was simulated by leakage nodes (fig. 11) which lie entirely within the active modeled area. At these nodes, inflow and outflow are simulated by head-dependent flow through a pond-bottom layer. The pond water level used in the model equals the estimated average water level of Ashumet Pond. The vertical hydraulic conductivity and thickness of the bottom sediments of the pond have not been measured. The pond has a sandy bottom near the shore, and marine-reflection profiles indicate that fine-grained sediments may cover the bottom of the center of the pond. On this basis, two zones of leakage nodes represent Ashumet Pond. The outer zone was assigned a leakance of 0.0001 (ft/s)/ft, equivalent to a 2-foot-thick layer with a vertical hydraulic conductivity of 19 ft/d. Leakance for the inner zone was 0.000002 (ft/s)/ft, equivalent to a 10-foot-thick layer with a conductivity of 2 ft/d.

A small stream, known locally as the Backus River, that drains a series of cranberry bogs in the southwest corner of the modeled area (fig. 11) was also simulated with leakage nodes. Leakage for the Backus River nodes was set equal to 0.00001 (ft/s)/ft.

Calibration

The path and shape of the plume are functions of the ground-water velocity distribution, which in turn is partly determined by the distribution of hydraulic head in the aquifer. The flow model computes the head distribution from the specified aquifer properties, boundaries, and inflows and outflows. To be a useful tool for studying the plume, the model should be able to simulate the flow system with reasonable accuracy, given the accuracy of the input data and assumptions made in applying the model. Therefore, the flow model was calibrated by comparing observed water-table altitudes with corresponding calculations by the model. During the calibration process, a "best-fit" between observations and computations was obtained by adjusting the input data within limits based on the precision and accuracy of the data.

The flow model was calibrated to the average water-table conditions shown in figure 5. A comparison of water-table maps drawn from the observed and computed water levels (fig. 12) shows close agreement in most areas. Direct comparison of observed and computed water levels was made at 49 wells. The computed heads were within 1 foot of the observed heads at 31 wells, and within 2 feet of the observed heads at 44 wells.

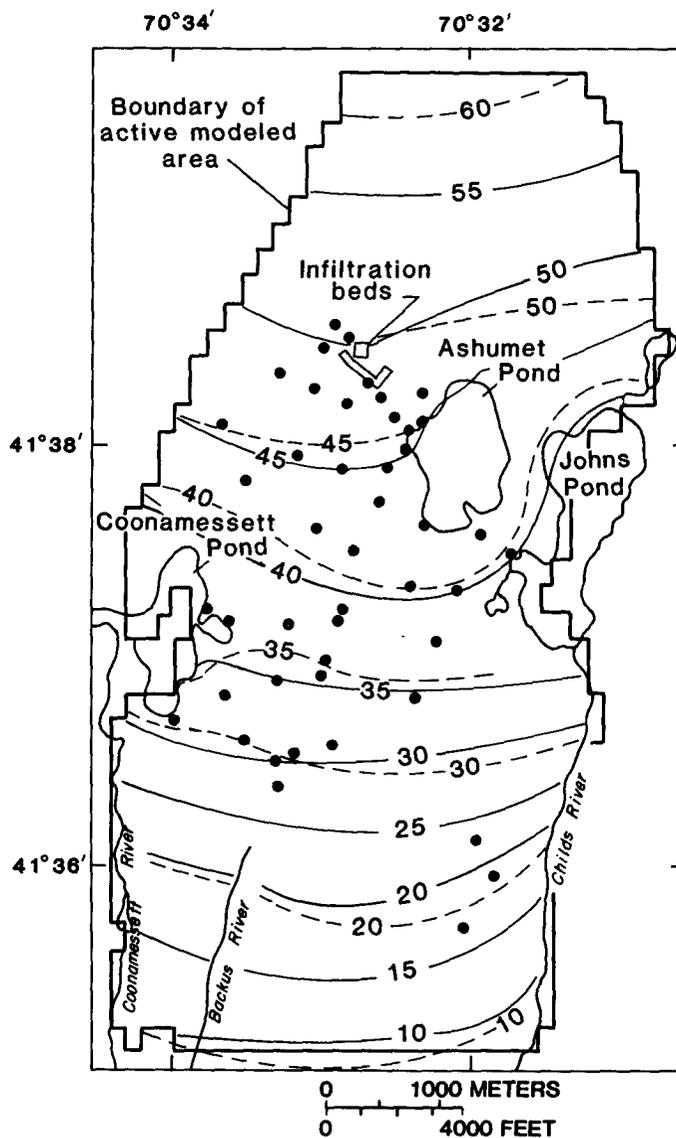
The computed heads are slightly higher than the observed heads north and east of Coonamessett Pond. At the three southernmost observation wells (fig. 12), the computed heads were 4 to 5 feet lower than the observed water levels. Little data on water levels, aquifer properties, and boundary characteristics were available for the southern part of the modeled area, so no adjustments were made to improve the water-level match in this area.

As an additional check on the accuracy of the calibrated flow model, the balance of inflow and outflow to the leakage nodes at Ashumet Pond was computed. Because the pond has no surface inlet or outlet, leakage from the pond to the aquifer should exceed leakage from the aquifer to the pond by the net input to the pond from precipitation. Based on the average annual precipitation, free-water-surface evaporation (Farnsworth and others, 1982, pl. 3), and the surface area of the pond, the net input from precipitation to the pond is estimated to be $0.4 \text{ ft}^3/\text{s}$. The net leakage of water from the pond to the aquifer calculated by the model is $0.77 \text{ ft}^3/\text{s}$, which is reasonably close to $0.4 \text{ ft}^3/\text{s}$.

The balance of inflow and outflow computed by the model is shown in table 5. Note that outflows to the Coonamessett River and the Childs River represent only contributions from the modeled area and cannot be compared directly to field measurements of total flow in the streams. As expected, however, the computed flows were less than the total measured flows in the streams.

During flow-model calibration, the sensitivity of the computed hydraulic heads and leakage-node flows to model input data was tested by varying hydraulic parameters, inflow and outflow specifications, and boundary characteristics. Several conclusions were reached from the sensitivity analysis:

1. The computed heads are sensitive to hydraulic conductivity and to areal recharge rate. If both parameters are changed simultaneously in the same proportion, however, the computed water levels change very little. Although the observed and computed water levels match closely, the hydraulic conductivity is not uniquely determined by the calibration process because the recharge rate is also imprecisely known. Because the ground-water velocity is directly proportional to hydraulic conductivity, better independent estimates of the conductivity are needed.



EXPLANATION

- 40--- WATER-TABLE CONTOUR, NOVEMBER 1979--
Shows altitude of water table. Contour interval 5, 10 feet. Datum is sea level.
- 40— COMPUTED WATER-TABLE CONTOUR,
FLOW-MODEL CALIBRATION--
Shows altitude of simulated water table.
Contour interval 5 feet. Datum is sea level.
- WATER-LEVEL OBSERVATION WELL--
Site where computed and observed water levels compared during calibration.

Figure 12.--Observed and computed water-table map and location of water-level observation wells for flow model calibration.

2. The computed head distribution in the area of the plume is insensitive to reasonable adjustment of the positions of the no-flow boundaries north of Coonamessett Pond and Johns Pond. Although the flow lines are not fixed physical boundaries, their specification in the model has little effect on the transport simulations.

3. The computed heads are sensitive to the assigned location and specified heads of the leakage nodes at Ashumet Pond and along the eastern and western model boundaries. The direction of the hydraulic gradient south of the infiltration beds is determined, in large part, by the heads specified at the leakage nodes. Changes in the relative specified heads along the Coonamessett and Childs Rivers within the accuracy of the topographic maps used to estimate the heads cause shifts in the direction of the hydraulic gradient. Consequently, the simulated path of the plume shifts eastward or westward. The leakage nodes at Ashumet Pond act as specified-head nodes unless the leakance is less than 0.00001 (ft/s)/ft. Specification of lower leakances causes distortion of the flow system around the pond, and solutes tend to spread over a broad front south of the pond and, at very low leakances [0.0000001 (ft/s)/ft], travel to Johns Pond.

Table 5.--Ground-water inflow and outflow rates computed by the calibrated flow model

	Cubic feet per second	Million gallons per day
Inflow		
Across northern model boundary	2.31	1.5
Recharge from precipitation	17.32	11.2
Recharge of treated sewage	.72	.5
Leakage from Ashumet Pond	3.75	2.4
Total inflow	24.10	15.6
Outflow		
Leakage to Ashumet Pond	2.92	1.9
Net leakage to Coonamessett Pond and Coonamessett River	4.60	3.0
Net leakage to Johns Pond and Childs River	11.10	7.2
Net leakage to Backus River	1.04	.7
Across southern model boundary	4.7	2.9
Total outflow	24.13	15.6
Inflow minus outflow (numerical error)	-0.03	

SIMULATION OF SOLUTE TRANSPORT

The solute-transport model computes concentrations of a given solute at each node in the active modeled area at specified time intervals. The ground-water velocities, inflows, and outflows computed by the flow model are used as input for the solute-transport simulations. The distribution of boron in the aquifer after 40 years of transport (1940 through 1979) was simulated first to test the ability of the two-dimensional model to reproduce the plume observed in 1978-79. Boron was selected for simulation because it seems to behave conservatively in the outwash, enters the aquifer in significant quantities only at the infiltration beds, and clearly delineates an extensive plume. The assumptions about the source history and concentrations are discussed below. Additional simulations were then run to test hypotheses about the plume's relationship to the flow system, to examine the movement of contaminants such as detergents that have a variable source history, and to predict future movement of the plume.

Model Application

In the method of characteristics, advective transport of solutes is simulated by tracking reference particles that move with the flowing ground water. The accuracy and precision of the solution generally are improved by using more particles (Konikow and Bredehoeft, 1978, p. 32-35). For all simulations, five particles were initially assigned to each active node. The solutions seemed to be reasonably accurate, and computer costs were reduced by limiting the number of particles that had to be tracked.

Because flow diverged strongly downgradient of Ashumet Pond due to leakage of pond water to the aquifer, nodes in this region tended to become void of particles. Regeneration of the initial distribution of particles, done automatically by the model code (Konikow and Bredehoeft, 1978, p. 18-19), occurred periodically during the simulations to minimize the number of void nodes. The regeneration did not introduce any perturbations or obvious inaccuracies in the solutions.

The numerical solution of the transport equations has several stability criteria that limit the size of the time step (Konikow and Bredehoeft, 1978, p. 11-13). For these simulations, the limiting stability criterion was the rate of inflow from leakage nodes along the downgradient sides of the ponds. To reduce the number of time increments needed to simulate the transport period, specified heads at the critical nodes were decreased 0.5 to 2.0 feet. These small adjustments had little effect on the computed flow system.

To help check the accuracy and precision of the numerical solution, solute-mass balance calculations are performed after specified time increments. The net sum of solute-mass inflow and outflow is compared to the mass stored in the aquifer. The percent difference, which should be small, is one measure of the numerical accuracy of the solution (Konikow and Bredehoeft, 1978, p. 14). For these simulations, the difference generally was less than 7 percent, although it tended to be slightly higher at early time steps. This error was acceptable given the nature of the solution method, the relatively coarse grid spacing, and the small number of particles.

Input Data and Assumptions

The solute, boron, was assumed to be conservative and to be absent in uncontaminated ground water, recharge from precipitation, and inflow from ponds, streams, and upgradient parts of the aquifer. Therefore, the only source of boron in the model was the treated sewage recharged at the infiltration beds. Although part of the plume discharges to Ashumet Pond in the simulations, the boron concentration in leakage from the pond to the aquifer was assumed to be zero. To test the validity of this assumption, the potential increase in solute concentration in the pond due to inflow of contaminated

ground water was estimated with a simple reservoir model. The pond was assumed to act as a fully mixed reservoir, and 60 percent of the treated sewage was assumed to discharge to the pond. The solute concentration in the pond as a function of time was computed from ground-water inflow and outflow rates obtained from the calibrated flow model. The computed concentrations in the pond water did not exceed 10 percent of the concentration in the treated sewage because the rate of inflow of contaminated ground water is much less than the total flow through the pond (table 5). This assumption is further substantiated by the relatively low concentrations of boron, 80 $\mu\text{g/L}$, measured in the pond water during the period 1975-78 (Vaccaro and others, 1979, p. 88-89).

For the initial simulations of the plume as observed in 1978-79, treated sewage recharged the aquifer at a rate of 0.72 ft^3/s at four nodes that represent the location of the infiltration beds. The boron concentration of the source was set at 500 $\mu\text{g/L}$ (table 1). The concentration and rate of recharge were assumed to remain constant during the simulation period. Because sewage flows were small prior to World War II (fig. 3), the simulation period extended from 1940 to 1979 (40 years).

Simulated Plume

The computed concentrations of boron after 9.8, 29.3, and 40 years of simulated disposal to four nodes at the infiltration beds are shown in figure 13. The simulated plume spreads longitudinally and, to a lesser extent, laterally from the source, and first intersects the western side of Ashumet Pond within 6 years. It continues to grow in a southerly direction, and at 40 years extends more than 11,000 feet downgradient of the beds.

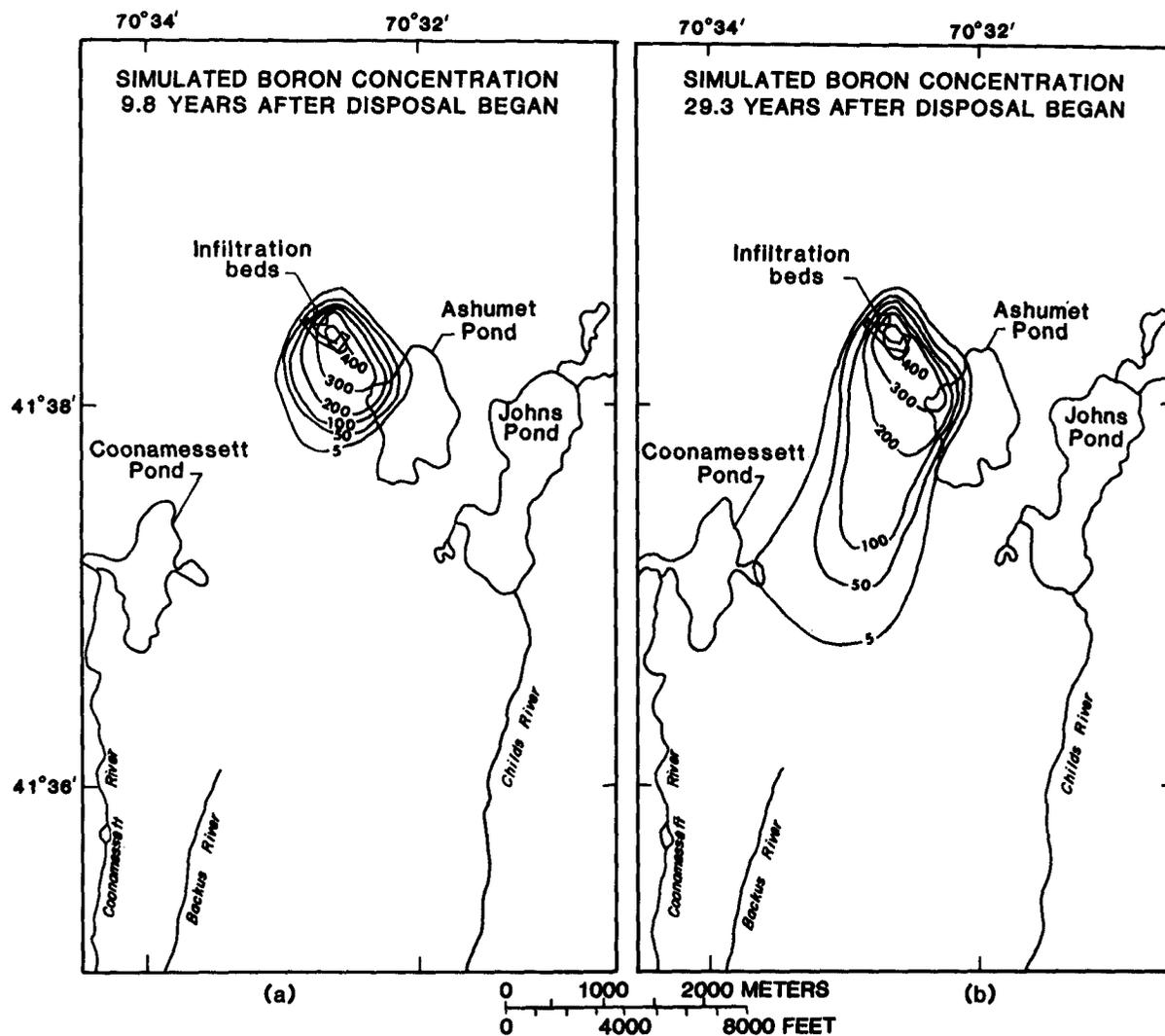
The simulated path of the plume agrees reasonably well with the location of the plume observed in 1978-79. The location of the observed plume in figure 13c represents the area in which detergents were detected or concentrations exceeded 20 mg/L chloride or 100 $\mu\text{g/L}$ boron. The simulated plume generally is wider than the observed plume, although the center of the simulated plume in which computed concentrations exceed 50 $\mu\text{g/L}$ boron (10 percent of the source concentration) matches the observed path more closely. The simulated plume also diverges eastward of the observed path and spreads farther southward than the observed plume.

The simulated plume intersects the leakage nodes that represent Ashumet Pond in an area where ground water discharges to the pond. Solutes discharge to the pond with the ground water, and the rate of mass discharge was calculated during the mass-balance computations. This rate, expressed as a fraction of the rate of mass input at the infiltration beds, increases rapidly as the simulated solute first reaches the pond (fig. 14) and gradually stabilizes at about 65 percent of the rate of inflow at the beds.

Differences Between Observed and Computed Paths

The simulated plume of boron generally seems wider and longer and diverges eastward of the observed plume. Several hypotheses were considered to explain these differences.

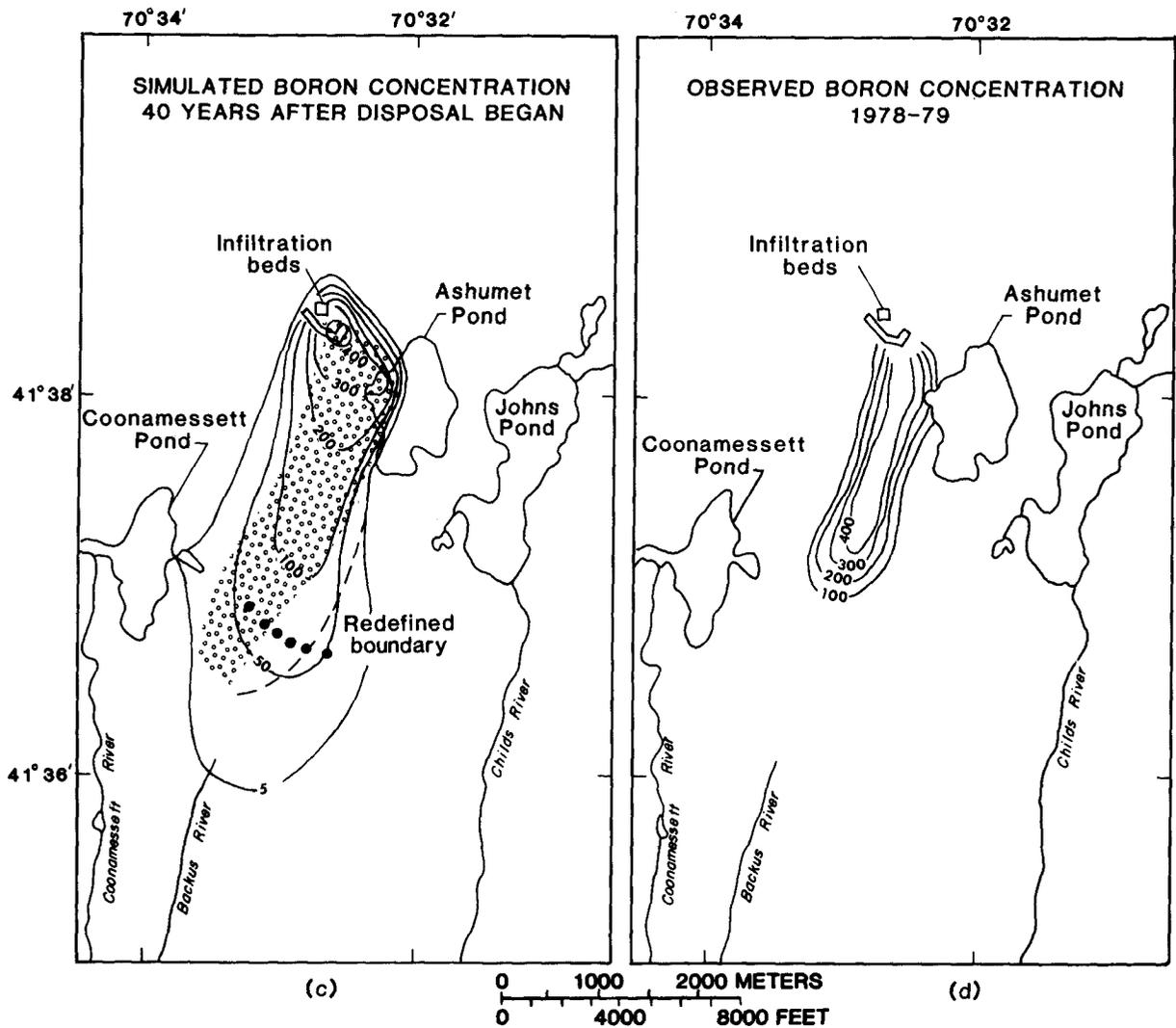
The greater width of the simulated plume compared to the observed plume (fig. 13c) may be due to several causes: (1) The apparent boundaries in 1978-79, delineated by the concentration contours, may not reflect the maximum extent of the contaminated zone. Identification of the boundaries of the plume from chemical analyses of ground water becomes uncertain as concentrations are attenuated by dilution near the boundaries (table 3) or as concentrations approach the detection limits of the laboratory analytical methods. The digital model, however, has a high apparent resolution of contaminated versus uncontaminated water. (2) The simulated flow system is only an approximation of the real flow system and may predict greater divergence of flow at the infiltration beds and toward the Coonamessett and Childs Rivers than occurs in the real



EXPLANATION

— 100 — LINE OF EQUAL BORON CONCENTRATION--
 Concentration in micrograms per liter.
 Interval varies.

Figure 13.--Computed boron concentrations after (a) 9.8 years, (b) 29.3 years, and (c) 40 years of disposal of treated sewage containing 500 µg/L boron, and (d) observed areal distribution of boron in 1978-79. Assumes that all sand infiltration beds (four nodes) were used for disposal.



EXPLANATION

- 100— LINE OF EQUAL BORON CONCENTRATION--
Concentrations in micrograms per liter.
Interval varies.
- - - - - EASTERN BOUNDARY OF PLUME REDEFINED BY
NOVEMBER 1983 TEST-WELL DRILLING
-  AREA OF PLUME DELINEATED IN 1978-79 --
Denoted by detection of detergents, or
concentrations exceeding 20 milligrams per liter
chloride or 100 micrograms per liter boron.
- OBSERVATION WELL-- Drilled in November 1983
to delineate plume boundaries.

Figure 13.--(continued).

system. (3) The dispersivity used in the model may be larger than the actual dispersivity and may predict more spreading of solutes by hydrodynamic dispersion than occurs in the aquifer. (4) The simulated spreading may be due in part to model error, especially numerical dispersion. Effects of dispersion are discussed in a later section of this report.

The apparent eastward divergence of the simulated plume from the observed plume may be due to several causes: (1) The model may simulate too much discharge to the Childs River and too little discharge to the Backus and Coonamessett Rivers. The computed heads are sensitive to inaccurate specification of heads along these boundaries, and an eastward bias in the water-table gradient may have been introduced in the model. Computed water levels at three wells in the southeastern corner of the modeled area are 4-5 feet lower than observed water levels. (2) Hydraulic conductivity may be laterally anisotropic or heterogeneous due to areal trends in the grain-size distributions in the outwash. Such variations could not be detected from the field data. Several hypothetical simulations were run in which hydraulic conductivity was assumed to decrease from 210 ft/d in the northwest corner of the modeled area to 150 ft/d in the southeast corner of the modeled area. Such a pattern would be consistent with observations by Mather and others (1942, p. 1153) that the outwash tends to become finer from northwest to southeast. However, these variations resulted in little change in computed hydraulic heads and did not affect the simulated path of the plume. (3) The apparent eastward divergence of the simulated plume may also be due partly to inaccurate field delineation of the plume along its eastern boundary. The wells that defined the eastern boundary in 1978-79 were widely spaced. This third hypothesis was tested by additional data collection in 1983. Ground electrical conductivity measurements, made in June 1983 with an electromagnetic induction device, suggested that the contaminated zone extends farther eastward than earlier thought (Gary Olhoeft, U.S. Geological Survey, oral commun., 1984). Also, additional wells were drilled in November 1983 at the sites shown in figure 13c. Water samples were collected and analyzed during drilling. Specific conductances greater than 190 $\mu\text{mhos/cm}$ and the presence of significant foaming at all but the easternmost drilling site show that the plume's eastern boundary lies 1,300 feet east of the original delineation and agrees more closely with the simulated plume (fig. 13c).

The length of the simulated plume generally agrees with the length of the zone in which detergents were detected or concentrations exceeded 20 mg/L chloride or 100 $\mu\text{g/L}$ boron (fig. 13c). Additional chemical analyses of water samples collected in 1983 (Thurman and others, 1984) confirm that contaminants from the disposal site are present in wells 11,000 feet from the infiltration beds. The observed boron plume seems to be shorter than the simulated boron plume, however (fig. 13d). This apparent difference may be due to several causes: (1) The apparent boundaries of the observed plume in 1978-79, shown as the 100 $\mu\text{g/L}$ concentration contour in figure 13d, may not reflect the maximum extent of boron movement in the aquifer. (2) Boron may not have been introduced into the treated sewage at present concentrations until some time after 1940. Data are not available to evaluate this hypothesis, but the association of boron with cleaners and detergents suggests that such a source variation may have occurred.

Two-Dimensional Simulation of a Three-Dimensional Plume

The computed concentrations in the center of the simulated plume decrease gradually from the infiltration beds downgradient to the toe (fig. 13c). In contrast, the observed concentrations of boron and other constituents, such as chloride, remain relatively unchanged in the center of the plume for 8,000 feet (fig. 13d). The inability of the model to simulate the observed concentrations, despite the good match between the observed and computed paths, is mostly due to the inherent limitations of the two-dimensional approach.

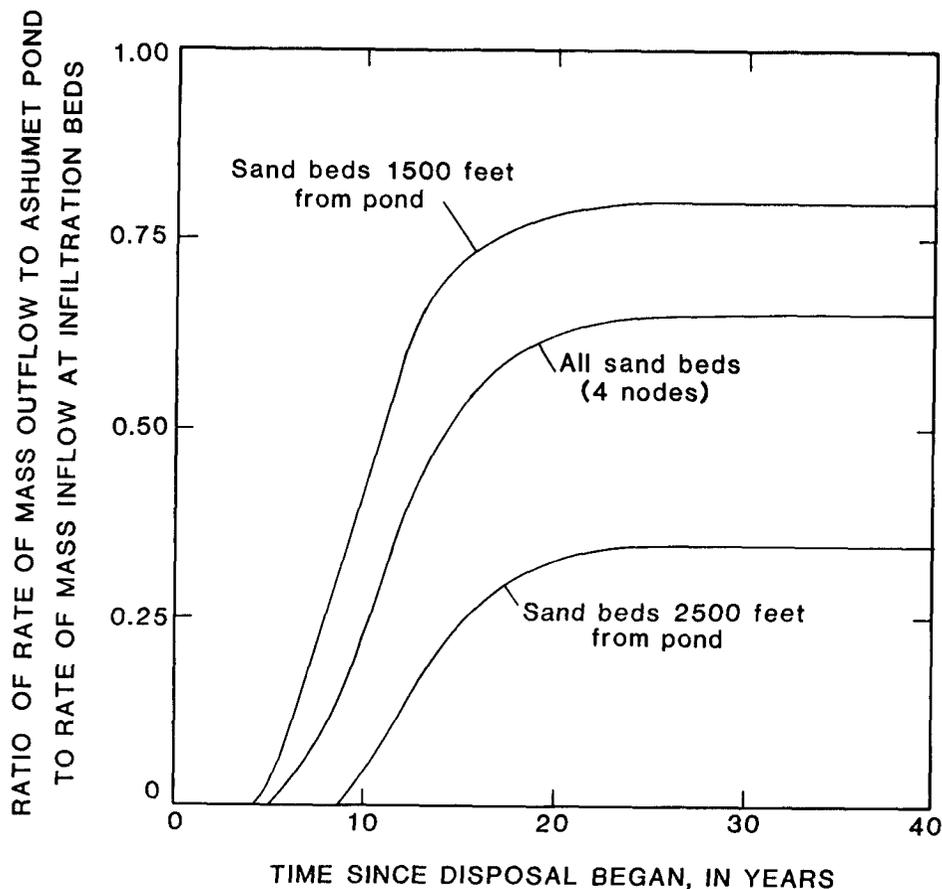


Figure 14.--Portion of total solute mass applied to the infiltration beds that discharges to Ashumet Pond in the simulations.

Typical observed and calculated vertical profiles of concentration through the plume are shown in figure 15. In the field, the contaminated ground water occupies only part of the aquifer thickness and is overlain by uncontaminated water from precipitation. Although some mixing occurs in a thin zone between contaminated and uncontaminated water, the two remain essentially separate. In the two-dimensional model, however, vertical variations of concentration are assumed to be negligible. The solute is evenly distributed through the thickness of the aquifer (fig. 15). Rather than overlying the plume, inflow from areal recharge or pond leakage immediately mixes through the full thickness of the aquifer in the model. Therefore, in the simulated plume, concentrations are diluted by recharge from precipitation and decrease away from the source.

An attempt was made to calculate equivalent vertically averaged concentrations from the field data for comparison with the simulated concentrations. In practice, however, concentration profiles and aquifer thickness were well defined at only a few observation sites, and reasonable estimates could not be obtained at a sufficient number of sites.

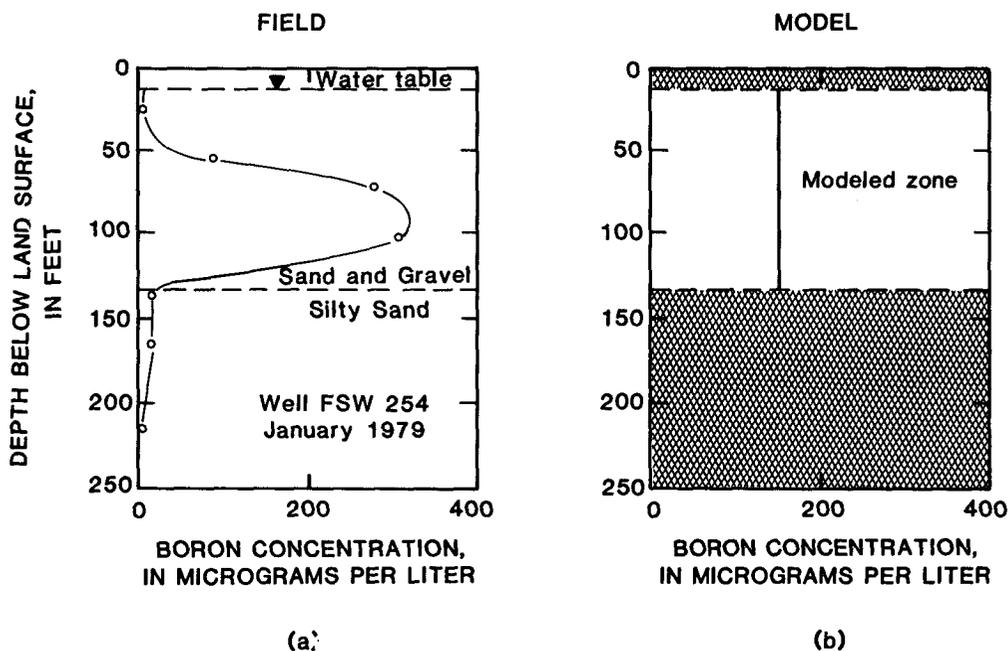


Figure 15.--Profiles of boron concentration with depth showing (a) typical vertical variation of concentration in the plume and (b) simulated vertically averaged concentration in the model. Location of well FSW 254 shown in figure 5.

Interaction of the Plume and Ashumet Pond

Ashumet Pond affects the simulated plume in two ways. First, the pond intercepts a portion of the treated sewage as it moves southward from the sand beds. In the calibration simulation, with the treated sewage applied to four nodes representing the entire sand-bed area, as much as 65 percent of the treated sewage discharges to the pond (fig. 14). The presence of contaminated water at the pond bottom was confirmed by two methods. Water samples collected from shallow wells driven into the pond bottom along the northwestern shore had specific conductances of over 400 μ mhos/cm and contained as much as 10 mg/L total nitrogen (William B. Kerfoot, K-V Associates, written commun., 1983). These levels are typical of wells screened in the plume within 200 feet of the pond. In addition, geophysical electromagnetic measurements of apparent ground conductivity along the shoreline show the presence of a contaminated zone having an elevated electrical conductance in the presumed area of discharge (Francis Frishneckt, U.S. Geological Survey, written commun., 1983).

The computed discharge of the plume to Ashumet Pond is very sensitive to the distance between the active infiltration beds and the pond. The sand beds cover a total area of 1,500 feet by 1,000 feet, and little data are available on past bed usage. The plume is likely a product of disposal to different beds at different times. Two simulations were run to test the effect of source location on the plume's path and rate of discharge to Ashumet Pond. In one simulation, all the treated sewage was applied to node (18,13) located 2,500 feet from the pond. In the other, the treated sewage was

applied to node (16,13) located 1,500 feet from the pond. The simulated plumes, after 40 years of transport, are shown in figure 16. The plume formed by disposal to the beds closest to the pond is much less extensive than the plume formed by disposal to the beds farthest from the pond. The difference in extent reflects the much greater rate of discharge of treated sewage to Ashumet Pond (fig. 14) when the closest beds are used.

These predicted effects of source location are reflected in the field data collected between 1978 and 1983. Since 1977, the treated sewage has been applied exclusively to two beds within 1,700 feet of the pond. Between 1978 and 1983, wells located west of the pond within 3,000 feet of the beds generally showed a drop in specific conductance and concentrations of constituents like boron (Thurman and others, 1984). Concentrations in wells located directly between the beds and Ashumet Pond remained at levels near the concentrations in the treated sewage. A similar pattern of lower apparent ground electrical conductivity west of the pond and elevated conductivity between the beds and the pond was inferred from geophysical measurements made in June 1983 (Gary Olhoeft, U.S. Geological Survey, written commun., 1984). As indicated by the simulations, the use of beds close to the pond since 1977 probably has caused contaminants to move more directly toward the pond. Concentrations have decreased west of the pond as contaminated water, representing disposal to more westerly beds prior to 1977, moves downgradient. In August 1984, the U.S. Air National Guard plans to shift disposal to eight sand beds located 1,700 to 2,600 feet from the pond. As a result, concentrations in wells west of Ashumet Pond should increase again as less treated sewage discharges to the pond.

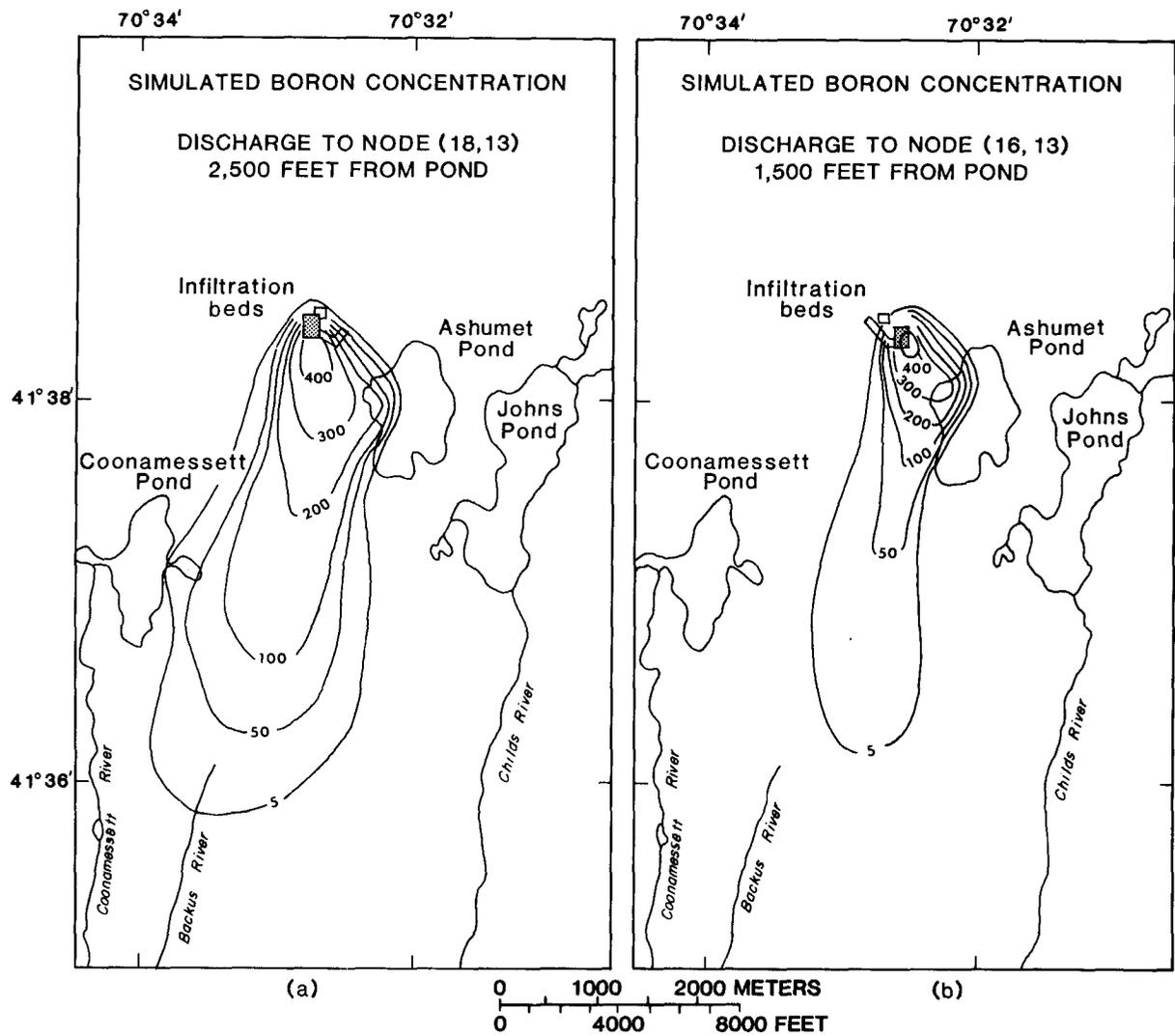
Ashumet Pond also affects the simulated plume by discharge of pond water to the aquifer along its southwest shoreline. A well cluster drilled to a depth of 100 feet below pond level at the southwestern corner of the pond did not detect the plume. The recharging pond water, in effect, creates a flow line that bounds the plume along its eastern side south of Ashumet Pond.

A more rigorous evaluation of the interaction between Ashumet Pond and the plume must consider the three-dimensional flow and transport system. In the two-dimensional model, concentrations of solute in ground water discharging to the pond are vertically averaged through the full thickness of the aquifer. Vertical flow patterns must be considered because discharge to the pond may include more of the uncontaminated water above the plume and less of the deeper contaminated water in the plume.

Sensitivity to Dispersivity

Dispersivity may be adjusted during transport simulations like other model parameters until an acceptable match is obtained between observed and computed solute concentrations. In these two-dimensional simulations, concentrations could not be compared directly, and no attempt was made to adjust dispersivity during comparison to the observed plume. Dispersivity was varied, however, to test its effect on computed concentrations.

With dispersivity set equal to zero, concentrations in the simulated plume decrease with distance from the infiltration beds due to dilution by areal recharge, divergence of flow toward the discharge boundaries, and perhaps numerical dispersion (fig. 17a). Additional spreading and dilution of the plume occurs when longitudinal dispersivity is set to 40 feet (fig. 13c) and 100 feet (fig. 17b), the range of dispersivity reported by other studies of large plumes (Anderson, 1979, p. 127). The changes in concentration which result by varying longitudinal dispersivity from 40 to 100 feet are small, however. The contours of computed concentration shift less than 500 feet (4 percent of the length of the plume) as longitudinal dispersivity is increased from 40 feet to 100 feet. Estimation of dispersivity by matching observed and computed concentrations would be hindered by this insensitivity of concentration to dispersivity within the range of expected values. Matching concentrations, if model-generated concentrations were not vertically averaged and could be compared directly to field values, would be further hindered by the wide spacing between observation points, the uncertainties associated with other aquifer characteristics, and the unknown source variations.



EXPLANATION

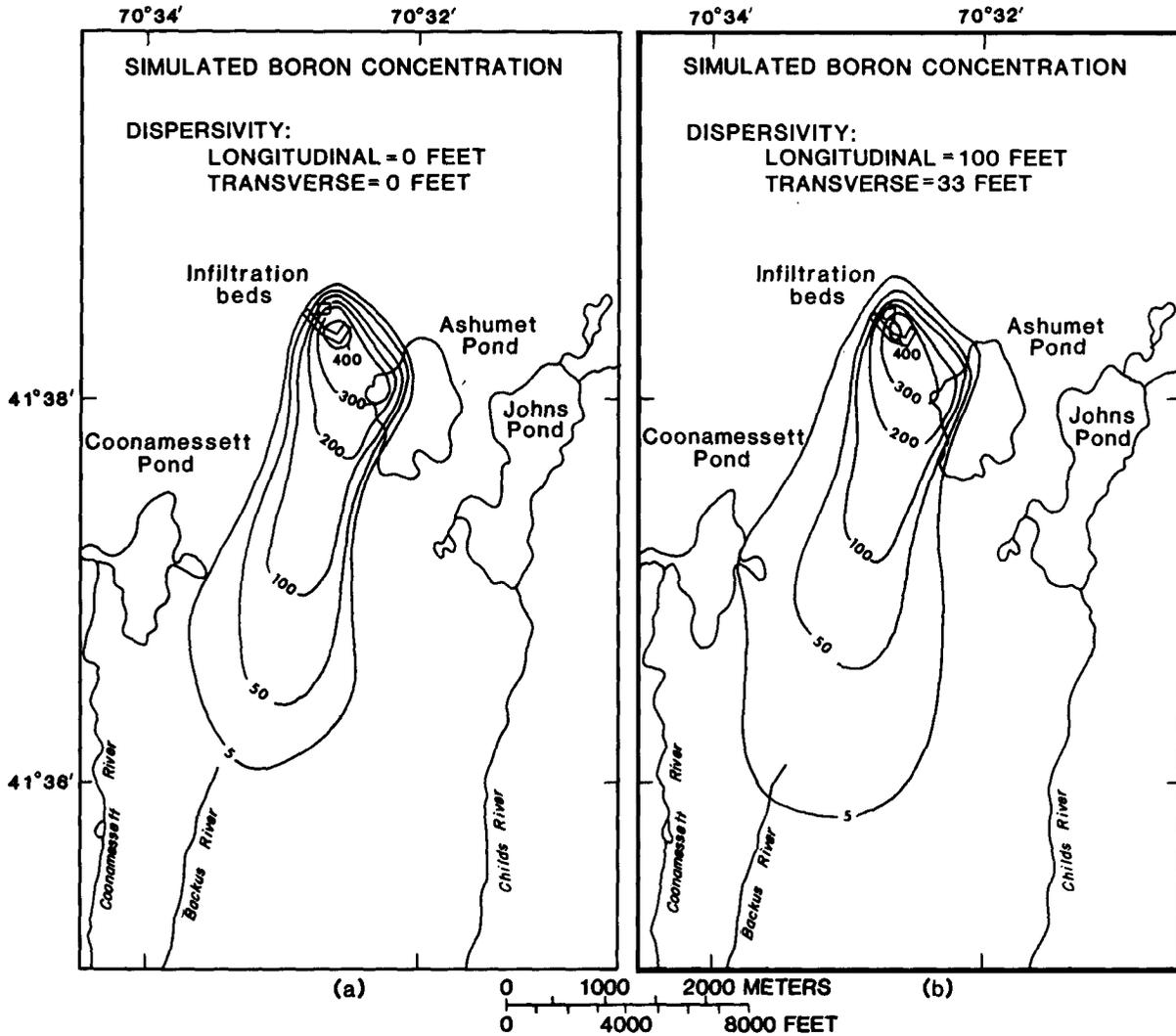
— 100 —

LINE OF EQUAL BORON CONCENTRATION--
 Concentrations in micrograms per liter.
 Interval varies.



NODE LOCATION OF TREATED-SEWAGE DISPOSAL

Figure 16.--Computed boron concentrations after 40 years of disposal of treated sewage containing 500 µg/L to infiltration beds (a) 2,500 feet and (b) 1,500 feet from Ashumet Pond.



EXPLANATION

————— 100 ————— LINE OF EQUAL BORON CONCENTRATION—
Concentrations in micrograms per liter.
Interval varies.

Figure 17.—Computed boron concentrations after 40 years of disposal of treated sewage containing 500 $\mu\text{g/L}$, assuming (a) zero dispersivity and (b) longitudinal dispersivity of 100 feet and transverse dispersivity of 33 feet.

Some dispersion in the simulations may be a result of the numerical methods used to solve the transport equation. Numerical dispersion may be caused by two factors: (1) The relatively coarse grid may result in some smearing of concentrations as reference particles are moved through the simulated flow system. (2) The regeneration of particles to minimize the number of void nodes also tends to smear concentrations within a given node, although the program includes an optimization routine to minimize this cause of numerical dispersion (Konikow and Bredehoeft, 1978, p. 19). The degree of numerical dispersion could not be evaluated from the simulated results.

PREDICTIVE CAPABILITY OF THE MODEL

If the transport model reasonably represents the observed field conditions, it also can be used to evaluate the effects of future source changes or other stresses on the plume. Two projections beyond the 40 years of transport shown in figure 13 were made to illustrate the predictive capability of the model. It is important to note, however, that the model was calibrated against a single set of observations made in 1978-79. Its ability to reproduce past changes is unverified because historical data on solute concentrations in the aquifer are unavailable. Also, little hydrologic and no chemical data are available for the area farther than 11,000 feet from the infiltration beds into which the contaminants move. Therefore, the reliability of the predictions cannot be assessed.

Constant and Continuous Source of Solute

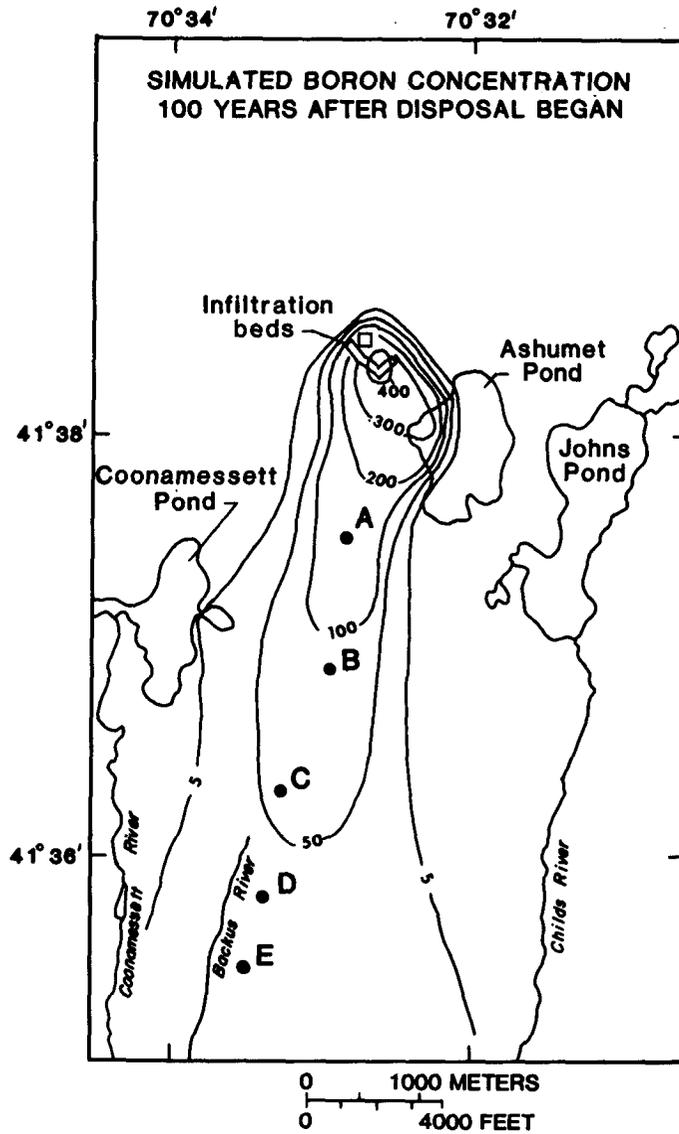
In the original set of simulations, treated sewage containing 500 $\mu\text{g/L}$ of boron continuously recharged the aquifer for 40 years at a rate of 0.72 ft^3/s . If disposal continues for 60 more years and all other hydrologic conditions remain the same, the simulated plume spreads along a broad front before discharging to the southern boundary of the modeled area (fig. 18). Concentrations at the toe are greatly diluted, although the dilution is due largely to mixing with areal recharge. In the actual three-dimensional flow and transport system, concentrations would be diluted much more slowly, and higher concentrations would reach the discharge areas.

Under the constant conditions assumed in the 100-year simulation, the simulated plume reaches a steady configuration. Concentrations stabilize after about 60 years from the start of disposal (fig. 19). Once a steady state is reached, solutes move continuously from the infiltration beds to the discharge areas, but the concentration pattern does not change with increasing time. This condition will probably never be observed because of variations at the source and changes in other stresses in the aquifer.

Changes in Concentrations of Solutes in the Source

Concentrations of some solutes in the treated sewage, such as detergents, have varied considerably since disposal began in 1936. The sewage also could receive additional treatment to remove selected contaminants that enter the aquifer at undesirable levels. To illustrate the change of concentrations of a constituent in the aquifer in response to the elimination of the constituent at the source, a simulation was run in which the concentration of boron in the treated sewage was suddenly and permanently decreased from 500 $\mu\text{g/L}$ to 0.0 $\mu\text{g/L}$. The simulated boron plume is gradually flushed from the aquifer (fig. 20). Because of the two-dimensional approximation, the concentrations of boron previously introduced into the aquifer also are diluted by mixing with recharge from precipitation as the contaminated ground water moves downgradient. Therefore, the simulated concentrations shown in figure 20 decrease more rapidly than they would in the real system where little vertical mixing occurs.

Boron concentrations remain relatively high in the simulated plume, even 20 years after boron is eliminated from the source. In 20 years, the simulated peak concentration is 6,000 feet downgradient of the infiltration beds. A second area of elevated concentration occurs at Ashumet Pond (fig. 20) that persists 40 years after boron is eliminated



EXPLANATION

- 100** **LINE OF EQUAL BORON CONCENTRATION--**
 Concentrations in micrograms per liter.
 Interval varies.

- D** **OBSERVATION SITE--**Location of nodes for
 which concentrations with time are
 plotted in figure 19.

Figure 18.--Computed boron concentrations after 100 years of continuous disposal of treated sewage containing 500 µg/L. Assumes constant hydrologic conditions.

from the treated sewage. This zone coincides with a leakage node at Ashumet Pond that is located at the boundary between areas where water leaks into and water leaks out of the pond. At this point, ground-water velocities generated by the model are very small, and the rate of solute transfer between this node and adjacent nodes is very slow. As the plume reaches the pond, solute concentrations increase much more slowly in the node containing the stagnant water than in adjacent nodes. As the plume is subsequently flushed from the aquifer, concentrations in the node containing the stagnant water decrease more slowly than in adjacent nodes. Therefore, a small area of high concentrations remains that is slowly attenuated. This zone may be an artifact of the two-dimensional simulation and the representation of Ashumet Pond essentially as a constant-head boundary. In the field situation, it is not known if such a stagnant area exists.

The simulated distribution of boron in figure 20 is very similar to the distribution of detergents observed in 1978-79 (fig. 8). Detergents, however, were never completely eliminated from the source because some foaming agents (MBAS) remain in the treated sewage (table 1). Detergent concentrations in 1978-79 in the plume exceeded 0.5 mg/L MBAS, the recommended concentration limit for foaming agents in drinking water (U.S. Environmental Protection Agency, 1979, p. 42198). A simulation of the transport of detergents was run to determine how rapidly the residual high concentration of detergents located 3,000 to 10,000 feet downgradient of the infiltration beds will be flushed out of the aquifer. The approximate history of concentration of detergents in the treated sewage, shown in table 1, was used for the simulations.

The simulated distribution of detergents (fig. 21) after 32 years of transport (1948 through 1979) is very similar to the observed distribution of detergents in 1978-79 (fig. 8). The computed concentrations are lower than the observed concentrations, partly due to the two-dimensional approximation, but exceed the 0.5 mg/L MBAS drinking water standard. After 20 years of additional transport, the simulated zone of elevated detergent concentrations has moved an additional 7,500 feet away from the infiltration beds. Although the maximum computed concentration of detergents in figure 21b is 0.35 mg/L MBAS, concentrations in the three-dimensional system would be diluted much more slowly.

The distributions of other contaminants in the plume seem to reflect a variable source history. These contaminants include strontium and volatile organic compounds (Thurman and others, 1984). The model may be a useful tool to evaluate the processes that affect the movement of these solutes in the aquifer and to test hypotheses concerning the source and period of disposal of these contaminants.

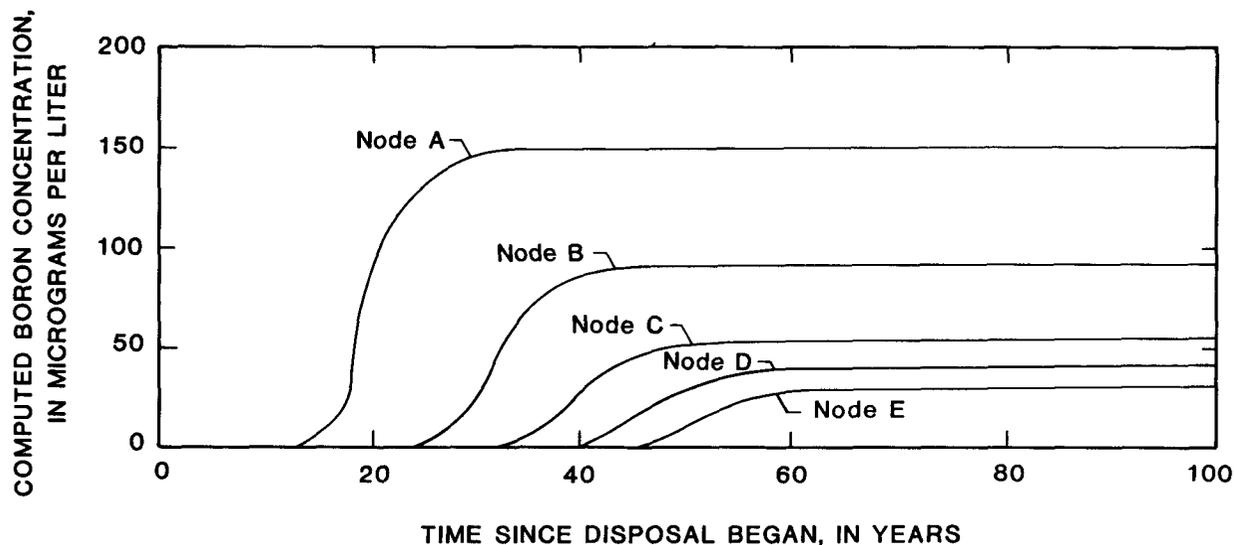
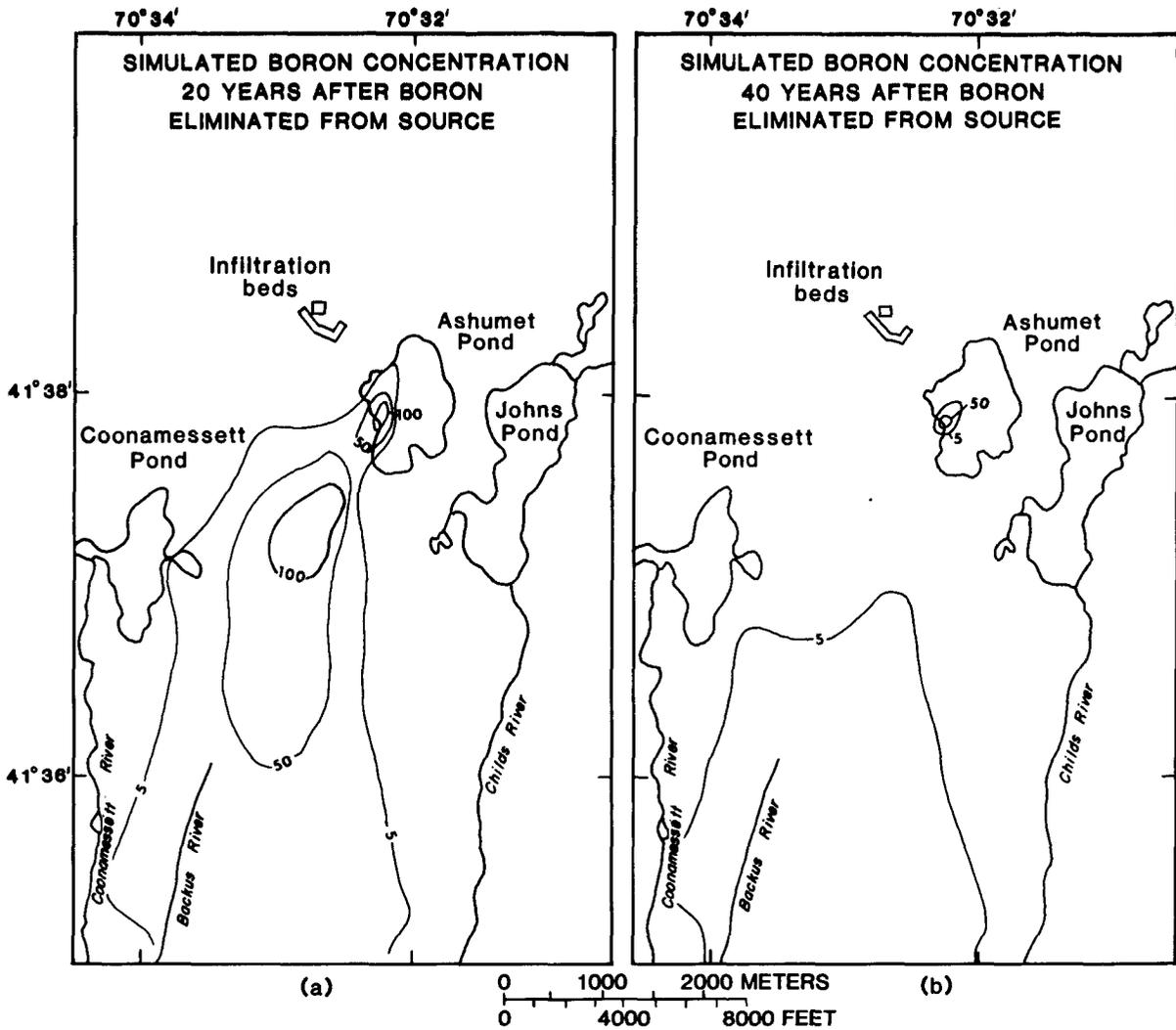


Figure 19.--Change in computed boron concentration at selected nodes if disposal of treated sewage continues for 100 years (node locations shown in figure 18).

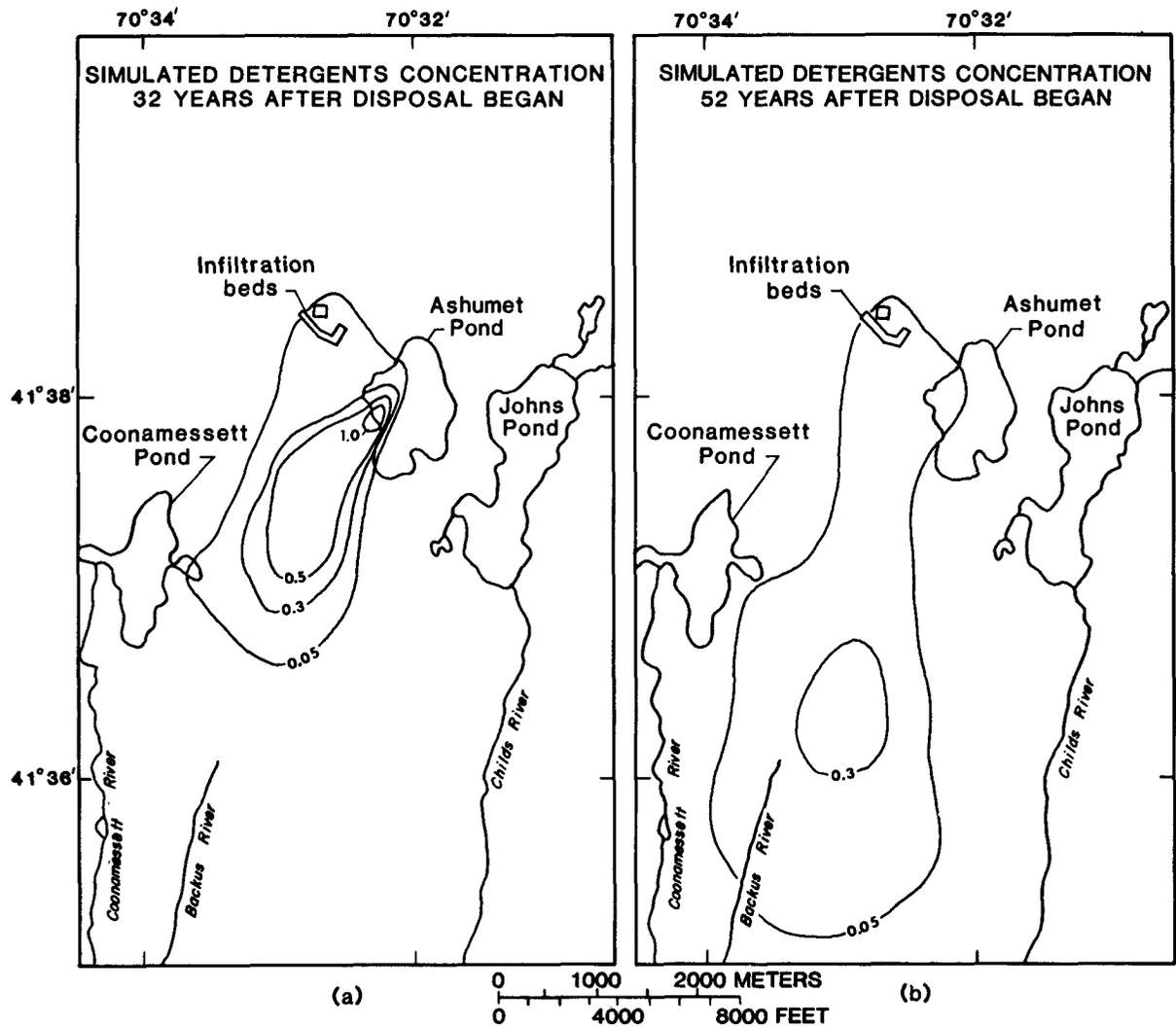


EXPLANATION

— 100 —

LINE OF EQUAL BORON CONCENTRATION--
Concentration in micrograms per liter.
Interval varies.

Figure 20.--Computed boron concentrations assuming 40 years of disposal of treated sewage containing 500 µg/L, followed by disposal of treated sewage containing no boron for (a) 20 years and (b) 40 years.



EXPLANATION

— 0.5 — LINE OF EQUAL DETERGENTS CONCENTRATION --
 Concentration in milligrams per liter methylene
 blue active substances (MBAS). Interval varies.

Figure 21.--Computed detergent (MBAS) concentrations assuming 18 years of disposal of treated sewage containing 3.0 mg/L MBAS, followed by disposal of treated sewage containing 0.3 mg/L MBAS for (a) 14 years and (b) 34 years.

SUMMARY AND CONCLUSIONS

A method-of-characteristics computer code (Konikow and Bredehoeft, 1978) was used to simulate two-dimensional solute transport in the sewage plume at Otis Air Base. The first step in the modeling process was calibration of a steady-state flow model against average water-table conditions. A hydraulic conductivity of about 190 ft/d and an average areal recharge rate of about 20 in/yr yielded the best match between observed and computed water levels. The ground-water velocity distribution from the flow model was used as input to the transport simulations.

The second step in the modeling process was simulation of solute transport. Boron was simulated because it is a good tracer of the plume and was believed to behave conservatively in the plume. The simulated plume was compared to the plume delineated by chemical analyses of water samples collected from wells in 1978-79, approximately 40 years after sewage disposal to the sand beds began at the base. The locations of the simulated and observed paths agree reasonably well, although the simulated plume is wider and spreads eastward of the observed plume. The differences may be due, in part, to inaccurate field delineation of the plume. Additional drilling and sampling should be coupled with geophysical methods to locate and characterize the plume more precisely, especially along its southern and eastern boundaries. The modeling results also suggest that boron may not delineate the entire plume. A better description of boron's source history, and identification of other tracers, such as trace-level nonreactive organic compounds, is needed for future modeling efforts.

The approximation of the aquifer as a two-dimensional system resulted in inadequate simulation of observed concentrations in the plume. The two-dimensional model vertically averages concentrations and mixes areal recharge from precipitation through the full aquifer thickness. The plume occupies only part of the aquifer thickness, however, and areal recharge forms an uncontaminated zone above the plume. The assumptions of the two-dimensional approach are not completely met at the Otis site, and the effects of three-dimensional flow on transport are not well represented. Future modeling efforts should focus on simulation of the three-dimensional features of the sewage plume.

Ashumet Pond affects the plume by intercepting a portion of the treated sewage as it moves southward from the sand beds. In the simulations, as much as 65 percent of the treated sewage discharges to the pond. The percentage of the plume that discharges to the pond is sensitive to the distance between the infiltration beds and the pond. Use of beds located farther from the pond than the beds in use during 1977-83 should reduce the rate of plume discharge to the pond and increase the western extent of the contaminated zone. The observed plume is the result of disposal to different beds at different times. The simulations were used to show how the plume-pond interaction has a significant effect on the response of the plume to these changes. Additional research is needed to understand the potential impacts of the three-dimensional movement of contaminants at Ashumet Pond on the pond water quality and on the extent and path of the plume.

The transport model is a useful tool for analyzing and interpreting field data and for evaluating possible changes in the plume. Although the simplifications inherent in the modeling process result in only rough agreement with the field situation, the model simulations give considerable insight into the complex interactions of geologic and hydrologic processes that affect the transport of solutes in the aquifer. Transport models should be an integral part of future research at the Otis site.

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CHAPTER C

The plume was originally described in 1978-79 by chemical analyses of water samples for major cations and anions, nutrients, and detergents. In this paper, additional chemical data collected in 1983 are presented that show movement of selected contaminants in the 4 years since 1979 and that describe the distributions of metals and organic compounds in the plume. This information adds to the base upon which hypotheses about the physical and chemical transport processes can be formulated and tested.

SEWAGE CONTAMINANTS IN GROUND WATER

by

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M. G. Brooks, M. P. Schroeder, R. J. Keck, A. J. Driscoll,
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ABSTRACT

The major cations and anions in the sewage plume at Otis Air Base, Massachusetts, are transported at the front of the plume and do not appear to be retained by the sand and gravel aquifer. Nutrients behave conservatively and nonconservatively. Nitrate moves rapidly while ammonia and phosphate are retarded. Organic constituents are present in the contaminated area of the aquifer, and detergents are a major component of the dissolved organic carbon. Volatile organic compounds are present in the aquifer, although not as far downgradient as the detergents. Also, the volatiles make only a small contribution to the dissolved organic carbon (less than 2 percent).

INTRODUCTION

Each year the Nation discharges 1 trillion gallons of wastewater and millions of tons of sludge to ground and surface waters. In coastal areas, wastewater is commonly discharged onto sand beds, and sludge is dried on land and disposed into landfills. Because many coastal communities dispose of wastewater and sludge onto sand beds, these wastes and their by-products, such as trace metals, nitrate, detergents, and nondegradable organic compounds, are continually being added to ground water. The fate of these compounds in an aquifer is an area of research in environmental chemistry of national significance and of specific interest to those who drink ground water in these areas. For these reasons we are studying geologic, hydrologic, chemical, and microbiological processes that control the fate and transport of treated sewage at Otis Air Base,¹ Falmouth, Massachusetts. This report summarizes the distribution and movement of inorganic solutes, nutrients, and organic compounds in ground water of this area in 1983.

EXPERIMENTAL PROCEDURES

Samples were collected from approximately 60 wells constructed of polyvinylchloride (PVC), which varied from 1.25 to 2.00 inches in diameter. Four of the wells were constructed of 2.50-inch diameter steel. The 1.25- and 2.50-inch wells were evacuated with a gasoline pump, then sampled with a peristaltic pump. The 2.00-inch wells were evacuated and sampled with a submersible stainless-steel pump. All wells were pumped until at least three casing volumes had been removed, and specific conductance was monitored to insure that stagnant water had been flushed from the well. Teflon tubing was used for discharge tubing for the peristaltic and submersible pumps.

Specific conductance, temperature, dissolved oxygen, and pH were measured in the field. Samples for major cations and anions were filtered through 0.45 micron Nucleopore filters. Samples for cations were preserved with nitric acid and stored in plastic bottles. After filtration both anions and nutrients were preserved without additives at 4 degrees C. Nutrients were analyzed within 3 days at a field laboratory near the site. Volatiles were sampled in a 40-mL sample bottle by removing all headspace and storing on ice at 4 degrees C. Samples for dissolved organic carbon and detergents were filtered through 0.45 micron silver filters and were stored on ice. Samples for semi-volatiles were taken by filling 1-gallon amber bottles with sample and spiking with three surrogate standards (see Barber and others, 1984). Samples were extracted by trapping the semi-volatiles on charcoal within 24 hours of sampling and were analyzed within one week at the laboratory.

Inorganic analyses, nutrients, and organic carbon were analyzed according to standard procedures of the U.S. Geological Survey (Skougstad and others, 1979), and trace metals were analyzed by inductively coupled plasma emission spectroscopy. Volatiles were analyzed by purge and trap followed by gas chromatography/mass spectrometry (Wershaw and others, 1983).

¹A description of the site, including its geologic and hydrologic setting, is given in Chapter A of this volume.

DISTRIBUTION AND MOVEMENT OF INORGANIC SOLUTES

Water samples were collected during the summer of 1983 and were analyzed for major cations and anions, trace metals, nutrients, and various organic constituents (dissolved organic carbon (DOC), volatiles, semi-volatiles, and detergents). The results of these analyses verified the general location of the plume that was reported previously (LeBlanc, 1982), but indicated that in three years the plume had moved southwest approximately 1000 feet, which is approximately one foot per day. The results of the chemical analyses for the 1983 field season confirm the hypothesis by LeBlanc (1982) that boron and detergents are nearly conservative tracers of the plume in this sand and gravel aquifer. Column experiments are planned for major and minor constituents to determine if field interpretations of conservative behavior can be confirmed in the laboratory.

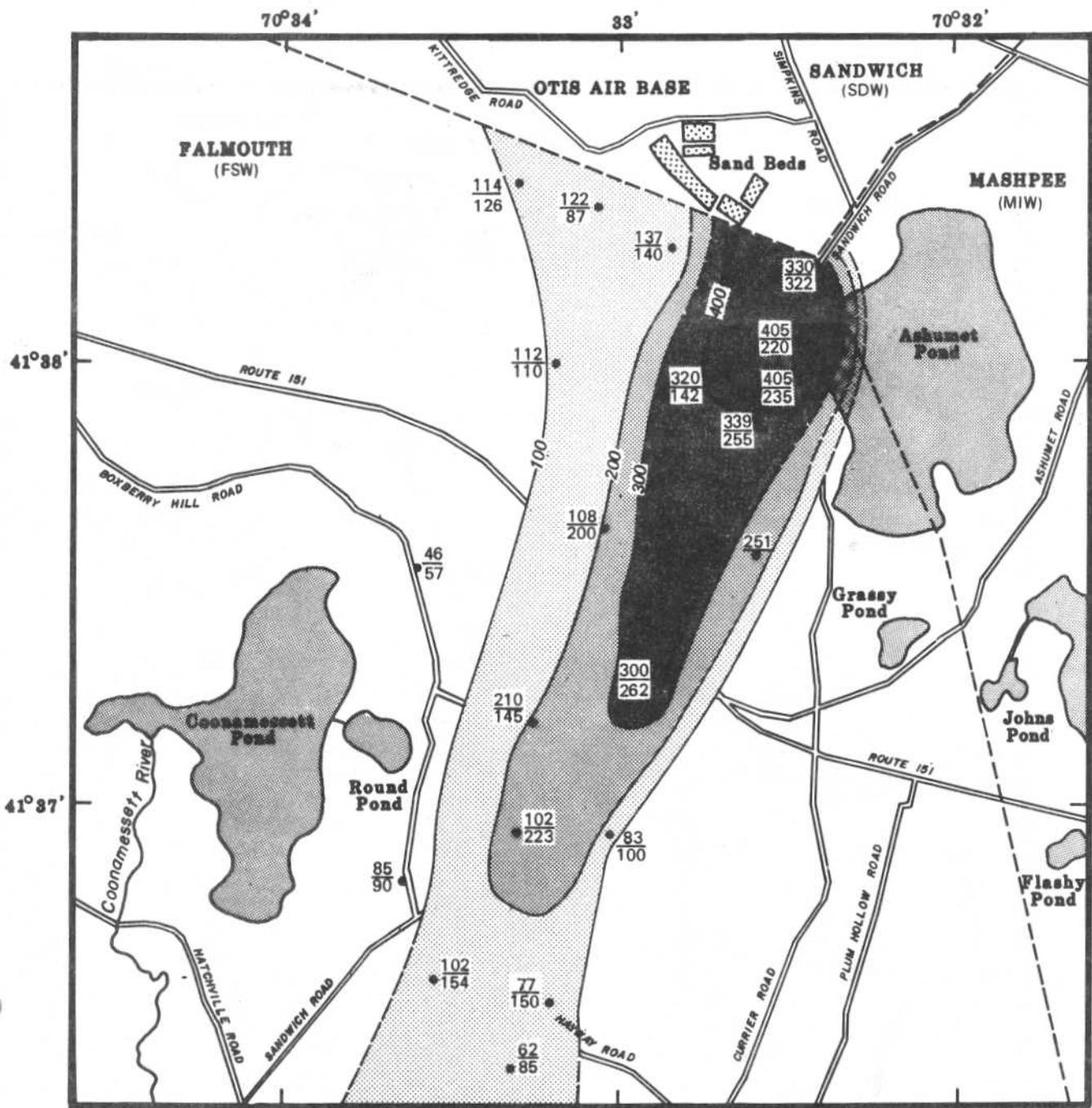
Furthermore, a series of different zones have been identified within the sewage plume. These results are discussed in two sections, inorganic and organic solutes. In each section there is a discussion of solute distribution, possible origins, and movement of the solutes in the aquifer. There are four tables of data at the back of this report. Table 6 contains the concentration of inorganic solutes found in the samples of ground water, table 7 contains the concentration of organic solutes, table 8 contains DOC fractionation analyses, and table 9 includes the concentration of volatile organic compounds that are present in the ground water. Finally, figure 22 shows the location of wells that were sampled during the 1983 field season.

Specific Conductance

Because the specific conductance of the effluent is 400 μmhos and the specific conductance of the native ground water is 50 to 80 μmhos , specific conductance is a good indicator of the zone of sewage-contaminated water of the aquifer. Using specific conductance as indicator of the plume, we found that conductances greater than 200 μmhos (50 percent effluent and 50 percent native ground water) extend 8000 feet from the beds and are 2000 feet wide (fig. 23). The concentration contours form an ellipse that is elongated in the direction of ground-water flow, which is from northeast to southwest.

Because specific conductance may come from any inorganic ions in the ground water, it is a nonspecific indicator of the sewage plume. The major usefulness of conductivity is as a field tool to locate the general vertical and horizontal pattern of the plume. When new wells are drilled, specific conductance is used by the field geologist to locate screens in the core of the plume. Also we used a stable reading of specific conductance during sampling of wells as an indicator of water from the aquifer rather than stagnant water from the casing of the well.

Since the last sampling period 3 years ago, the specific conductance has increased at the toe of the plume. Wells FSW 282-70, FSW 282-94, FSW 282-123, and FSW 294-89 increased slightly in conductance with increases in major cations and anions. This suggests that contaminated ground water has moved southwest over the past few years. This is chemical evidence showing plume migration. Later sections will show this movement in more dramatic terms (see section on boron and detergents).



0 500 1000 1500 METERS
 0 2500 5000 FEET

EXPLANATION

—100— LINE OF EQUAL SPECIFIC CONDUCTANCE -- Interval is 100 micromhos per centimeter at 25 °Celsius for 1978-79 data.

•137/140 FSW WELL -- Numbers show specific conductance in micromhos per centimeter in 1978-79 (upper) and 1983 (lower).

Figure 23.—Areal distribution of specific conductance in ground water, 1978-79 and 1983.

Not only has there been an increase in specific conductance at the toe of the plume, there has also been a decrease in conductance in wells near the sand beds just west of Ashumet Pond (see wells FSW 237-88, FSW 239-64, FSW 244-90, FSW 254 series). Figure 23 shows the ratio of conductances collected during the 1979 and 1983 field seasons. The lower conductances probably reflect the current use of the beds closest to Ashumet Pond (LeBlanc, 1984). The plume is moving more directly toward Ashumet Pond, and the conductance in wells just west of Ashumet Pond is decreasing as contaminated water moves toward the south. The decrease in conductance in these wells just west of Ashumet Pond is further corroborated by decreases in the concentrations of major cations, anions, and boron, which has been used as a tracer of the plume by LeBlanc (1982).

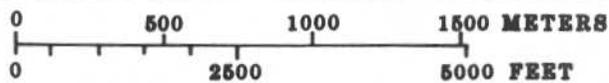
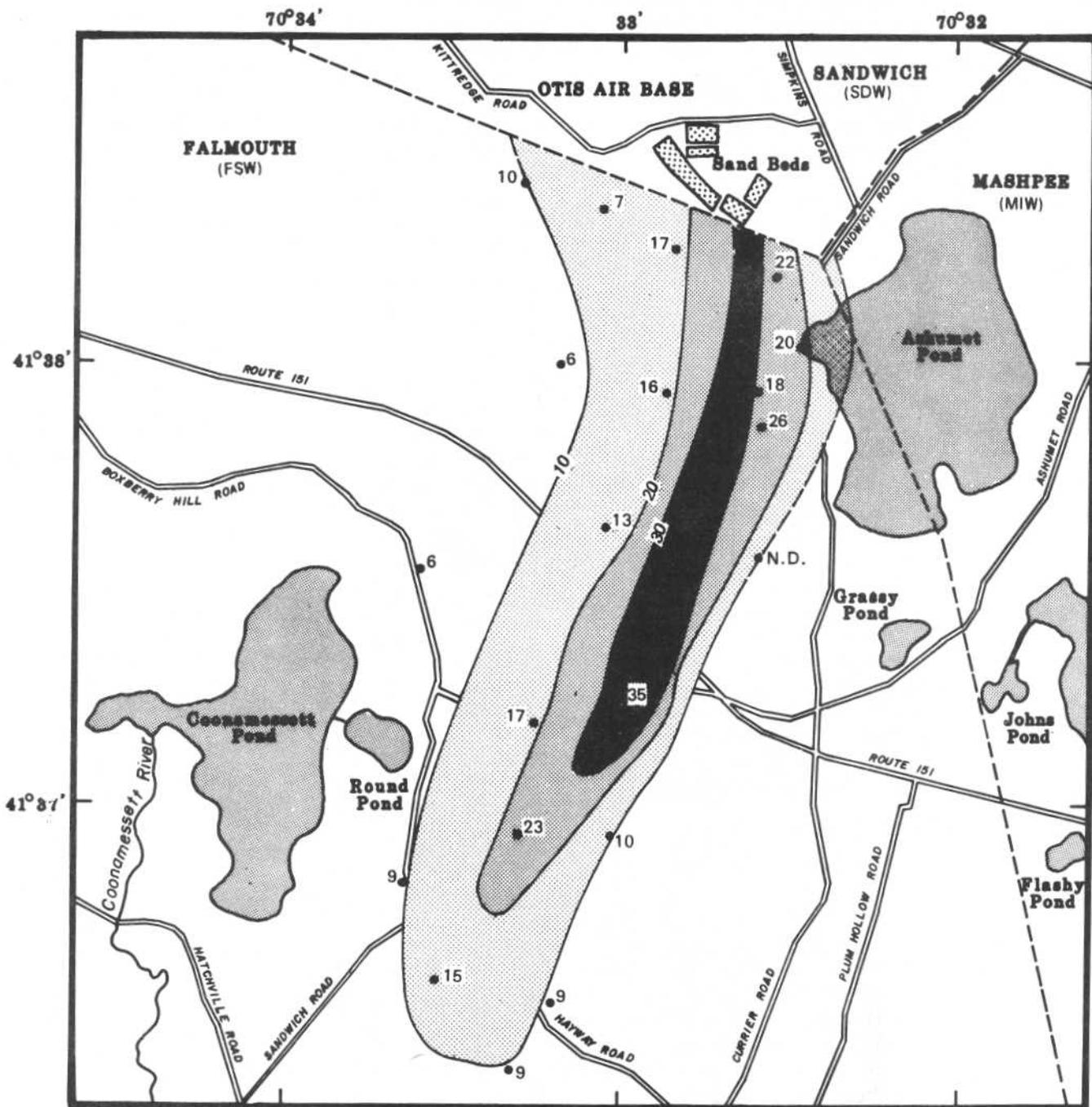
Major Cations

The ratio of major cations (Na/Ca), although not distributed identically in the effluent and ground water, does not show a trend in the plume of contaminated ground water that would indicate that cation exchange is occurring. The concentration of sodium is generally greater than the concentration of calcium, which is not a typical distribution for ground water. Commonly, the concentration of calcium is greater than the concentration of sodium. Because the concentration of sodium is greater than calcium both in the effluent and in the native ground water, there are multiple sources for sodium. Sodium is a major cation in the sewage and may also come from road salt introduced into the aquifer (LeBlanc, 1982). A natural source for sodium in the aquifer is sea spray that makes its way into the aquifer with recharging groundwater from precipitation. For these reasons, sodium and calcium are of limited use as tracers of the effluent plume in the ground water. Figure 24 and 25 show the distributions of sodium and chloride, which do follow the general location of the conductivity plume. Because there is only a five-fold change in concentration from the core of the plume to the native ground water, it is difficult to locate the boundaries of the plume from the distributions of sodium and chloride.

Major Anions

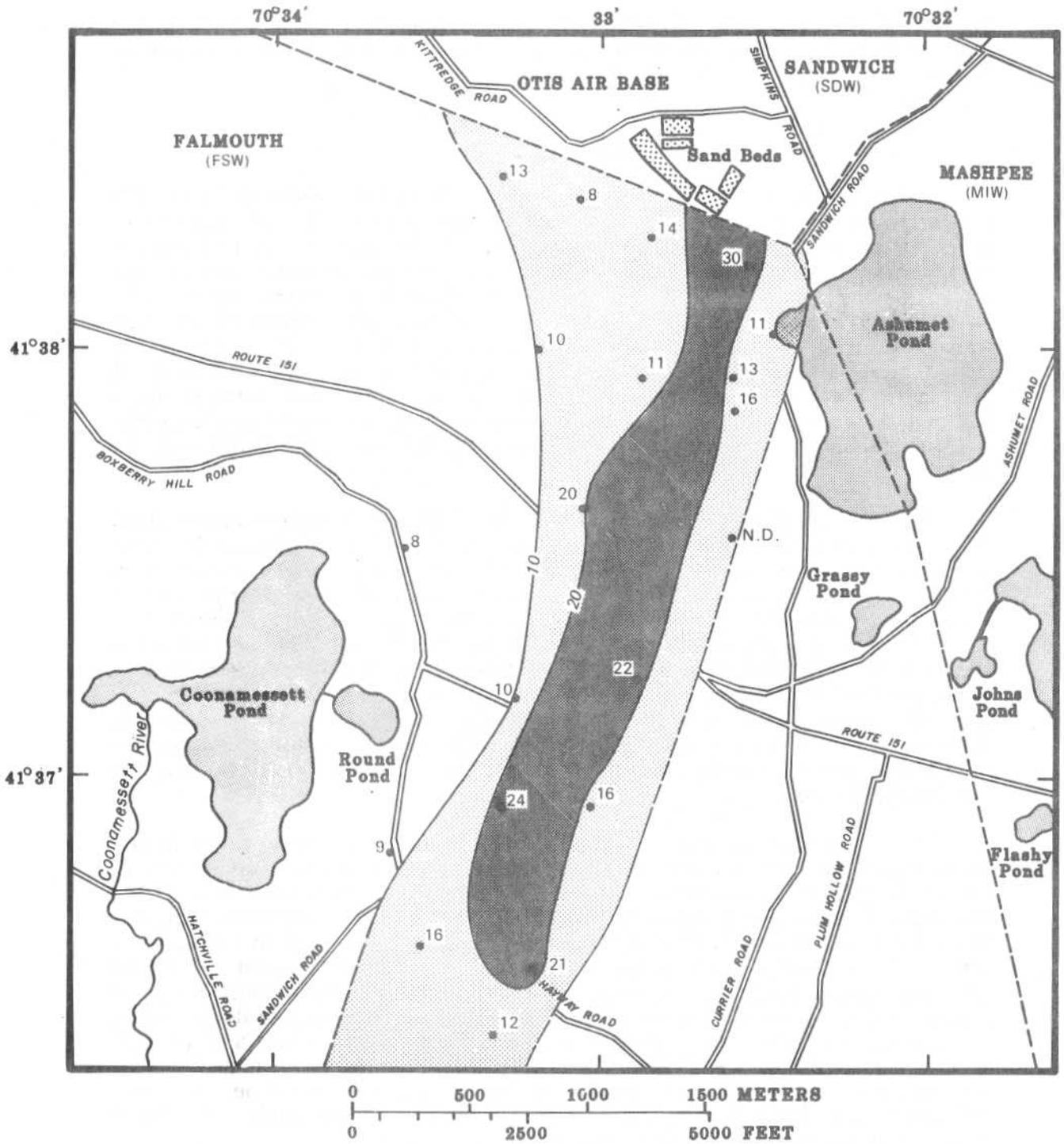
Major anions (SO_4^{4-} , Cl, and HCO_3^-) are present in approximately equal distributions in the effluent and contaminated and native ground waters. The major difference is an increase in alkalinity just downgradient from the infiltration beds. Alkalinity (as HCO_3^-) increases from 0.5 to 1.0 meq in the first 1000-2000 feet of contaminated ground water. Organic carbon is converted to inorganic carbon in this zone through microbial respiration (carbon dioxide, which then forms carbonate alkalinity), and approximately 0.75 meq of organic carbon is removed. Thus, nearly a 1:1 stoichiometry is maintained in this process. Microbiological studies are underway to better understand these conversions (Ceazan and others, 1984; Smith and Duff, 1984).

Chloride and sulfate are moving conservatively in the aquifer based on Cl/ SO_4^{4-} ratios of 1.0 to 1.5 throughout the core of the plume. There are no significant trends in these ratios with distance from the beds. For example, if preferential sorption of sulfate or sulfate reduction were occurring, the ratios of Cl/ SO_4^{4-} should increase with distance from the beds. Sulfate removal in ground water commonly occurs through microbial sulfate reduction to sulfide. Although



- EXPLANATION**
- 10— LINE OF EQUAL CONCENTRATION OF SODIUM - Interval is 10 milligrams per liter
 - 10 FSW WELL - Number shows concentration of sodium in milligrams per liter
 - N.D. NO DATA

Figure 24.—Areal distribution of sodium in ground water, 1983.



EXPLANATION

— 10 —	LINE OF EQUAL CONCENTRATION OF CHLORIDE - Interval is 10 milligrams per liter	● 12	FSW WELL - Number shows concentration of chloride in milligrams per liter
		N.D.	NO DATA

Figure 25.--Areal distribution of chloride in ground water, 1983.

hydrogen sulfide was not detected, sulfate reduction may be occurring near the sand-filtration beds, and new wells have been drilled near the beds to determine if this is the case.

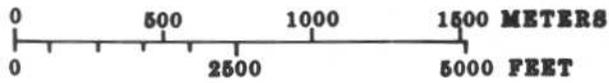
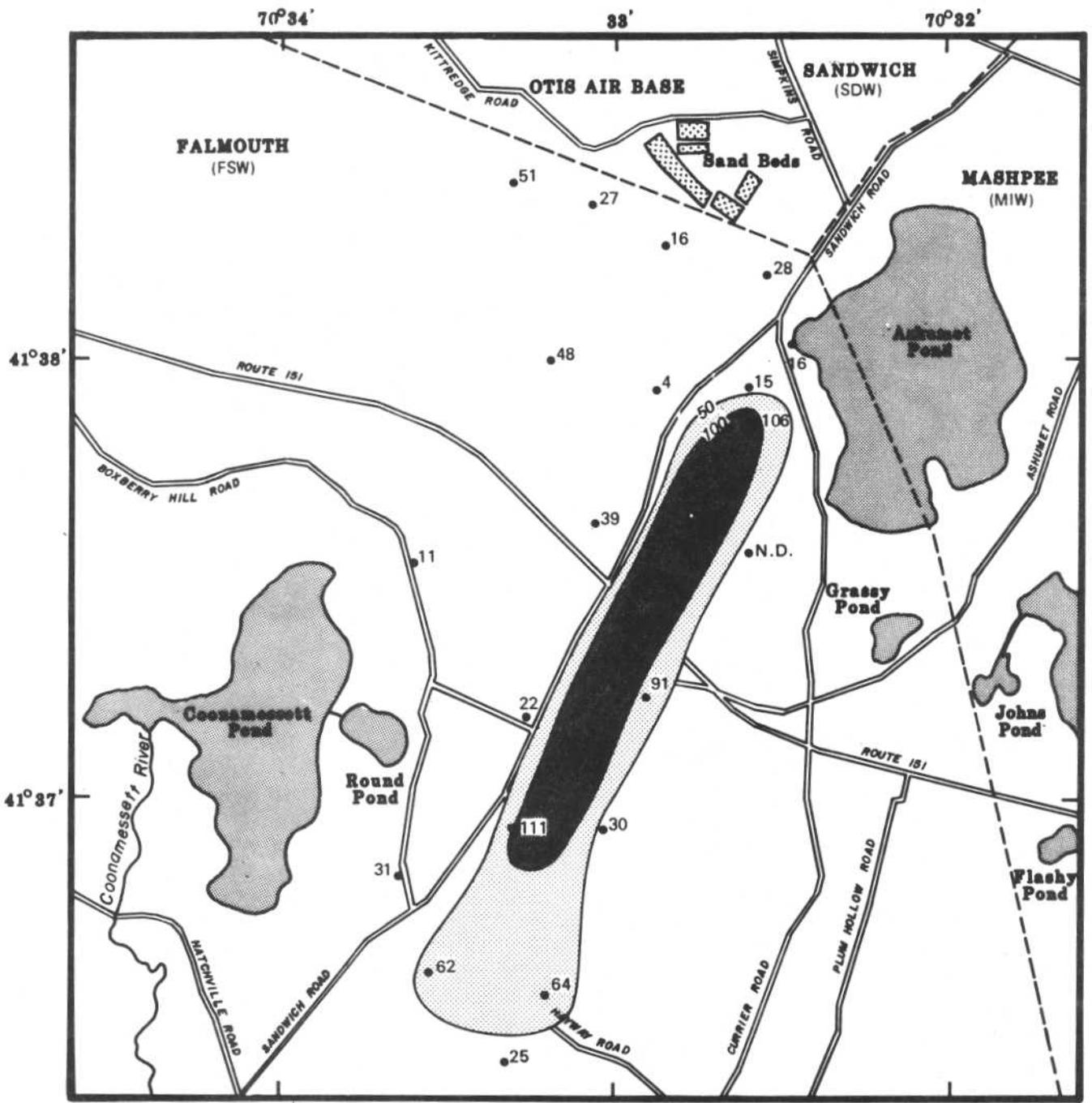
Trace Elements

Trace metals are present in low concentration in the effluent and in the aquifer. Locally, there are increased concentrations of iron and manganese, which appear to be leaching from the sediment of the aquifer. This conclusion was reached from three lines of evidence. First, manganese concentrations are low in the treated sewage (20 $\mu\text{g/L}$), but concentrations in certain wells in the plume are 1-3 mg/L. Second, there is no systematic distribution of iron and manganese in the plume that follows the concentration of other solutes in the plume, such as boron, detergents, and conductivity. Finally, field evidence of leaching of manganese and iron from cobbles along the beach of Ashumet Pond and in gravel pits near the infiltration beds suggest that the source of manganese is from leaching of the sediments by the anaerobic (reducing) waters of the plume.

Strontium, which previously had not been measured in water samples from the aquifer, forms a plume similar to sodium, chloride, and specific conductance (fig. 26). Strontium is a minor alkaline earth cation with concentrations that vary from approximately 10-100 $\mu\text{g/L}$ in the aquifer. The distribution of strontium suggests that it may behave conservatively, but this conclusion is based only on the distribution of strontium in the plume, and column experiments are underway to test this hypothesis. From theoretical considerations of strontium, which is a divalent cation of large size, one would predict that strontium would be retained by ion exchange. The fact that the strontium distribution resembles the distribution of detergents suggests that there may be relationship between these two constituents, which may be related to origin in the sewage effluent.

The trace element that has been a good indicator of the plume is boron, which is present in the effluent at 500 $\mu\text{g/L}$ and is present at less than 30 $\mu\text{g/L}$ in the native ground water. Boron is used as an additive in soaps and detergents, and based on several analyses of the effluent seems to be of relatively constant concentration over the short history of our sampling (from 1979 to 1983). Thus, boron is being used as a conservative tracer of the plume for solute-transport modeling (LeBlanc, 1984). In fact, boron may generally be a good tracer of sewage in ground water. However, column studies are underway to determine if boron behaves conservatively in the ground water. Because boron is a weak acid, it will be sorbed by weakly basic sites, such as aluminum-oxide coatings or perhaps on clay minerals. The aquifer solids contain less than 1 percent clay, and quartz and feldspar are the principal minerals of the sand. For these reasons, we hypothesize that boron moves conservatively.

Figure 27 shows the distribution of boron in 1978-1979 and again in the 1983 sampling. Notice that the concentrations of boron have increased near the toe of the plume from less than 20 $\mu\text{g/L}$ to 380 $\mu\text{g/L}$ (for example, wells FSW 166-67, FSW 282, FSW 290, FSW 294, and FSW 182-69). These data show that the plume has moved approximately 1000 feet over the past 3 years. Perhaps more interesting is the sharpness of the boron-concentration front, where concentrations increase from 10 to 400 $\mu\text{g/L}$ over a distance of 1000 feet. This



- EXPLANATION**
- 50 — LINE OF EQUAL CONCENTRATION OF STRONTIUM - Interval is 50 micrograms per liter
 - 4 FSW WELL - Number shows concentration of strontium in micrograms per liter
 - N.D. NO DATA

Figure 26.—Areal distribution of strontium in ground water, 1983.

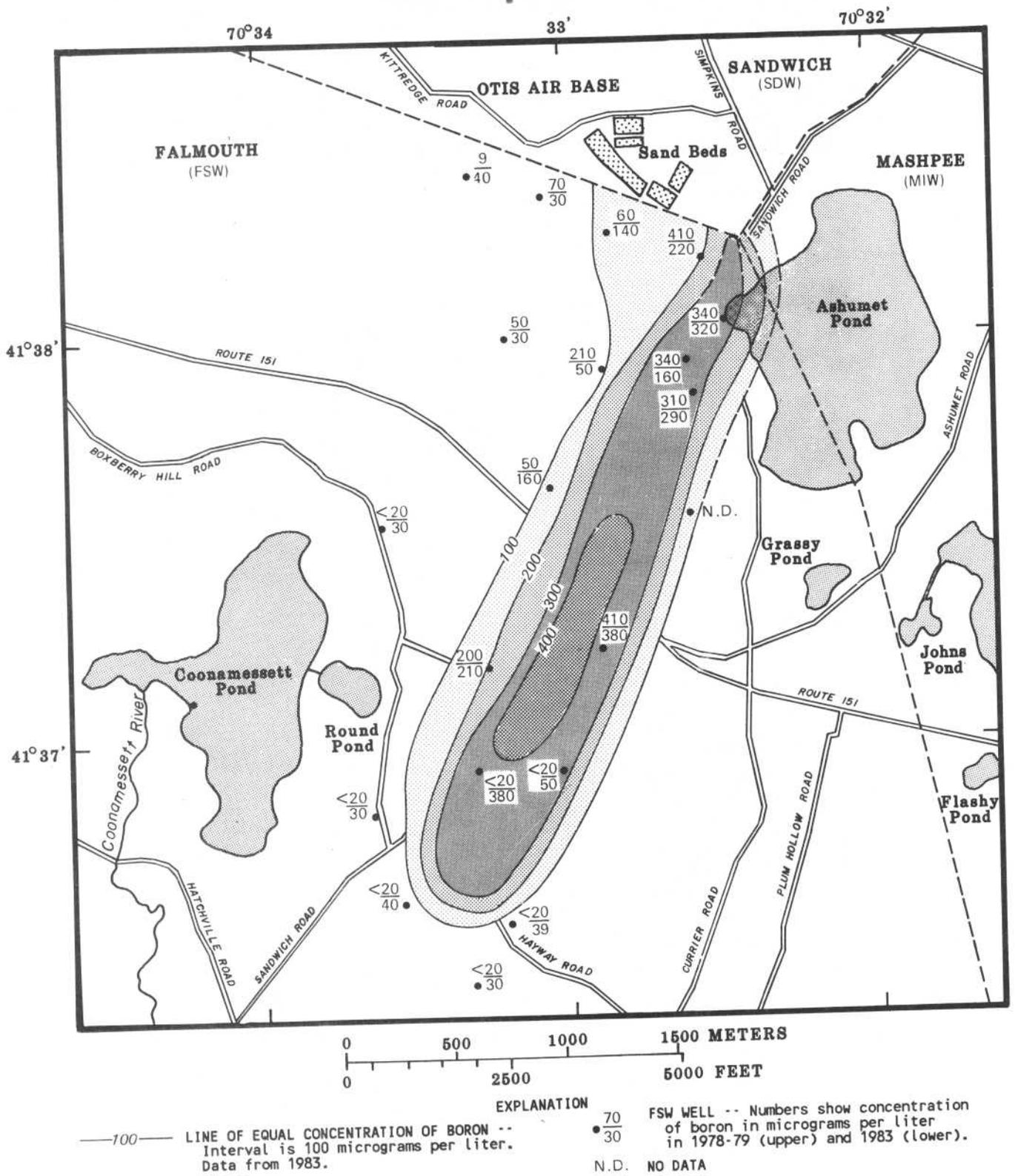


Figure 27.--Areal distribution of boron in ground water, 1978-79 and 1983.

suggests that longitudinal dispersion is small throughout the flow path of the boron plume.

Nutrients

The distribution of nutrients (N and P) are discussed in a separate section (Ceazan and others, 1984). Two major findings that should be emphasized are the nonconservative behavior of phosphate and ammonia. On the other hand, nitrate does not appear to be retained by the aquifer. This conclusion is based on the finding of nitrate at the furthest toe of the plume. Phosphate shows the greatest retardation and has moved less than 1000 feet from the infiltration beds. Ammonia has traveled further downgradient and the core of the ammonia plume is approximately 3000 to 4000 feet from the beds. Finally, nitrate is present as far as 10,000 feet from the infiltration beds. Because of microbiological transformations of nitrogen, such as nitrification from ammonia to nitrate, it is difficult to separate the mechanisms that are the cause of the retention of ammonia. Both sorption and nitrification may be responsible for the apparent retardation of ammonia in the aquifer.

DISTRIBUTION AND MOVEMENT OF ORGANIC SOLUTES

This section discusses organic solutes and is divided into three parts: dissolved organic carbon (DOC), detergents (MBAS), and volatiles. Semi-volatiles are discussed in a separate report by Barber and others (1984).

Dissolved Organic Carbon

Dissolved organic carbon is a good indicator of the amount of organic matter in the plume. It is a measure of all nonvolatile organic compounds in the ground water which includes the natural organic matter as well as the organic compounds from the treated sewage. The concentration of dissolved organic carbon varied from 0.7 mg/L, which was a background concentration for natural organic matter in the ground water, to 4.2 mg/L at the center of the plume at well FSW 282. Table 7 shows the concentration of dissolved organic carbon in all the wells sampled during the 1983 field season. The range in concentration of DOC found in the plume (from 0.7 to 4.2 mg/L), is within the range of dissolved organic carbon found naturally in ground waters. These low concentrations of organic carbon in the plume present a challenge for the analytical work of identification of specific organic compounds.

In spite of low concentrations of dissolved organic carbon in the ground water, the plume is easily recognizable. Figure 28 shows the distribution of dissolved organic carbon in the ground water. There are two areas in which DOC concentrations exceed 2 mg/L. The first is located within 1500 ft of the infiltration beds at well FSW 347-67. The DOC in this zone is as high as 4 mg/L, which is well below the DOC of the treated sewage (12 mg/L). The decrease in DOC is caused by microbial decomposition, which converts organic carbon to inorganic carbon. This conversion is suggested by increasing alkalinity in the waters of the plume. The second zone of increased DOC is located at wells FSW 262 and 282, which corresponds to the location of the detergent maximum (see figure 29). The concentration of DOC increases to 4 mg/L in this second zone. This increase in DOC is caused by the nondegradable detergents that are present

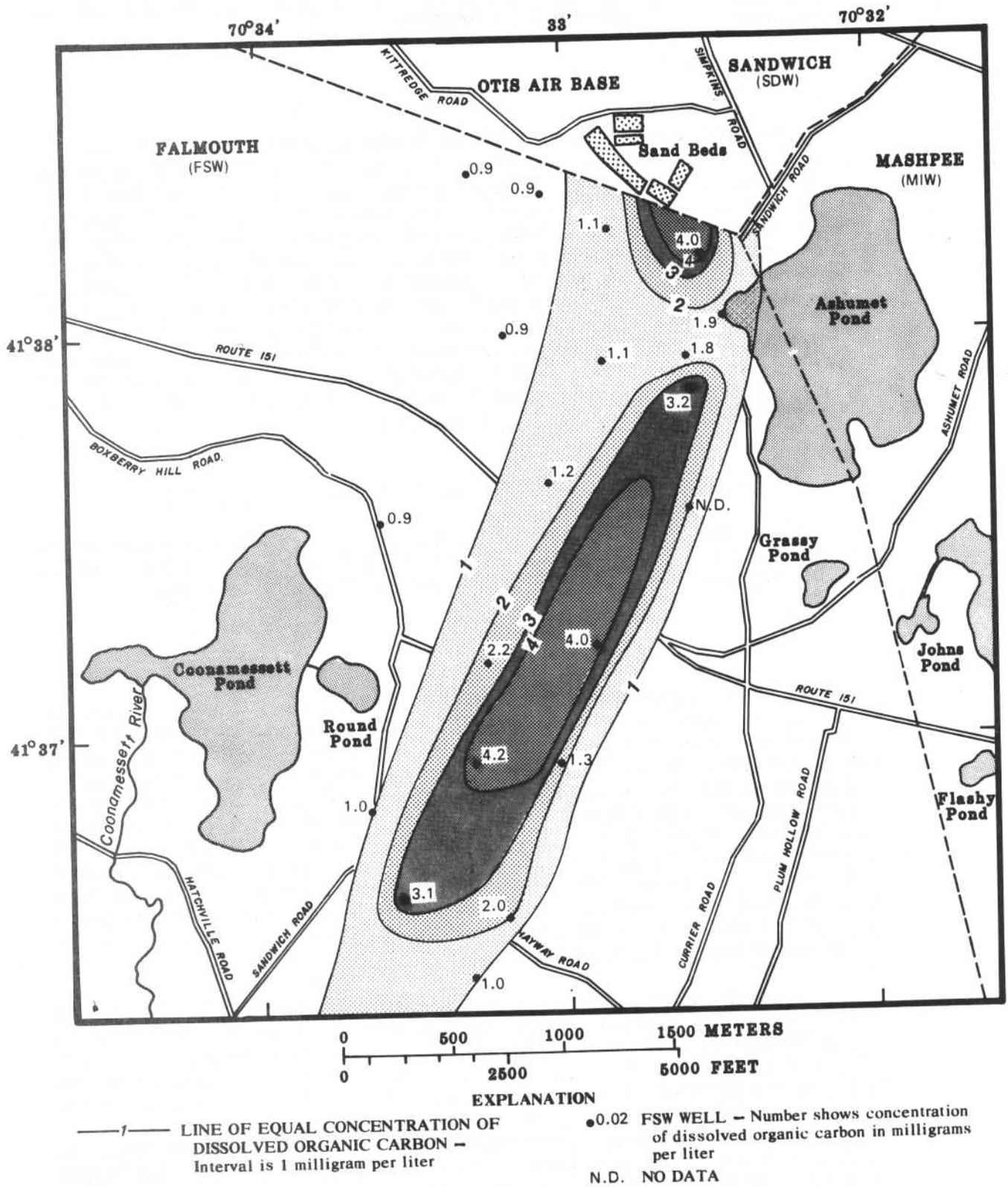


Figure 28.--Areal distribution of dissolved organic carbon in ground water, 1983.

in this part of the plume. Detergents account for approximately 50 percent of the DOC in this zone based on DOC fractionation analyses, which separate the detergent component of the DOC. DOC fractionation analysis is explained in the following section.

Detergents

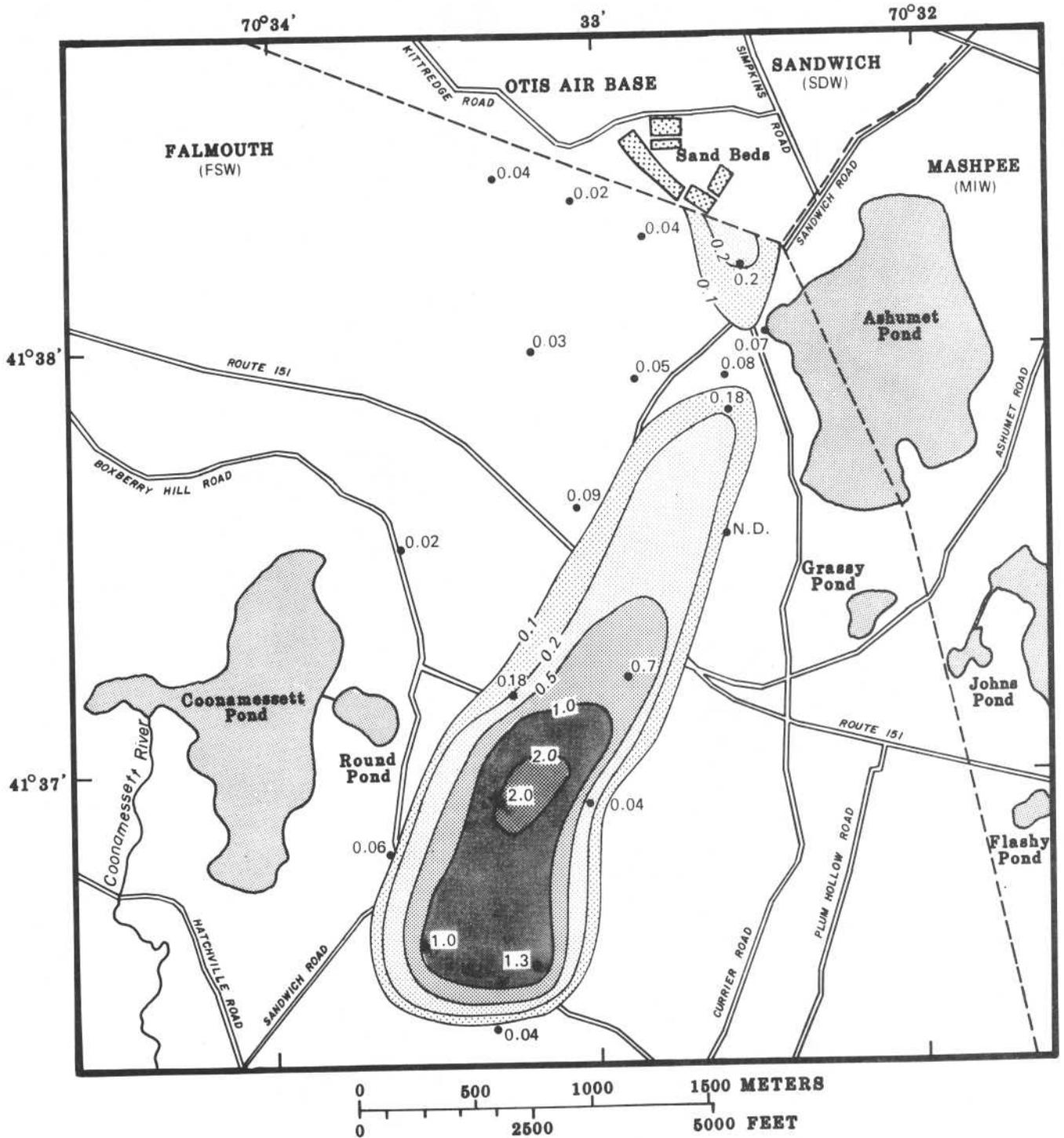
The use of nonbiodegradable detergents began in approximately 1946 and continued through 1964. After 1964 biodegradable detergents were used. Because of the switch to degradable detergents, there is an 18-year pulse of nondegradable detergents that forms a plume centered at well FSW 282 (LeBlanc, 1982) and is shown in figure 29. The purpose of the 1983 sampling was to measure the amount of detergents present, their contribution to DOC, and any movement since the last sampling in 1979.

The detergents were measured this past field season by two methods. First was the methylene blue active substances (MBAS) test, which was also used by LeBlanc in the 1978-1979 sampling period. The second method was DOC fractionation analysis to measure the amount of organic carbon contributed by the detergents. Using DOC fractionation, we found that the hydrophobic neutral fraction contained the detergents. For example, table 8 shows the difference in hydrophobic neutrals between the native ground water (FSW 242-77) and the core of the detergents (FSW 282-70). Well FSW 282-70 contained 2.8 mg/L as DOC in the hydrophobic neutral fraction and the native ground water contained no DOC in the hydrophobic neutral fraction. Combination of the DOC-fractionation and MBAS analyses shows that approximately 50 percent of the dissolved organic is contributed by the detergents. By difference, 2 mg/L of organic carbon is not accounted for. Identification of this organic carbon is the subject of further research.

Volatile Organic Compounds

Approximately 32 samples were analyzed for volatile organic compounds (table 9). The purge and trap technique, which is reported in this section, identified from 1-10 compounds in the samples with a detection limit of 0.1 µg/L. Table 9 shows the compounds identified and their concentration in the ground water. The compounds that were detected frequently include: trichloroethene (trichloroethylene), tetrachloroethene (tetrachloroethylene), and tetra- and trichloroethanes. Nine of the wells had concentrations exceeding 10 µg/L (fig. 30). The core of the volatiles was found approximately 3000 feet downgradient from the sand beds at well cluster FSW 254. This core of volatiles is well upgradient of the toe of the plume delineated by boron and detergents. This difference may be caused by several factors. First, the volatiles may be coming from a different source than the boron and detergents. Another source might be a spill or septic tank, where volatile organic compounds are commonly used as degreasing solvents. However, the distribution of the volatile organics in the ground water suggests an origin that is similar in location to the other compounds in the plume.

A second factor that may explain the difference in the distribution of volatiles is sorption of the volatile compounds on the sediments of the aquifer. Given the center of the volatile plume near well FSW 254, the retardation of

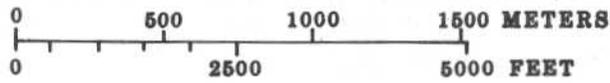
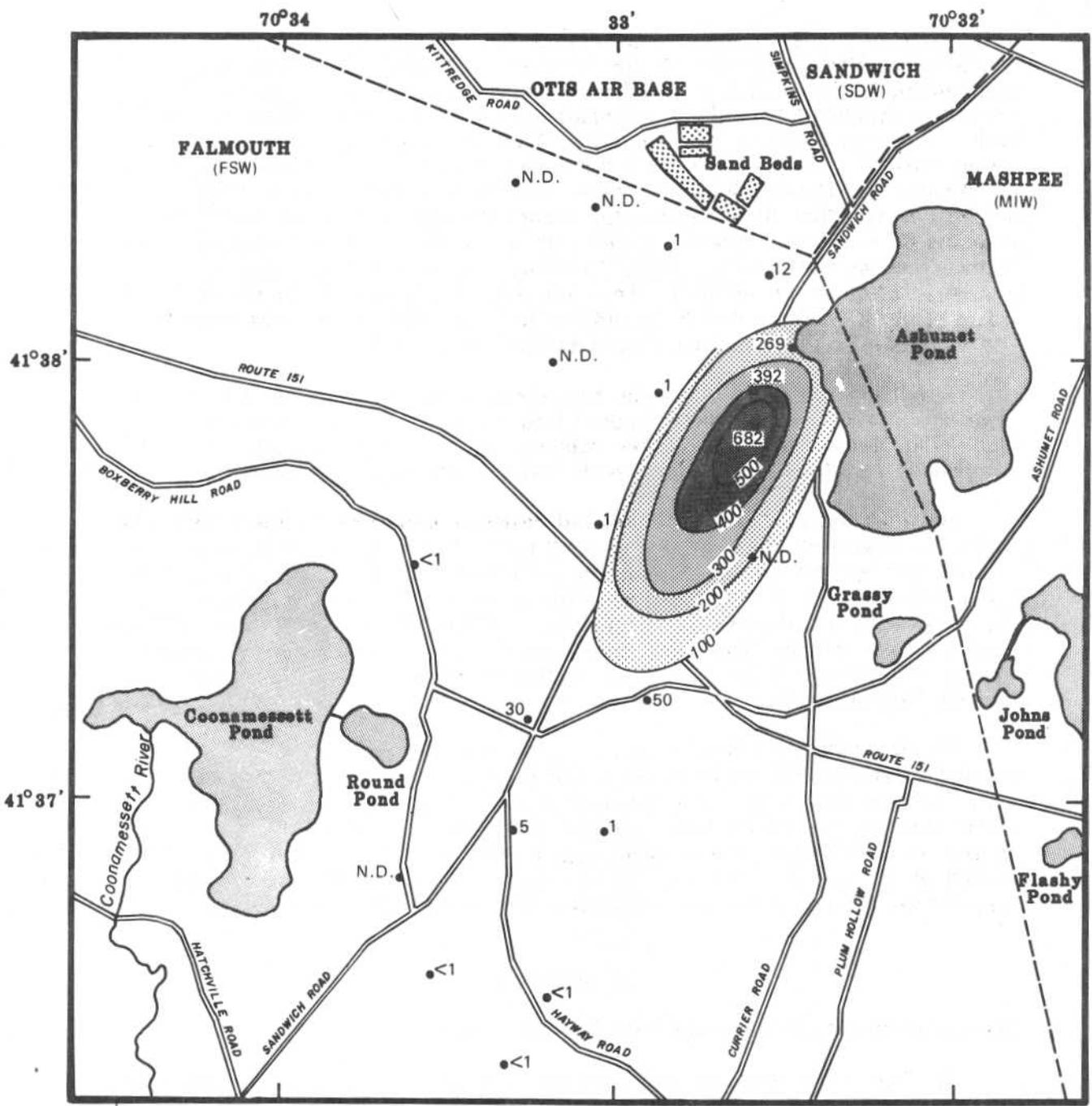


— 0.1 — LINE OF EQUAL CONCENTRATION OF MBAS DETERGENTS — Interval in milligrams per liter is variable

● 0.02 FSW WELL — Number shows concentration of MBAS in milligrams per liter

N.D. NO DATA

Figure 29.—Areal distribution of MBAS detergents in ground water, 1983.



EXPLANATION

—100— LINE OF EQUAL CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS — Interval is 100 micrograms per liter

•1 FSW WELL — Number shows concentration of volatiles in micrograms per liter

N.D. NO DATA

Figure 30.--Areal distribution of volatile organic compounds in ground water, 1983.

volatiles would be a factor of 3 to 4 times that of the boron and detergents in the plume. Previous studies on the removal of tetrachloroethene, and similar compounds, by bank filtration (Schwartzbach and others, 1983), showed that tetrachloroethene and similar compounds are mobile in ground water and do not sorb onto the aquifer sediments. This is expected from theoretical considerations. Water solubility is a simple measure of sorptive potential of an organic compound. Because these volatile compounds have large water solubilities (greater than 300 mg/L), theory predicts that they would not be retained on a sand and gravel aquifer with less than 0.5 percent organic carbon (Schwartzbach and others, 1983). Therefore, this second hypothesis of sorption and retardation seems unlikely. The fact that detergents, which are of similar water solubility and, by inference, similar sorptive capacity, are not retained by the aquifer, is further evidence that retention is not occurring.

A third possibility, and the one that seems most likely, is that the volatiles have only more recently been disposed into the sewage. Given the distance of 3000-4000 feet and a ground-water velocity of 1 ft/d, we estimate that these compounds may have entered the ground water in the past 10-15 years.

Because there are no wells located between wells FSW 254 and FSW 262, which are separated by a distance of 3000 feet, the center of the volatile plume may be further downgradient than the data now indicate. The area between these two wells is an important zone for more sampling in order to determine the exact location of the volatile plume. Also, additional wells east and up-gradient from the sand beds may give more exact information on the source of the volatile contaminants. Therefore, further sampling for volatiles should focus on these two locations.

Finally, we found that sampling by peristaltic pump loses approximately one half of the volatile organic compounds present in the sample when compared with a submersible pump. This means that concentrations in the volatile organic plume may be 1.5 to 2.0 times greater than shown in figure 30, because the central well, FSW 254, was sampled with a peristaltic pump. This difference is caused by degassing of the sample. In future work we plan to investigate a simple down-hole sampler, such as a bailer versus the submersible pump.

CONCLUSIONS

The major conclusions from the 1983 field study are:

1) The concentrations of inorganic solutes in the ground water are consistent with the previous study of LeBlanc (1982) with respect to the location of the plume based on major cations and anions and boron. A new tracer, strontium, was found in the plume.

2) Metals, such as manganese and iron, are being mobilized from the aquifer solids near the sand-infiltration beds by the anaerobic (reducing) conditions of the ground water.

3) The plume has moved approximately 1000 feet over the past 3 years in the direction of ground-water flow, from northeast to southwest.

4) The organic plume was investigated by DOC, DOC fractionation, and volatile organic analysis. Detergents accounted for 50-60 percent of the dissolved organic carbon in the plume at its most southern extent. Tetrachloroethene and other volatile organic solutes were discovered in well cluster FSW 254.

5) The type of pump used for sampling affects the concentration of volatile organic compounds in the sample. Because of degassing of the sample, the submersible pump gives a greater concentration of volatiles by a factor of two than the peristaltic pump.

6) Finally, the organic compounds in the plume are affected more by microbial processes than by sorption, which seems to play a small role, if any, in the movement of organic solutes in the ground water.

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Table 6. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	pH (lab)	pH (field)	Sp. Cond	Sp. Cond	Temp (field) (C°)	Br (mg/L)	Cl (mg/L)	F (mg/L)	NH ₄ ⁺ + organic N (mg/L) ¹	NO ₃ ⁻ (mg/L) ¹
			(lab) (µmhos/cm)	(field) (µmhos/cm)						
FSW										
166-67	6.2	5.8	96	100	9.5	0.05	16.0	0.03	0.4	0.92
167-55	6.1	6.0	49	48	9.0	0.03	7.4	0.01	0.3	<0.06
173-69	5.7	5.9	69	122	10.0	0.05	20.0	0.04	1.1	2.2
182-69	5.9	5.7	85	80	9.0	0.05	12.0	0.03	0.5	1.6
194-57	6.0	5.6	151	145	11.5	0.05	14.0	0.07	1.9	1.7
214-60	5.8	5.6	96	83	13.5	0.05	11.0	0.03	0.9	2.3
230-48	5.6	5.4	123	115	10.5	0.05	6.3	0.11	1.0	3.4
231-57	6.0	--	160	145	12.0	--	--	--	1.5	6.4
232-58	6.3	5.9	160	153	12.0	0.05	4.8	0.2	0.8	4.6
234-99	5.6	6.4	126	122	12.5	0.05	13.0	0.04	0.5	2.2
235-94	5.5	--	87	81	11.0	0.03	7.9	0.03	0.4	1.3
236-106	5.4	4.9	140	126	10.0	0.05	14.0	0.05	0.7	1.1
237-88	6.6	6.4	142	128	14.0	0.05	11.0	0.10	6.0	2.6
238-106	6.1	5.2	110	95	10.0	0.05	10.0	0.04	0.8	2.0
239-64	6.8	6.6	220	190	13.0	0.08	11.0	0.20	10.0	<0.06
240-95	5.9	5.8	55	57	10.0	--	9.5	--	0.20	0.07

¹ Milligrams per liter as nitrogen.

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	pH (lab)	Sp. Cond		Temp (field) (C ^o)	Br (mg/L)	Cl (mg/L)	F (mg/L)	NH ₄ ⁺ + organic N (mg/L) ¹	NO ₃ ⁻ (mg/L) ¹	
		pH (field)	Sp. Cond (lab) (µmhos/cm)							Sp. Cond (field) (µmhos/cm)
FSW 241-98	5.9	5.8	68	62	10.0	--	6.9	--	0.20	0.06
242-77	5.6	5.4	57	51	10.0	0.04	7.9	0.06	0.5	0.21
243-45	5.7	6.2	57	38	9.0	0.03	7.4	0.06	0.5	0.29
244-90	6.9	6.6	235	230	11.0	0.30	13.0	0.20	15.0	<0.06
245-25	4.7	4.7	224	200	10.0	0.05	28.0	0.06	0.7	1.2
246-35	6.0	5.6	158	152	12.0	0.05	14.0	0.06	0.6	5.0
247-70	5.5	5.4	119	120	--	0.06	20.0	0.13	1.00	1.4
254-216	6.5	6.9	80	59	10.0	0.02	6.8	0.08	0.2	<0.06
254-168	6.4	6.4	121	115	10.0	0.02	11.0	0.10	0.2	<0.06
254-140	6.7	6.3	163	175	10.5	0.11	15.0	0.09	0.2	0.31
254-107	6.7	6.2	250	235	10.5	0.12	16.0	0.15	1.0	1.0
254-72	6.9	6.7	255	225	11.0	0.46	13.0	0.21	12.0	0.08
254-54	6.7	6.3	241	220	10.5	0.04	7.5	0.11	10.0	0.57
254-26	5.8	4.9	79	70	10.0	0.04	11.0	0.04	0.4	0.80
262-159	7.1	6.7	152	125	10.0	0.04	4.0	0.12	0.3	0.32
262-85	6.5	5.9	262	255	11.0	0.14	22.0	0.13	0.2	0.32
262-69	5.9	5.7	213	200	11.0	0.05	16.0	0.10	4.0	2.9

¹Milligrams per liter as nitrogen.

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	pH (lab)	pH (field)	Sp. Cond	Sp. Cond	Temp (field) (C°)	Br (mg/L)	Cl (mg/L)	F (mg/L)	NH ₄ ⁺ + organic N (mg/L) ¹	NO ₃ ⁻ (mg/L) ¹
			(lab) (µmhos/cm)	(field) (µmhos/cm)						
FSW 262-41	5.3	5.0	90	90	10.0	0.05	10.0	0.04	0.2	1.4
267-155	6.6	6.7	117	122	9.0	0.03	8.8	0.10	0.2	0.19
267-136	6.9	6.0	97	95	9.0	0.05	11.0	0.05	0.3	1.8
267-111	6.3	5.9	125	120	9.0	0.05	11.0	0.06	0.4	3.7
267-88	5.8	5.5	200	195	9.0	0.05	20.0	0.07	11.0	3.5
271-165	7.1	6.9	117	125	9.0	0.03	10.0	0.36	0.20	<0.06
271-141	6.8	6.9	139	132	9.0	0.04	14.0	0.08	0.50	0.56
271-85	5.8	5.0	164	150	10.0	0.07	21.0	0.06	0.30	0.98
271-41	5.4	5.2	55	55	10.0	0.03	9.5	0.01	0.30	0.07
279-86	5.6	--	79	76	11.0	0.06	10.0	0.04	0.20	0.42
279-61	5.6	--	84	73	11.0	0.04	11.0	0.03	0.20	0.25
282-123	6.3	5.9	155	143	9.0	0.05	16.0	0.08	0.30	0.28
282-94	6.6	5.7	219	208	9.0	0.08	20.0	0.09	0.60	0.78
282-70	6.3	5.4	223	215	10.0	0.08	24.0	0.09	0.60	1.36
282-49	6.3	6.0	97	100	9.0	0.05	22.0	0.04	0.40	<0.06
288-97	6.8	6.3	145	142	9.0	0.05	10.0	0.08	3.70	3.8

¹ Milligrams per liter as nitrogen.

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	pH (lab)	pH (field)	Sp. Cond	Sp. Cond	Temp (field) (C°)	Br (mg/L)	Cl (mg/L)	F (mg/L)	NH ₄ ⁺ + organic N (mg/L) ¹	NO ₃ ⁻ (mg/L) ¹
			(lab) (µmhos/cm)	(field) (µmhos/cm)						
FSW										
290-91	6.8	5.9	91	90	10.0	0.05	8.5	0.04	0.50	2.1
294-89	6.4	6.0	154	139	9.5	0.05	16.0	0.05	0.40	1.4
299-20	6.2	5.2	83	76	10.0	0.18	8.4	0.28	0.30	3.1
300-30	7.1	6.5	422	410	11.5	0.01	19.0	0.04	8.50	14.0
300-10	5.6	5.2	141	138	13.0	0.04	33.0	0.06	0.20	0.26
347-67	6.7	6.3	322	302	10.0	0.06	30.0	0.26	3.8	<0.06
SDW										
305-32	5.7	6.2	126	122	9.5	0.13	9.0	0.23	0.4	3.8
313-60	6.1	--	105	100	10.0	0.02	8.4	0.04	0.2	0.90

¹Milligrams per liter as nitrogen.

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	NO ₂ ⁻ (mg/L) ²	NH ₄ ⁺ (mg/L) ²	Total-N (mg/L) ²	Diss O ₂ ¹ (mg/L)	Diss P ³ (mg/L) ³	SO ₄ (mg/L)	Alkalinity (meq/L)	Al (µg/L)	B (µg/L)	Ba (µg/L)
FSW										
166-67	<0.06	<0.10	1.09	0.8	0.01	5.6	0.16	19.0	50.0	15.0
167-65	<0.06	<0.10	<0.25	10.8	0.01	3.6	0.19	<10.0	20.0	11.0
173-69	<0.06	<0.10	2.04	--	0.01	4.2	0.22	20.0	50.0	22.0
182-69	<0.06	<0.10	1.54	--	0.02	3.8	0.12	10.0	30.0	10.0
194-57	<0.06	1.6	3.42	4.4	0.02	16.0	0.44	19.0	140.0	44.0
214-60	<0.06	0.11	2.40	--	0.01	8.2	0.15	11.0	90.0	20.0
230-48	<0.06	<0.10	4.30	--	0.29	21.0	0.15	38.0	50.0	10.0
231-57	<0.06	<0.10	--	--	0.50	--	0.26	31.0	60.0	10.0
232-58	<0.06	<0.10	4.79	--	0.74	24.0	0.25	33.0	60.0	9.0
234-99	<0.06	<0.10	2.10	--	0.02	14.0	0.14	17.0	40.0	18.0
235-94	<0.06	<0.10	1.12	--	0.01	16.0	0.08	13.0	30.0	15.0
236-106	<0.06	<0.10	1.48	--	0.01	24.0	0.10	16.0	140.0	18.0
237-88	<0.06	3.8	8.20	--	0.05	6.5	0.51	12.0	50.0	13.0
238-106	<0.06	<0.10	1.90	--	0.03	17.1	0.15	18.0	30.0	12.0
239-64	<0.06	7.0	12.0	0.0	0.11	15.0	1.35	13.0	320.0	16.0
240-95	--	<10.0	--	--	0.01	6.0	8.00	<10.0	<10.0	15.0

¹Dissolved oxygen data collected in 1979 (LeBlanc, 1982).

²Milligrams per liter as nitrogen.

³Milligrams per liter as phosphorus.

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	NO ₂ ⁻ (mg/L) ²	NH ₄ ⁺ (mg/L) ²	Total-N (mg/L) ²	Diss O ₂ ¹ (mg/L)	Diss P ₃ (mg/L)	SO ₄ (mg/L)	Alkalinity (meq/L)	Al (µg/L)	B (µg/L)	Ba (µg/L)
FSW										
241-98	--	<0.10	--	--	0.02	10.0	11.0	<10.0	20.0	--
242-77	<0.06	<0.10	0.40	--	0.04	6.0	0.09	11.0	30.0	11.0
243-45	<0.06	<0.10	0.40	--	0.02	8.1	0.09	19.0	20.0	9.7
244-90	<0.06	10.7	15.0	--	0.11	16.0	1.29	16.0	160.0	19.0
245-25	<0.06	<0.10	1.45	--	0.02	9.4	0.06	426.0	40.0	117.0
246-35	<0.06	<0.10	6.5	--	0.36	16.0	0.22	30.0	130.0	40.0
247-70	<0.06	0.60	--	2.6	0.02	5.8	0.26	33.0	40.0	49.0
254-216	<0.06	<0.10	0.30	0.1	0.09	13.0	0.34	20.0	20.0	10.0
254-168	<0.06	<0.10	<0.25	0.0	0.05	17.0	0.45	21.0	20.0	12.0
254-140	<0.06	<0.10	0.50	--	0.08	14.0	0.94	51.0	30.0	11.0
254-107	<0.06	<0.10	2.09	0.0	0.04	23.0	1.32	30.0	290.0	13.0
254-72	<0.06	9.10	12.0	0.0	0.07	11.0	1.57	31.0	250.0	17.0
254-54	<0.06	7.6	10.0	0.0	0.03	16.0	1.10	15.0	240.0	23.0
254-26	<0.06	0.15	1.31	8.1	0.01	7.4	0.11	54.0	40.0	33.0
262-159	<0.06	<0.10	3.80	--	0.12	22.0	0.82	--	30.0	14.0

¹Dissolved oxygen data collected in 1979 (LeBlanc, 1982).

²Milligrams per liter as nitrogen.

³Milligrams per liter as phosphorus.

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	NO ₂ ⁻ (mg/L) ²	NH ₄ ⁺ (mg/L) ²	Total-N (mg/L) ²	Diss O ₂ ¹ (mg/L)	Diss P (mg/L) ³	SO ₄ (mg/L)	Alkalinity (meq/L)	Al (µg/L)	B (µg/L)	Ba (µg/L)
FSW										
262-85	<0.06	<0.10	0.50	0.0	0.04	23.0	1.26	10.0	380.0	16.5
262-69	<0.06	2.1	5.81	0.0	0.02	23.0	0.57	10.0	360.0	22.0
262-41	<0.06	<0.10	--	8.0	0.01	9.2	0.17	72.0	30.0	64.0
267-155	<0.06	<0.10	--	--	0.38	15.0	0.58	66.0	30.0	13.0
267-136	<0.06	<0.10	1.81	8.2	0.06	7.5	0.30	18.0	20.0	10.9
267-111	<0.06	<0.10	--	0.0	0.05	12.0	0.31	<10.0	40.0	12.0
267-88	<0.06	7.6	--	0.0	0.05	25.0	0.22	8.6	160.0	24.3
271-165	<0.06	<0.10	--	--	0.11	12.0	0.58	13.0	20.0	12.7
271-141	<0.06	<0.10	--	--	0.01	11.0	0.53	23.0	20.0	12.2
271-85	<0.06	<0.10	--	--	0.08	14.0	0.36	14.0	150.0	13.7
271-41	<0.06	<0.10	--	--	0.01	5.8	0.08	39.0	20.0	17.2
279-86	<0.06	<0.10	--	4.3	0.01	12.0	0.12	13.0	50.0	16.6
279-61	<0.06	<0.10	--	7.3	0.01	12.0	0.14	13.0	40.0	16.5
282-123	<0.06	<0.10	--	0.8	0.01	12.0	0.58	101.0	20.0	10.7
282-94	<0.06	<0.10	--	0.1	0.03	27.0	0.72	112.0	270.0	15.2
282-70	<0.06	<0.10	--	0.2	0.03	29.0	0.33	25.0	380.0	21.4
282-49	<0.06	<0.10	--	11.4	0.01	3.9	0.09	19.0	30.0	11.7

¹Dissolved oxygen data collected in 1979 (LeBlanc, 1982).

²Milligrams per liter as nitrogen.

³Milligrams per liter as phosphorus.

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	NO ₂ ⁻ (mg/L) ²	NH ₄ ⁺ (mg/L) ²	Total-N (mg/L) ²	Diss O ₂ ¹ (mg/L)	Diss P ₃ ³ (mg/L)	SO ₄ (mg/L)	Alkalinity (meq/L)	Al (µg/L)	B (µg/L)	Ba (µg/L)
FSW										
288-97	<0.06	2.3	--	0.0	0.05	10.0	0.47	<10.0	210.0	--
290-91	<0.06	<0.10	--	0.3	0.05	6.6	--	<10.0	30.0	12.0
294-89	<0.06	<0.10	--	0.4	0.06	9.9	0.54	669.0	40.0	17.0
299-20	<0.06	<0.10	--	--	0.01	7.6	0.09	28.0	30.0	39.0
300-30	<0.06	5.3	22.0	0.0	1.20	31.0	1.77	<10.0	530.0	12.0
300-10	<0.06	<0.10	--	5.9	0.03	5.1	0.07	67.0	40.0	52.0
347-67	<0.06	2.1	4.60	0.0	1.70	26.0	1.52	18.0	220.0	20.0
SDW										
305-32	<0.06	<0.10	--	--	0.23	19.0	0.14	220.0	70.0	11.0
313-60	<0.06	<0.10	--	10.0	0.02	22.0	0.14	22.0	30.0	20.0

¹Dissolved oxygen data collected in 1979 (LeBlanc, 1982).

²Milligrams per liter as nitrogen.

³Milligrams per liter as phosphorus.

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	Be (µg/L)	Ca (mg/L)	Cd (µg/L)	Co (µg/L)	Cu (µg/L)	Fe (µg/L)	K (mg/L)	Li (µg/L)	Mg (mg/L)	Mn (µg/L)	Mo (µg/L)
FSW											
166-67	<0.5	2.4	<1.0	<3.0	<10.0	1393.0	0.7	<4.0	2.4	35.0	<10.0
167-65	<0.5	1.0	<1.0	<3.0	<10.0	1295.0	0.6	4.0	1.0	35.0	<10.0
173-69	<0.5	4.2	<1.0	<3.0	<10.0	378.0	0.9	<4.0	3.4	13.0	<10.0
182-69	<0.5	2.6	<1.0	<3.0	<10.0	423.0	0.6	5.0	2.0	15.0	<10.0
194-57	<0.5	2.9	<1.0	<3.0	<10.0	25.0	2.0	4.0	2.0	457.0	<10.0
214-60	<0.5	1.9	<1.0	<3.0	13.0	39.0	1.0	<4.0	1.9	14.0	<10.0
230-48	<0.5	8.7	<1.0	29.0	<10.0	14.0	3.1	5.0	2.7	435.0	<10.0
231-57	<0.5	13.0	2.8	6.6	<10.0	325.0	3.5	<4.0	3.2	411.0	<10.0
232-58	<0.5	12.0	<1.0	5.0	<10.0	116.0	4.5	<4.0	3.5	248.0	<10.0
234-99	<0.5	4.9	<1.0	<3.0	<10.0	15.0	1.8	<4.0	3.4	10.0	<10.0
235-94	<0.5	2.7	<1.0	<3.0	<10.0	10.0	0.7	<4.0	2.5	3.0	<10.0
236-106	<0.5	3.1	<1.0	<3.0	<10.0	29.0	0.8	<4.0	2.3	141.0	<10.0
237-88	<0.5	0.4	<1.0	<3.0	<10.0	21.0	2.6	<4.0	0.3	12.0	<10.0
238-106	<0.5	5.1	<1.0	<3.0	<10.0	37.0	1.0	<4.0	4.2	5.0	<10.0
239-64	<0.5	1.5	<1.0	<3.0	<10.0	24.0	4.5	<4.0	1.3	723.0	12.0
240-95	<0.5	1.4	<1.0	<3.0	<10.0	9.0		5.0	1.5	2.0	<10.0

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	Be (µg/L)	Ca (mg/L)	Cd (µg/L)	Co (µg/L)	Cu (µg/L)	Fe (µg/L)	K (mg/L)	Li (µg/L)	Mg (mg/L)	Mn (µg/L)	Mo (µg/L)
FSW											
241-98	--	--	--	--	--	--	--	--	--	--	--
242-77	<0.5	1.0	<1.0	<3.0	<10.0	4.0	0.4	7.0	1.2	2.8	<10.0
243-45	<0.5	1.4	<1.0	<3.0	<10.0	15.0	0.7	8.0	2.0	5.0	<10.0
244-90	<0.5	1.6	<1.0	<3.0	<10.0	38.0	5.4	9.0	1.2	50.0	<10.0
245-25	<0.5	4.5	<1.0	<3.0	<10.0	17.0	2.0	8.0	1.6	374.0	<10.0
246-35	<0.5	5.5	<1.0	<3.0	85.0	12.0	3.1	7.0	2.9	387.0	<10.0
247-70	<0.5	3.4	<1.0	<3.0	<10.0	1.4	1.3	6.0	2.3	840.7	<10.0
254-216	<0.5	3.4	<1.0	<3.0	<10.0	3320.0	1.1	8.0	1.9	63.0	<10.0
254-168	<0.5	6.7	<1.0	<3.0	<10.0	2934.0	1.0	10.0	3.2	31.0	<10.0
254-140	<0.5	9.6	<1.0	<3.0	<10.0	7657.0	1.8	9.0	3.9	335.0	<10.0
254-107	<0.5	12.0	<1.0	<3.0	<10.0	216.0	1.9	7.0	6.4	18.0	<10.0
254-72	<0.5	1.8	<1.0	<3.0	<10.0	870.0	5.4	6.0	1.6	372.0	<10.0
254-54	<0.5	1.4	<1.0	<3.0	<10.0	57.0	8.1	9.0	1.8	53.0	<10.0
254-26	<0.5	1.6	<1.0	<3.0	<10.0	29.0	1.0	9.0	1.4	28.0	<10.0
262-159	<0.5	11.0	<1.0	<3.0	<10.0	1656.0	2.6	12.0	3.9	158.0	<10.0
262-85	0.9	10.2	<1.0	<3.0	<10.0	55.0	1.2	7.6	5.3	10.0	<10.0
262-69	<0.5	1.3	<1.0	<3.0	<10.0	34.0	2.4	5.1	1.3	20.0	<10.0

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	Be (µg/L)	Ca (mg/L)	Cd (µg/L)	Co (µg/L)	Cu (µg/L)	Fe (µg/L)	K (mg/L)	Li (µg/L)	Mg (mg/L)	Mn (µg/L)	Mo (µg/L)
FSW											
262-41	<0.5	1.5	<1.0	<3.0	<10.0	9.0	0.7	<4.0	4.0	386.0	<10.0
267-155	0.6	8.0	<1.0	<3.0	<10.0	4.0	1.5	6.6	3.3	308.0	<10.0
267-136	<0.5	5.3	<1.0	<3.0	<10.0	37.0	0.8	8.0	2.2	1.9	<10.0
267-111	<0.5	7.4	<1.0	<3.0	<10.0	22.0	0.8	4.8	3.8	4.9	<10.0
267-88	<0.5	3.3	<1.0	<3.0	<10.0	6.5	3.0	5.8	2.2	17.0	<10.0
271-165	<0.5	7.9	<1.0	<3.0	<10.0	4.1	1.5	7.2	3.0	219.9	<10.0
271-141	<0.5	8.1	<1.0	<3.0	<10.0	147.2	1.2	8.3	3.9	4.0	<10.0
271-85	<0.5	6.6	<1.0	<3.0	<10.0	6.0	1.0	4.0	4.8	3.1	<10.0
271-41	<0.5	1.3	<1.0	<3.0	<10.0	8.0	0.7	7.0	1.2	15.9	<10.0
279-86	<0.5	1.9	<1.0	<3.0	<10.0	6.1	0.5	6.9	1.8	6.7	<10.0
279-61	<0.5	2.0	<1.0	<3.0	<10.0	53.4	0.7	7.4	2.1	5.2	<10.0
282-123	<0.5	9.4	<1.0	4.4	<10.0	146.4	1.2	8.3	4.2	5.7	<10.0
282-94	<0.5	13.2	<1.0	4.9	<10.0	127.8	1.2	5.6	6.4	22.2	<10.0
282-70	0.6	8.5	<1.0	28.8	<10.0	14.3	1.2	<4.0	6.6	27.1	<10.0
282-49	<0.5	0.9	<1.0	<3.0	<10.0	6.0	0.6	5.3	1.1	2.9	<10.0
288-97	<0.5	2.1	<1.0	<3.0	<10.0	7.0	2.2	6.0	1.3	5.0	<10.0

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	Be (µg/L)	Ca (mg/L)	Cd (µg/L)	Co (µg/L)	Cu (µg/L)	Fe (µg/L)	K (mg/L)	Li (µg/L)	Mg (mg/L)	Mn (µg/L)	Mo (µg/L)
FSW											
290-91	<0.5	4.1	<1.0	<3.0	<10.0	< 3.0	0.7	5.0	2.0	< 1.0	<10.0
294-89	<0.5	7.8	<1.0	<3.0	<10.0	910.	1.3	9.0	4.2	110	<10.0
299-20	<0.5	5.4	<1.0	<3.0	<10.0	6.0	0.7	8.0	1.3	9.0	<10.0
300-30	<0.5	5.8	<1.0	<3.0	<10.0	< 3.0	5.5	8.0	4.3	8.0	30.0
300-10	<0.5	3.0	<1.0	<3.0	<10.0	< 3.0	1.4	8.0	2.1	32.0	<10.0
347-67	<0.5	17.0	<1.0	7.0	<10.0	101.0	3.4	6.0	9.4	2662.0	<10.0
SDW											
305-32	<0.5	8.4	<1.0	7.0	50.0	29.	2.8	10.0	3.0	100.	<10.0
313-60	<0.5	3.5	<1.0	<3.0	<10.0	12.	1.2	8.0	4.2	9.	<10.0

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	Na (mg/L)	Pb (µg/L)	Si (mg/L)	Sr (µg/l)	V (µg/L)	Zn (µg/L)
FSW						
166-67	9.7	<10.0	8.1	30.0	<6.0	216.0
167-55	5.5	<10.0	5.6	14.0	<6.0	130.0
173-69	11.0	<10.0	9.5	41.0	<6.0	210.0
182-69	8.5	<10.0	9.1	25.0	<6.0	158.0
194-57	17.0	<10.0	7.2	28.0	<6.0	4.0
214-60	11.0	<10.0	7.5	23.0	<6.0	30.0
230-48	4.7	<10.0	12.0	120.0	<6.0	639.0
231-57	6.4	<10.0	13.0	115.0	<6.0	113.0
232-58	6.6	<10.0	13.0	126.0	<6.0	65.0
234-99	10.0	<10.0	12.0	51.0	<6.0	10.0
235-94	7.2	<10.0	9.0	27.0	<6.0	9.0
236-106	17.0	<10.0	9.4	16.0	<6.0	28.0
237-88	16.0	<10.0	12.0	4.0	<6.0	14.0
238-106	6.2	<10.0	9.3	48.0	<6.0	63.0
239-64	20.0	<10.0	11.0	16.0	<6.0	14.0
240-95	6.2	<10.0	8.4	14.0	<6.0	9.0

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	Na (mg/l)	Pb (µg/L)	Si (mg/l)	Sr (µg/L)	V (µg/L)	Zn (µg/L)
FSW						
241-98	--	--	--	--	--	--
242-77	5.5	<10.0	8.0	11.0	<6.0	11.0
243-45	4.3	<10.0	7.4	17.0	<6.0	21.0
244-90	18.0	<10.0	6.3	15.0	<6.0	23.0
245-25	28.0	<10.0	4.6	27.0	<6.0	13.0
246-35	15.0	11.0	11.0	27.0	<6.0	64.0
247-70	11.6	<10.0	7.2	38.9	<6.0	46.6
254-216	7.2	<10.0	19.0	29.0	<6.0	3.0
254-168	9.9	<10.0	19.0	36.0	<6.0	6.0
254-140	14.0	<10.0	17.0	92.0	<6.0	5.0
254-107	26.0	<10.0	8.7	106.0	<6.0	< 3.0
254-72	25.0	<10.0	5.4	24.0	<6.0	4.0
254-54	23.0	<10.0	4.9	18.0	<6.0	6.0
254-26	9.2	<10.0	6.2	21.0	<6.0	3.0
262-159	11.0	<10.0	19.0	66.0	<6.0	11.0
262-85	35.0	<10.0	10.0	91.0	<6.0	6.1
262-69	30.0	<10.0	7.0	18.0	<6.0	22.0

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	Na (mg/l)	Pb (µg/L)	Si (mg/l)	Sr (µg/L)	V (µg/L)	Zn (µg/L)
FSW						
262-41	6.6	<10.0	8.4	33.0	<6.0	20.0
267-155	8.4	<10.0	22.0	46.0	<6.0	25.0
267-136	8.8	<10.0	14.9	34.2	<6.0	51.4
269-111	8.8	<10.0	8.9	58.0	<6.0	2.4
267-88	13.0	<10.0	14.6	39.3	<6.0	9.9
271-165	9.4	<10.0	19.5	44.7	<6.0	12.6
271-141	11.2	<10.0	18.3	48.6	<6.0	7.0
271-85	15.2	<10.0	11.0	63.5	<6.0	11.6
271-41	6.0	<10.0	5.8	22.9	<6.0	15.8
279-86	8.9	<10.0	3.1	22.4	<6.0	3.6
279-61	8.7	<10.0	3.9	27.9	<6.0	7.5
282-123	12.1	<10.0	18.3	53.8	<6.0	7.8
282-94	18.2	<10.0	12.4	110.6	<6.0	14.2
282-70	22.8	<10.0	10.6	84.5	<6.0	28.8
282-49	15.8	<10.0	6.9	10.6	<6.0	17.4
288-97	17.0	<10.0	7.8	22.0	<6.0	16.0

Table 6. Continued. Inorganic analyses for samples from 1983 field season.
 [-- is for no data]

Well No.	Na (mg/l)	Pb (µg/L)	Si (mg/l)	Sr (µg/L)	V (µg/L)	Zn (µg/L)
FSW						
290-91	9.1	<10.0	13.0	31.0	<6.0	6.0
294-89	15.0	<10.0	18.0	62.0	<6.0	9.0
299-20	6.1	<10.0	6.5	28.0	<6.0	8.0
300-30	59.0	<10.0	18.0	35.0	<6.0	< 3.0
300-10	17.0	<10.0	6.8	34.0	<6.0	< 3.0
347-67	22.0	<10.0	13.0	28.0	<6.0	12.0
SDW						
305-32	6.6	<10.0	13.0	68.0	<6.0	250.0
313-60	7.6	<10.0	9.4	43.0	<6.0	8.0

Table 7. Organic analyses for samples from 1983
field season
[na = not analyzed; nd = not detected]

Well No.	DOC (mg/L)	MBAS (mg/L)	Total volatiles (μ g/L) (DCE, TCE, PCE)
FSW			
166-67	1.3	0.04	0.5
167-65	1.0	0.01	na
173-69	1.0	0.52	na
182-69	1.0	0.04	nd
194-57	2.3	0.20	1.1
214-60	1.4	0.09	na
230-48	2.0	0.10	na
231-57	3.0	na	na
232-58	3.2	0.11	0.8
234-99	0.9	0.04	na
235-94	0.9	0.02	na
236-106	1.1	0.04	1.0
237-88	1.1	0.05	0.9
238-106	<1.0	0.03	na
239-64	1.9	0.07	268.4
242-77	0.9	0.02	nd
243-45	0.8	0.01	na
244-90	1.8	0.08	390.6
245-25	1.0	0.04	nd
246-35	2.0	0.09	na
247-70	1.0	0.06	na
254-216	1.0	0.04	1.0
254-168	1.1	0.04	1.3
254-140	1.9	0.16	4.5
254-107	2.3	0.25	93.7
254-72	2.8	0.14	681.7
254-54	3.2	0.18	8.1
254-26	1.2	0.03	nd
262-159	2.0	0.03	na
262-109	4.0	0.10	na
262-85	3.7	0.69	46.7
262-69	2.8	0.48	3.7
262-41	1.0	0.04	na
267-155	2.0	0.04	na
267-136	1.0	0.04	na
267-111	1.0	0.07	na
267-88	1.2	0.09	9.6
271-165	1.0	0.03	nd
271-141	2.0	0.05	nd
271-85	2.0	1.3	nd

Table 7. Continued. Organic analyses for samples from 1983
field season
[na = not analyzed; nd = not detected]

Well No.	DOC (mg/L)	MBAS (mg/L)	Total volatiles (μ g/L) (DCE, TCE, PCE)
271-41	1.0	0.05	nd
279-86	1.0	0.05	na
279-61	<1.0	0.04	na
282-123	3.1	0.06	nd
282-94	4.0	2.00	5.9
282-70	4.2	2.00	nd
282-49	1.9	0.05	na
288-97	2.2	0.18	30.8
290-91	1.0	0.06	na
294-89	3.1	0.96	0.5
299-20	2.0	0.05	nd
300-30	3.5	0.27	3.9
300-10	1.0	0.04	na
347-67	4.0	0.21	11.7
SDW			
305-32	3.0	0.13	na
313-60	1.0	0.05	na

Table 8. DOC fractionation analyses for native ground water containing 0.02 mg/L MBAS (Well FSW 242-77) and for a ground water containing 2.0 mg/L MBAS (well FSW 282-70)

DOC fraction	FSW 242-77 (mg/L organic carbon)	FSW 282-70 (mg/L organic carbon)
Hydrophobic		
Acids	0.1	0.3
Bases	0.0	0.1
Neutrals	0.0	2.8
Hydrophilic		
Acids	0.1	0.0
Bases	0.3	0.3
Neutrals	0.4	0.6
Total organic carbon	0.9	4.2

Table 9. Organic analyses by purge/trap and gas chromatography/mass spectrometry for samples from the 1983 field season
 [nd = none detected]

Well No.	Compound	Concentration ($\mu\text{g/L}$)
FSW		
166-67	Trichloroethene	0.3
	Tetrachloroethene	0.2
182-69	nd	
194-57	Trichloroethene	0.7
	Tetrachloroethene	0.4
232-58	1,1,1-Trichloroethane	0.2
	Trichloroethene	0.5
	Tetrachloroethene	0.1
236-106	Trichloroethene	0.1
	Tetrachloroethene	0.9
237-88	Trichloroethene	0.1
	Tetrachloroethene	0.8
239-64	1,1,1-Trichloroethane	0.1
	Trichloroethene	94.5
	Tetrachloroethene	133.6
	1,2-Dichloroethene	34.5
	1,1-Dichloroethane	4.7
	1,1-Dichloroethene	0.2
	1,2-Dichloroethane	0.2
	Carbontetrachloride	0.1
	1,2-Dichloropropane	0.2
	1,1,2-Trichloroethane	0.1
	Chlorobenzene	0.2
240-95	1,1,1-Trichloroethane	0.2
241-98	1,1,1-Trichloroethane	1.4
242-77	nd	
244-90	1,1,1-Trichloroethane	0.5
	Trichloroethene	30.2
	Tetrachloroethene	244.7
	1,2-Dichloroethene	113.5
	1,2-Dichloroethane	0.6
	Carbontetrachloride	0.2
	1,2-Dichloropropane	0.3

Table 9.--Organic analyses by purge/trap and gas chromatography/mass spectrometry for samples from the 1983 field season--Continued
 [nd = none detected]

Well No.	Compound	Concentration ($\mu\text{g/L}$)
244-90 --Continued	1,1,2-Trichloroethane	0.1
	Chlorobenzene	0.3
	Ethylbenzene	0.2
247-70	nd	
254-216	Trichloroethene	0.3
	Tetrachloroethene	0.7
254-168	Trichloroethene	0.3
	Tetrachloroethene	0.7
	1,2-Dichloroethene	0.3
254-140	Trichloroethene	4.5
254-107	1,1,1-Trichloroethane	2.8
	Trichloroethene	47.9
	Tetrachloroethene	16.2
	1,1-Dichloroethane	1.0
	1,2-Dichloroethene	25.8
254-72	Trichloroethene	65.0
	Tetrachloroethene	416.8
	1,1-Dichloroethane	3.3
	1,2-Dichloroethene	196.6
254-54	Trichloroethene	1.4
	Tetrachloroethene	3.6
	1,2-Dichloroethene	3.1
254-26	nd	
262-85	1,1,1-Trichloroethane	1.7
	Trichloroethene	26.8
	Tetrachloroethene	13.6
	1,2-Dichloroethene	4.6
262-69	Trichloroethene	1.9
	Tetrachloroethene	0.3
	1,2-Dichloroethene	1.5
267-88	1,1,1-Trichloroethane	2.5
	Trichloroethene	0.6
	Tetrachloroethene	6.2
	Carbontetrachloride	0.1
	1,1,2-Trichloroethane	0.1
	Chlorobenzene	0.1

Table 9.--Organic analyses by purge/trap and gas chromatography/mass spectrometry for samples from the 1983 field season--Continued
[nd = none detected]

Well No.	Compound	Concentration ($\mu\text{g/L}$)
271-141	nd	
271-85	nd	
271-41	nd	
282-123	nd	
282-94	1,1,1-Trichloroethane	1.3
	Trichloroethene	3.2
	Tetrachloroethene	1.1
	1,2-Dichloroethene	0.3
282-70	nd	
288-97	1,1,1-Trichloroethane	1.1
	Trichloroethene	10.0
	Tetrachloroethene	19.2
294-89	Trichloroethene	0.5
299-20	nd	
300-30	Trichloroethene	2.1
	Tetrachloroethene	0.8
	1,2-Dichloroethene	0.9
	Chlorobenzene	0.1
347-67	1,1,1-Trichloroethane	0.5
	Trichloroethene	4.4
	Tetrachloroethene	5.1
	1,1-Dichloroethane	0.1
	1,2-Dichloroethene	1.6
Tap Water Otis Air National Guard Base		
	1,1,1-Trichloroethane	0.3
	Chloroform	5.0
	Bromodichloromethane	9.9
	Dibromochloromethane	7.3
	Bromoform	1.0
Ashumet Pond Boat Landing		
	1,2-Dichloroethene	0.3
	Trichloroethene	0.1

CHAPTER D

Low concentrations of organic chemicals are a critical consideration in studies of ground-water contamination. Even at very low concentrations, these chemicals can render a water supply unsuitable for use as drinking water. This paper describes a technique that was tested at the Otis field site for detecting extremely low concentrations of organic compounds in ground water. These organic constituents may be ideal tracers of the plume which can be simulated with solute transport models.

CLOSED-LOOP STRIPPING, COMBINED WITH CAPILLARY GAS CHROMATOGRAPHY/MASS SPECTROMETRY ANALYSIS TO DEFINE A SEMI-VOLATILE ORGANIC CONTAMINANT PLUME

By

Larry B. Barber, II, E. Michael Thurman, and Michael P. Schroeder

Abstract

Thirty-two wells were sampled using closed-loop stripping combined with capillary gas chromatography/mass spectrometry analysis, to establish whether or not semi-volatile organic compounds are present in a plume of sewage contaminated ground water at Otis Air Base, Cape Cod, Massachusetts. Approximately 40 different organic compounds were tentatively identified in the ground water at the site. Of these substances, trichloroethene and tetrachloroethene were present in all wells sampled within the plume delineated by inorganic constituents. Dichlorobenzene, alkylated phenols, and alkylated benzenes were also present in many of the wells. Contaminant distributions were quite complex, and probably reflect variations in source composition. The closed-loop stripping technique allowed determination of organic compounds at the low nanogram per liter (ng/l) concentration level. The semi-volatile plume defined by the closed-loop stripping technique is considerably larger in areal extent than the plume determined by a purge and trap method; the latter has a detection limit in the low microgram per liter ($\mu\text{g/l}$) range. Based on this study, it was concluded that closed-loop stripping combined with capillary gas-chromatography/mass spectrometry is an effective method for determination of semi-volatile organic contaminants at the part per trillion (ng/l) level in ground water.

INTRODUCTION

Fifty percent of all residents in the United States rely on ground water as their primary source of drinking water (McCarty and others, 1981). Until recently, this vast natural resource had been considered pristine, and received little or no treatment prior to human consumption. Once contaminated, subsurface waters may remain so for hundreds to thousands of years. The problem of ground-water contamination by trace-level synthetic organic chemicals has been reviewed by a number of workers including McCarty and others (1981), Council on Environmental Quality (1981), and Pettyjohn and Hounslow (1983).

An extensive plume of contaminated ground water resulting from 40 years of disposal of secondary treated wastewater onto sand-infiltration beds was investigated. Of the various land-treatment methods in use today, rapid infiltration is one of the most efficient in terms of the required acreage to disposal volume ratios.

Currently, there are more than 360 rapid infiltration sites in the United States, and many more are planned for the near future (Scheaffer, 1979). Although the effectiveness of these sites for removing refractory-organic compounds from wastewater is not yet known, several recent papers have addressed the problem (Hutchins and Ward, 1983; Clark and Baxter, 1982; Tomson and others, 1981; Bouwer and others, 1981; Schwarzenbach and others, 1983). These studies indicate that many semi-volatile organic compounds (operationally defined as compounds that are extractable from water and are amenable to gas chromatography analysis) are not completely removed during infiltration. Once contamination occurs, natural reclamation of the aquifer is slow because of the reduction or absence of degradative processes such as photolysis, oxidation, volatilization, sorption, biodegradation and dilution. Relatively small amounts of contaminants have the potential of polluting vast quantities of ground water at the microgram per liter ($\mu\text{g/L}$) level. Thus, it is important to understand and evaluate the effectiveness of rapid-infiltration processes on the reclamation of wastewater containing refractory organic compounds, and to examine the nature and extent of ground-water contamination resulting from such disposal practices.

This report discusses a method of analyzing for trace-level, semi-volatile organic substances in ground water using a closed-loop stripping (CLS) apparatus for concentrating the organic substances, followed by capillary gas chromatography/mass spectrometry (GC/MS) analysis. The purpose of the investigation is four fold: (1) To determine whether or not semi-volatile organic substances are present in the ground water at the field site; (2) to evaluate the CLS method for sample concentration; (3) to evaluate CLS GC/MS analysis as a tool for contaminant mapping; and (4) to determine the distribution of semi-volatile organic compounds within the plume previously delineated by

inorganic and gross-organic measurements. The data presented in this report are the result of the 1983 field season at the Cape Cod Ground-Water Contamination Research site.

1

The study area is located at Otis Air Base (OAB), Cape Cod, Massachusetts. The base has a wastewater treatment plant from which secondary treated effluent recharges a sand and gravel aquifer through rapid infiltration sand beds (Vaccaro and others, 1979). An earlier water-quality study by LeBlanc (1982) documented the presence of a contamination plume that extends over 11,000 ft downgradient from the disposal beds, and has a width of over 3000 ft. The plume was delineated on the basis of specific conductance and concentrations of chloride, boron, detergents (as MBAS), sodium, and other inorganic constituents. Figure 31 is a map of the site showing the extent of the plume.

Although the location of the contamination source can be restricted to a relatively small area, little is known about the volume and chemical composition of the effluent prior to the late 1970's. The unknown chemical nature of the source complicates interpretation of the chemical data and understanding of compound distribution within the plume. Observed distribution patterns and concentrations of particular compounds may result from: (1) variations in source composition; (2) accidental spills; or (3) high-volume discharge during peak periods of base use.

Geology of the study area is characterized by Pleistocene glacio-fluvial deposits that overlie less permeable crystalline igneous and metamorphic rocks (Oldale, 1976). The hydrology of the area is fairly well understood. The top 90 to 140 feet of the aquifer consists of stratified glacial sand-and-gravel outwash deposits. Ground water moves through the permeable outwash towards the south at about 1 foot per day (ft/d). Details of the hydrology are given by LeBlanc (1984, 1982).

EXPERIMENTAL PROCEDURES

Sample Collection

At the beginning of the 1983 field season, 66 observation wells were in place at the OAB site. Of these, 55 were sampled for inorganic and gross organic constituents as well as for volatile organic analysis (Thurman and others, 1984). Thirty-two of the wells were sampled for analyses by CLS with GC/MS (fig. 31).

1

A description of the site, including its geologic and hydrologic setting, is given in Chapter A of this volume.

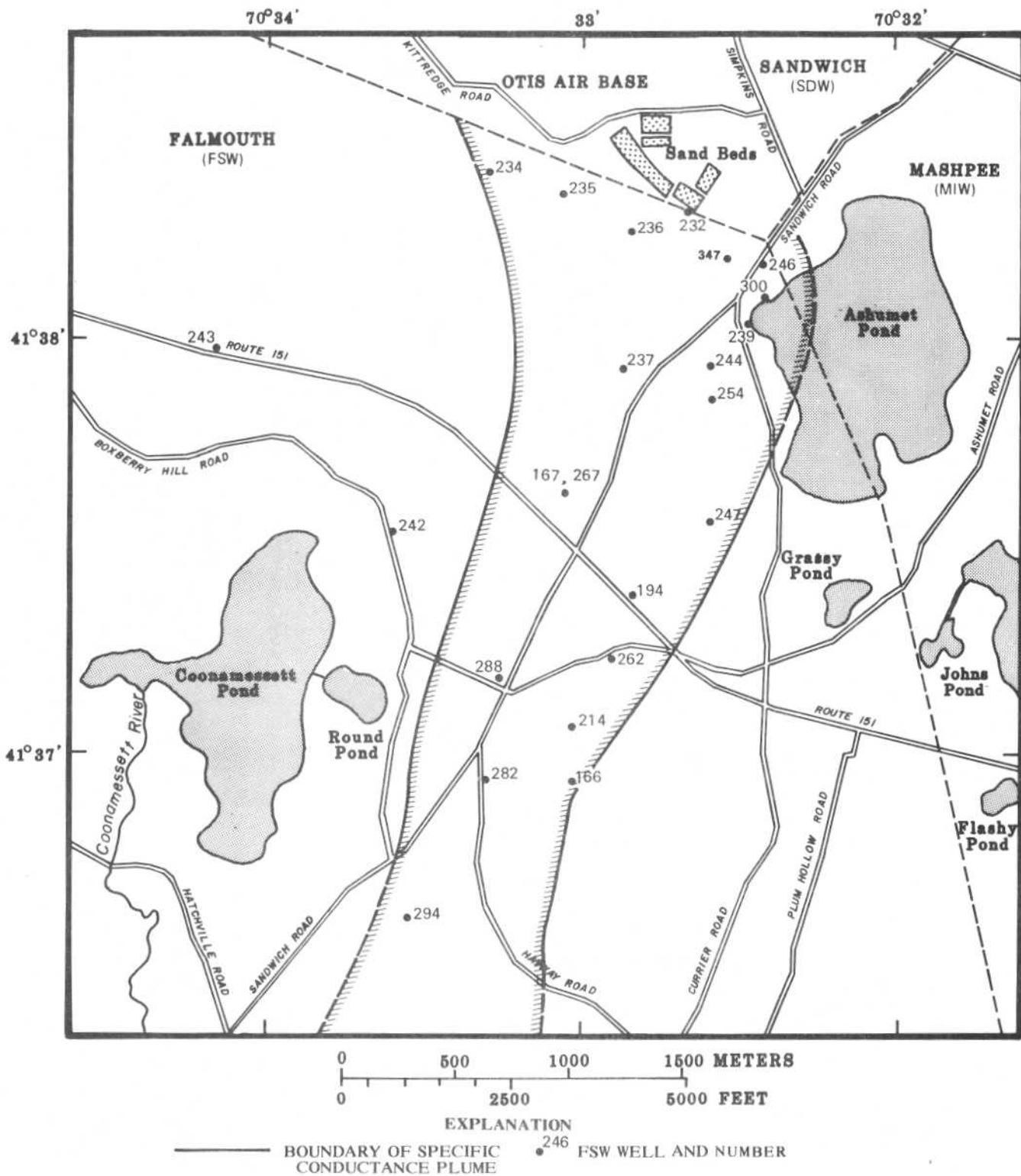


Figure 31.-- Specific conductance plume and location of wells.

Because of the ability of CLS to detect organic compounds at the nanogram per liter (ng/l) level, questions have been raised about the ability to obtain representative samples that have not been contaminated by the sample collection process. This problem has been considered by a number of workers including Clark and Baxter (1982), Keely and Wolf, (1983), Nacht (1983), Pettyjohn and others (1981), and Scalf and others (1981). The following cleaning procedure was used to minimize contamination from sample containers and processing equipment. Samples were collected in 4-liter amber bottles with Teflon-lined screw caps. The bottles were first washed with hot soapy water and rinsed. Next, they were rinsed with a 20 percent hydrochloric acid/distilled water solution, followed by low-organic distilled water. Finally the bottles were baked for 12 hours at 300 degrees C. This cleaning procedure removed all purgeable organic compounds from the sampling containers and processing equipment.

Ground-water samples were collected by (1) a small diameter stainless-steel submersible pump fitted with Teflon tubing; and (2) a peristaltic pump equipped with Teflon tubing. When the peristaltic pump was used, the well was first evacuated with a gasoline-powered suction pump. In both types of sampling, a minimum of three well-casing volumes were discharged before sampling was initiated. After evacuation, the site was cleared of vehicles and other potential sources of contamination, and was left undisturbed for 4 hours. Before sample collection, the pumping system was flushed for 30 minutes with native well water. Sample bottles were rinsed three times, then filled to the top with a minimum of turbulence and headspace; immediately prior to capping, the samples were spiked with a surrogate standard solution containing 1-chlorohexane ($C_6H_{13}Cl$), 1-chlorododecane ($C_{12}H_{25}Cl$), and 1-chlorooctadecane ($C_{18}H_{37}Cl$). After collection, the samples were stored at 4 degrees C. In all cases, the semi-volatile compounds were stripped from the sample within 12 hours of the time of collection; GC/MS analysis was performed within 1 to 2 weeks. Preliminary data indicate that no significant loss of organic components occurred between the time of stripping (and trapping on charcoal) and the time of analysis. However, the subject of loss both during sample collection and during trap storage and transport is currently being investigated in more detail.

Closed-Loop Stripping

The application of closed-loop stripping (CLS), as developed by Grob (1973), has been established as a valuable tool for the analysis of trace-level semi-volatile organic compounds in water (Coleman and others, 1981; Schwarzenbach and others, 1978; McCarty and Reinhard, 1980). Closed-loop stripping involves purging headspace air through a water sample, trapping the organic fraction onto a solid adsorbent (activated charcoal), and then repurging the water-saturated vapor back through the sample in an air-tight glass-Teflon system (fig. 32). Organic compounds with a significant vapor pressure over water are partitioned from

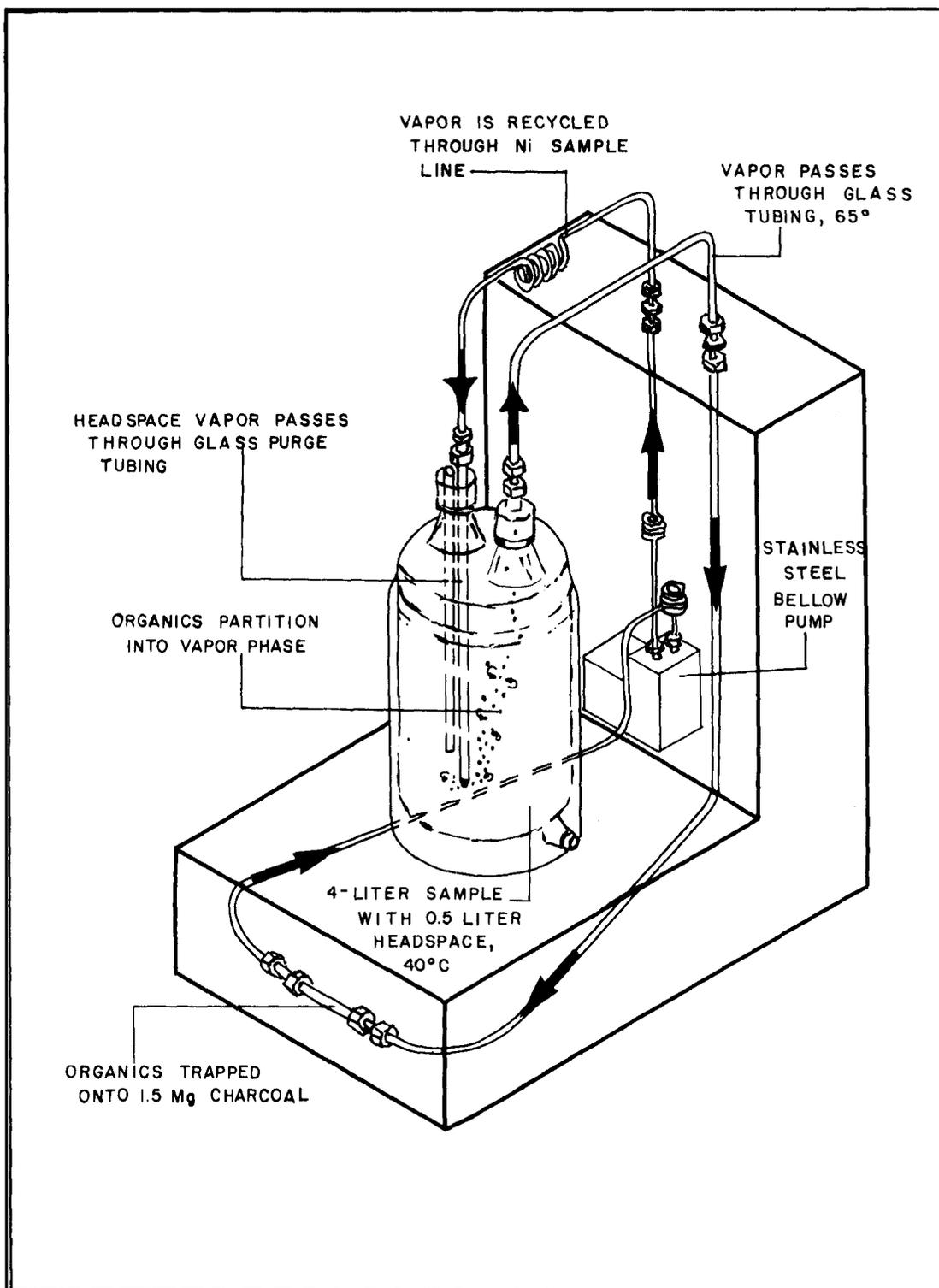


Figure 32.--Schematic diagram showing operation of closed-loop stripping apparatus. Arrows indicate direction of vapor movement.

the aqueous phase into the vapor phase during the purging process. The saturated water vapor containing the stripped organics is pumped through glass tubing to an activated carbon trap. The glass tubing and the trap are maintained at 20 to 30 degrees C above the temperature of the water sample to prevent water condensation in the trap which reduces trapping efficiency. As the water vapor passes through the charcoal filter, the organic components are partitioned onto the solid phase and retained, and the vapor is recycled through the sample, repeating the purge process. After the sample has been stripped of its semi-volatile components, the trap is removed, and the organics are extracted with a small volume of solvent. For this study 15 μ l of distilled-in-glass methylene chloride was used to elute the 1.5 mg charcoal traps. The methylene chloride extract containing the desorbed organics is ready for direct injection into the GC/MS system. Assuming an average recovery of 90 percent (which is reasonable based on published data), a 4-liter sample volume, and a final extract volume of 10 μ l, the concentration factor will be 360,000. Because of the high concentration factor, CLS allows the detection of organic compounds at extremely low levels.

Although this method is capable of concentrating organic compounds with a wide range of volatilities (boiling points range from less than 70 to greater than 300 degrees C), substances that are strongly ionic or that have low vapor pressures (humic acids, detergents, urea and carbohydrates) are not concentrated by the procedure (Grob and Grob, 1974). Advantages of CLS include (1) high reproducibility; (2) minimal influence by water sample conditions; (3) wide range of sensitivity; (4) suitability of extracts for GC/MS analysis; and (5) good recovery of moderately polar substances (Grob and Zurcher, 1976). Closed-loop stripping is most effective for low to medium molecular weight organic compounds, from C₂ up to about C₁₈ in the n-alkane series. Highly volatile substances coelute with the methylene chloride and cannot be separated from the solvent peak and thus are not determined by this method.

The CLS apparatus used in this study is a commercially available unit manufactured by Tekmar². This semi-automated device allows ready standardization of purge time, sample temperature, trap temperature, and line temperature. All samples were run under the conditions listed in table 10. These conditions are optimal for the recovery of the surrogate standards used in this study, and for a wide range of semi-volatile environmental contaminants (Coleman and others, 1983). Based on data from preliminary sample analysis, it was concluded that because of the trace level of organic substances in the ground water at the Otis site, a 4-liter sample volume was necessary to attain a sufficient concentration factor for consistent detection of low-level compounds.

2

Use of brand names is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

All solvents and chemicals used for the preparation of standards were reagent grade or better. A surrogate-standard solution consisting of approximately 49 ng/ μ L each of 1-chlorohexane, 1-chlorododecane, and 1-chlorooctadecane was prepared in methanol. A 10- μ l aliquot of the 1-chloroalkane standards was spiked into the water samples with a microliter syringe by injecting below the meniscus at the time of collection, so that the standards underwent all phases of sample processing. The reference amount of surrogate standard added to the samples resulted in a final concentration of 122 ng/L for each of the 1-chloroalkanes.

Table 10. Closed-loop stripping operational conditions used in this study.

Sample size	4-liter
Sample temperature	40 degrees C
Line temperature	65 degrees C
Trap size	1.5 mg
Trap temperature	50 degrees C
Purge time	2 hours

Standards and Blanks

Procedural blanks were incorporated into the analytical scheme because of the potential for sample contamination. Before analysis of actual samples, carbon-filter blanks and CLS system blanks of low-organic distilled water containing the surrogate standards were analyzed. In addition, distilled water blanks were run after any suspected highly contaminated samples to evaluate the possibility of cross-contamination.

Gas Chromatography/Mass Spectrometry Analysis

After the semi-volatile organic component of each sample was concentrated by CLS, specific compound identification was performed using a Hewlett Packard 5985 GC/MS system. The gas chromatograph was equipped with a 0.21 mm internal diameter, 25 meter capillary column (Hewlett Packard SE-54 (Ultra II) cross-linked 5 percent phenyl-methyl silicone). One microliter of CLS extract was injected with the spitless injector purge vent closed. The injector vent was opened after 30 seconds. The helium carrier-gas had a linear velocity through the GC column of 28 cm/second. The injector temperature was maintained at 250 degrees C. Samples were injected with the column temperature lowered to 30 degrees C by cooling the GC oven with liquid nitrogen. After a 10 minute hold at 30 degrees C the oven temperature was programmed to increase to 300 degrees C at a rate of 6 degrees C/minute. Temperature was held at 300 degrees C for 5 minutes. Mass spectra were acquired from 40 to 450 amu at a

rate of 2 scans per second. The electron energy was 70 eV, and the source temperature was 200 degrees C. Source pressure was approximately 0.000003 torr when the GC temperature was 25 degrees C. Data acquisition was terminated after 60 minutes.

Identification of organic compounds was based solely on computerized matching of sample mass spectra with those in the NBS (National Bureau Of Standards) and Wiley libraries, using a Hewlett-Packard 1000 data system. The computerized matches were evaluated by the mass spectrometer operator to assure the quality of identification. This method of identification is only tentative, and further work is in progress to confirm the identity of compounds by analyzing authentic standards under identical analytical conditions, and comparing mass spectra and retention indices of the analyte with those of the authentic standards.

Quantification

Concentrations of the organic compounds tentatively identified in the CLS extracts have not yet been quantified. However, semi-quantitative values have been calculated using an internal standard method by which concentrations are determined relative to the reference standard compound 1-chlorododecane, spiked into the sample at 122 ng/L. The formula used is shown in equation 1; calculations were made using baseline corrected total ion current peak areas.

$$\text{Amount Z} = \frac{\text{corrected area compound Z}}{\text{corrected area surrogate standard}} \times 122 \text{ (1)}$$

Due to the preliminary nature of this study, insufficient data are available to determine the absolute recovery of the surrogates and the analytes of interest. Likewise, precision data for the semi-quantitative values given in this report have not yet been determined. Work is underway to evaluate both recovery and precision.

RESULTS

Approximately 40 semi-volatile organic compounds were tentatively identified in the plume of contaminated ground water at the OAB site (table 11). These compounds generally fall into the following classes: (1) aliphatic hydrocarbons; (2) chlorinated aliphatic hydrocarbons; (3) chlorinated aromatics; (4) alkyl-substituted aromatics; (5) alkyl-substituted phenols; (6) aldehydes; (7) phthalates; and (8) miscellaneous. Three of these compounds were present in most of the wells screened within the plume identified by inorganic contaminants: (1) trichloroethene

Table 11. Partial list of organic compounds tentatively identified by mass spectra library fits from gas chromatography/mass spectrometry analysis of closed-loop stripping extract.

Alkyl Substituted Aromatics

benzene
methyl benzene
C2 benzene isomers
C3 benzene isomers
C4 benzene isomers
C5 benzene isomers
1-methyl-3-(4-methylphenyl) benzene
propyl benzene

Aliphatic Hydrocarbons

2-methyl-1-propene
trimethylpentane isomers
trimethylpentene isomers
1,1-dimethylcyclohexane
1,1,3-trimethylcyclohexane
1-methyl-4-(methylethyl)-cyclohexane
4-ethyl-3-heptene
3,5-dimethyloctane
1-octene

Chlorinated Hydrocarbons

trichloroethene
trichloroethane
tetrachloroethene
tetrachloroethane

Chlorinated Benzenes

dichlorobenzene isomers
chlorobenzene
1-chloro-2-methyl benzene

Phthalates

bis-(2-ethylhexyl)-phthalate
dibutyl phthalate
butyl-2-methylpropyl phthalate

Alkyl Substituted Phenols

4-(2,2,3,3-tetramethylbutyl)-phenol
nonyl phenol isomers

Table 11. Partial list of organic compounds tentatively identified by mass spectra library fits from gas chromatography/mass spectrometry analysis of closed-loop stripping extract-- continued.

Miscellaneous

- 2,3-dihydro-1-methyl-1H-indene
- 2,3-dihydro-1,1-dimethyl-1H-indene
- 2,6-bis-di-t-butyl-p-benzoquinone
- 7-methyl-3,4-octadiene
- cyclooctanone
- decahydro-trans-napthalene
- 2-beta-pinene
- 2-propenylidene-cyclobutane
- butyl ester thiocyanic acid
- 2,2,4,4-tetramethyl-3-pentanone
- 3-methyl-1-butanolbenzoate

Aldehydes

- nonanal
- decanal
- octanal
- hexanal

(2) tetrachloroethene; and (3) dichlorobenzene. These compounds are common in both industrial and domestic wastewater. Dichlorobenzene is a common component of toilet-bowl cleansers and many other household products; trichloroethene and tetrachloroethene are both widely used as degreasing solvents.

Mapping the plume using the chromatograms from CLS GC/MS analysis proved to be useful in determining the distribution of the different classes of semi-volatile compounds. Each well had a relatively unique chromatographic signature indicating which compounds were present. Four distinct semi-volatile organic subplumes existed within the overall plume (fig. 33): (1) A zone of tri- and tetrachloroethene of considerable extent that corresponds to the detergent and boron plumes; (2) a zone of alkylated phenols near the source area; (3) a zone of alkylated benzenes near the source area; and (4) a zone of dichlorobenzene extending along the core of the plume. The observed distribution of the chlorinated ethene compounds is similar to the boron plume and suggests that these compounds are moving in a somewhat conservative manner. The boron plume coincides approximately with that of the conservative ion, chloride; thus boron appears to behave conservatively in this particular aquifer (Thurman and others, 1984). Dichlorobenzene appears to be retained relative to tri- and tetrachloroethene, and the alkylated benzenes and phenols are restricted to a small portion of the total plume. The similarity of the distribution of the semi-volatile organics with the distribution of detergents (MBAS) and boron is shown in figures 33 and 34. It is apparent that the semi-volatile organics can be used in conjunction with these parameters to identify and characterize the plume.

The discrete plumes of individual classes of organic compounds could be the result of several factors. It is possible that separation of compounds is the result of different rates of movement in the aquifer, in particular for tri- and tetrachloroethene, and dichlorobenzene. The different rates could be due to varying degrees of hydrophobicity as expressed by the octanol/water partition coefficients (K_{ow}) (trichloroethene $K_{ow}=2.3$; dichlorobenzene $K_{ow}=3.4$). However, such separations are difficult to achieve even in an analytical chromatography column. The apparent variable retention of the organic compounds needs to be evaluated in detail by column experiments using native aquifer material to determine if different retardation factors exist for the various classes of compounds. Another possible cause for the discrete plumes is variation in the source input in time, space, and concentration. This seems likely, particularly for the alkylated benzene and phenol compounds near the beds. A third possibility is that specific compound movement may be influenced by the presence of detergents and the formation of micelles.

One of the most significant observations from the data is the difference in the tri- and tetrachloroethene plumes defined by two separate analytical methods: (1) CLS GC/MS and (2) purge and trap GC/MS (Thurman and others, 1984). The CLS GC/MS

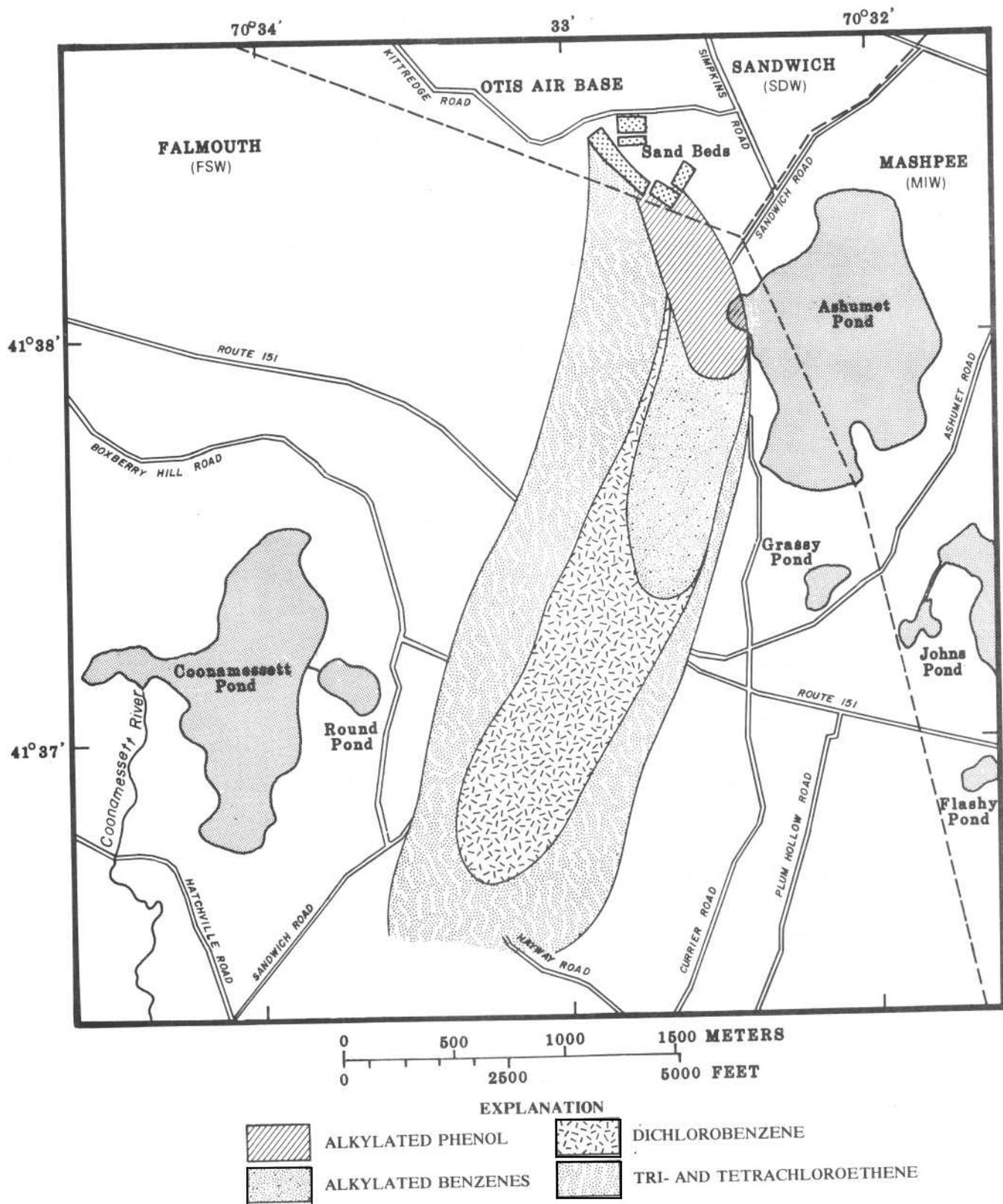


Figure 33.--Distribution of semi-volatile organic substances in ground water, 1983, by closed loop-stripping technique.

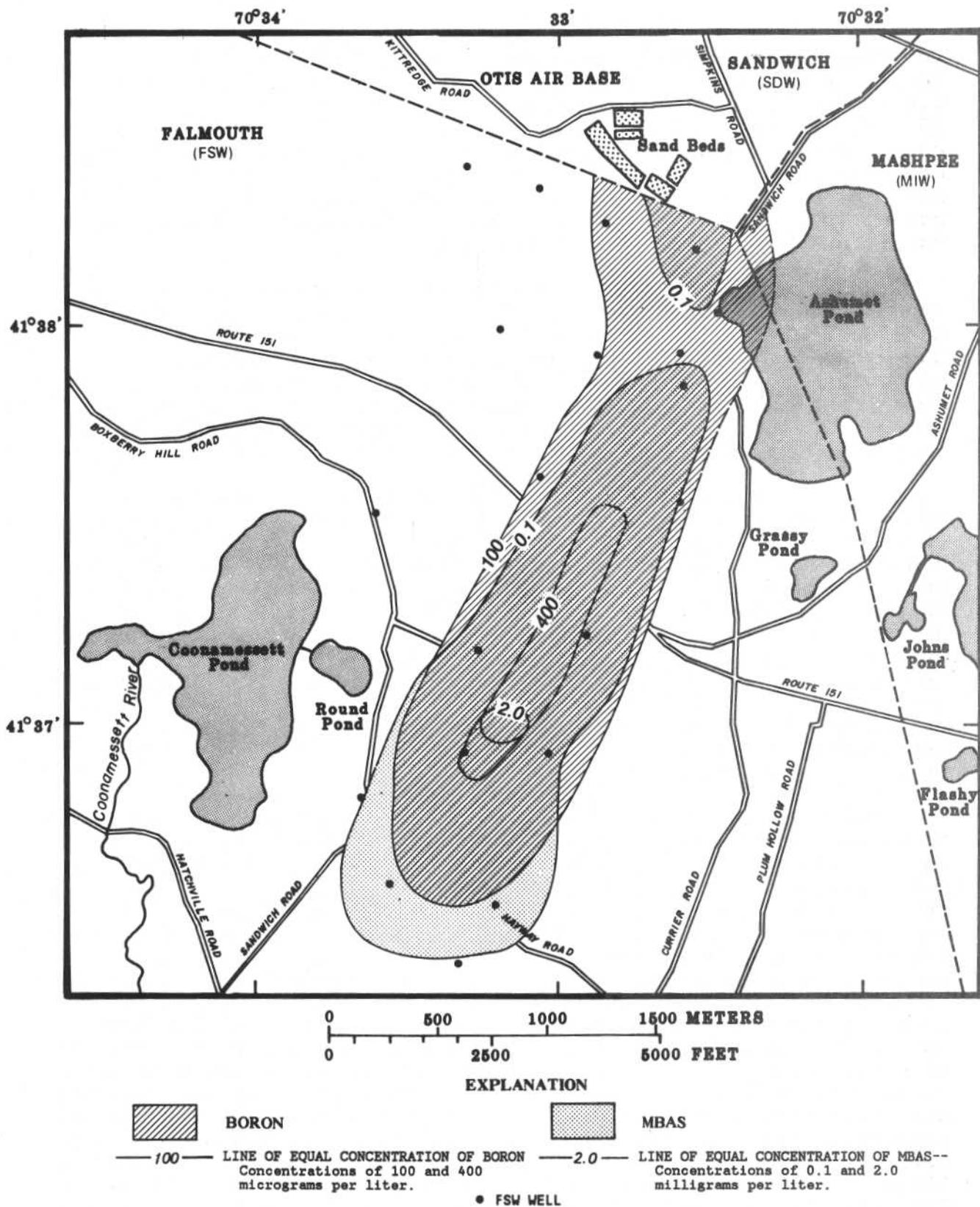


Figure 34.--Distribution of detergents (as MBAS) and boron in ground water, 1983.

technique is capable of detecting compounds in the 1 to 10 ng/L level, whereas the purge and trap GC/MS method has a detection limit of 1 to 5 µg/L. As can be seen by comparing figures 33 and 35, the areal definition of the plume based on CLS GC/MS is considerably greater in extent than the plume defined on purge and trap data. This has important implications in determining the rate of transport of organic compounds in the aquifer. It also points out the ability for early detection of trace level contamination by using the CLS method.

Well number FSW 242-77 yields uncontaminated ground water from a control site (based on inorganic measurements). The clean baseline of the chromatogram for this well (fig. 36) shows that the water is uncontaminated by semi-volatile substances. The lack of organic compounds at the ng/L level suggest minimal contamination from well construction materials or from sample collection and processing. Well FSW 242-77 contained less semi-volatile compounds than laboratory-distilled waters.

The FSW 254 series is a cluster of wells located in the core of the plume that is representative of the type of contamination observed at other locations within the plume. The vertical distribution of semi-volatile substances relative to boron and MBAS is shown in figure 37. At this well cluster, the greatest extent of organic contamination occurs in the upper part of the plume, possibly the result of changes in the source composition or the location of the infiltration bed used, or the influence of geologic structure in the aquifer. At other locations where vertical profiles were constructed, slightly different distribution patterns were observed for the semi-volatile substances, confirming the existence of several sub-plumes of organic contamination.

Compounds tentatively identified on mass spectra for CLS GC/MS analysis of key wells in the FSW 254 series are summarized in figures 38 to 40 and tables 12 to 14. Although the concentrations reported are semi-quantitative, reproducible results were obtained for samples that were run in duplicate. It is interesting to note the presence of several aldehydes throughout the well series, both in the contaminated and uncontaminated waters, suggesting that they may be naturally occurring compounds. Schwarzenbach and others (1978), in an investigation of volatile organic compounds in surface waters in the same general area of this study reported a similar set of aldehyde compounds at concentrations comparable to those reported here. The reversal of concentration levels for tetrachloroethene and trichloroethene between wells FSW 254-54 and FSW 254-140 indicates that these compounds occur as two subplumes with tetrachloroethene overlying trichloroethene at this location. Alkylated benzene compounds are present in wells FSW 254-54 to FSW 254-140 but their levels decrease rapidly with increasing depth. Single well points are insufficient to accurately define the plume as can be seen by the rapid vertical variations both in

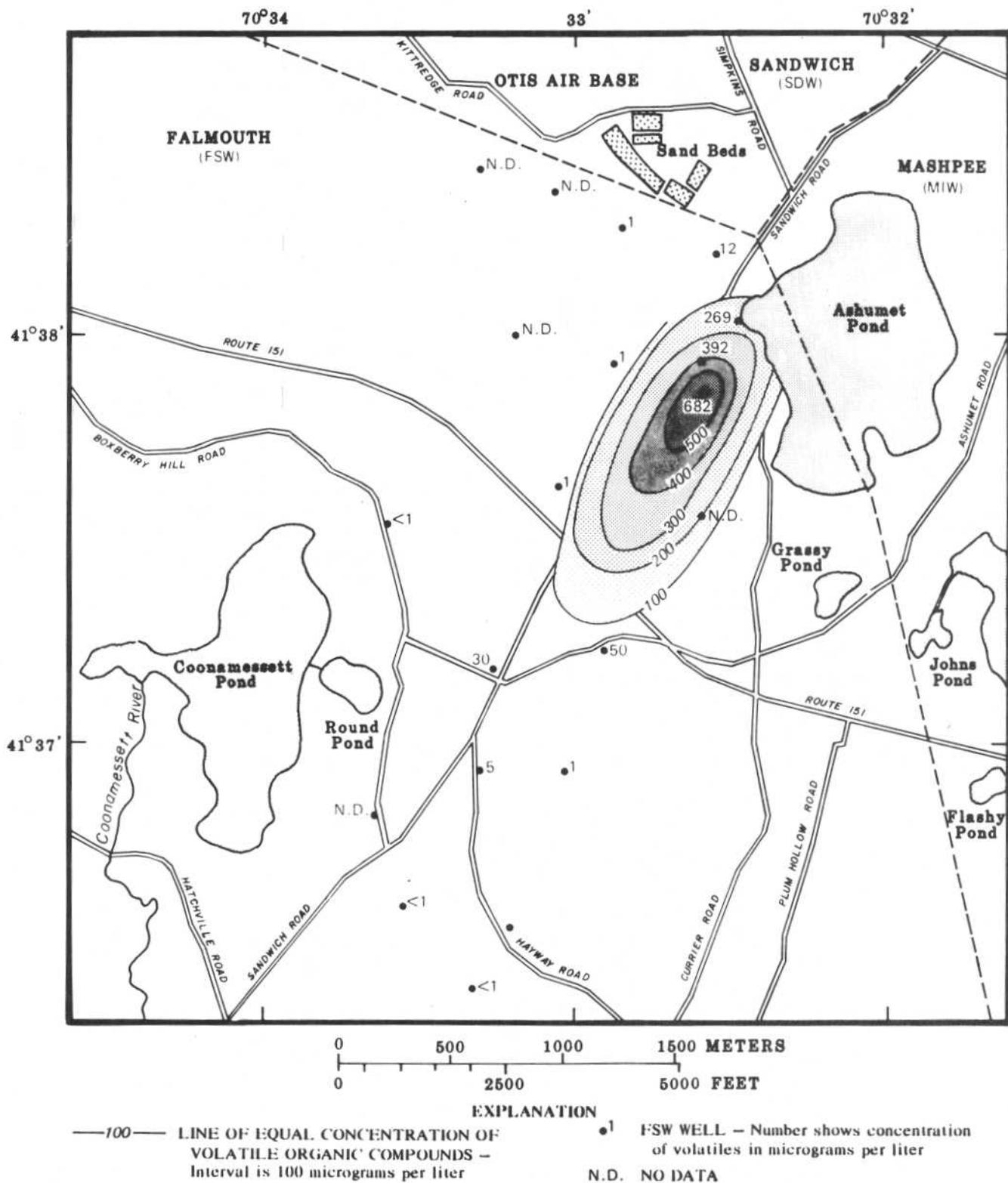


Figure 35.--Distribution of tri- and tetrachloroethene in ground water, 1983, by purge and trap technique.

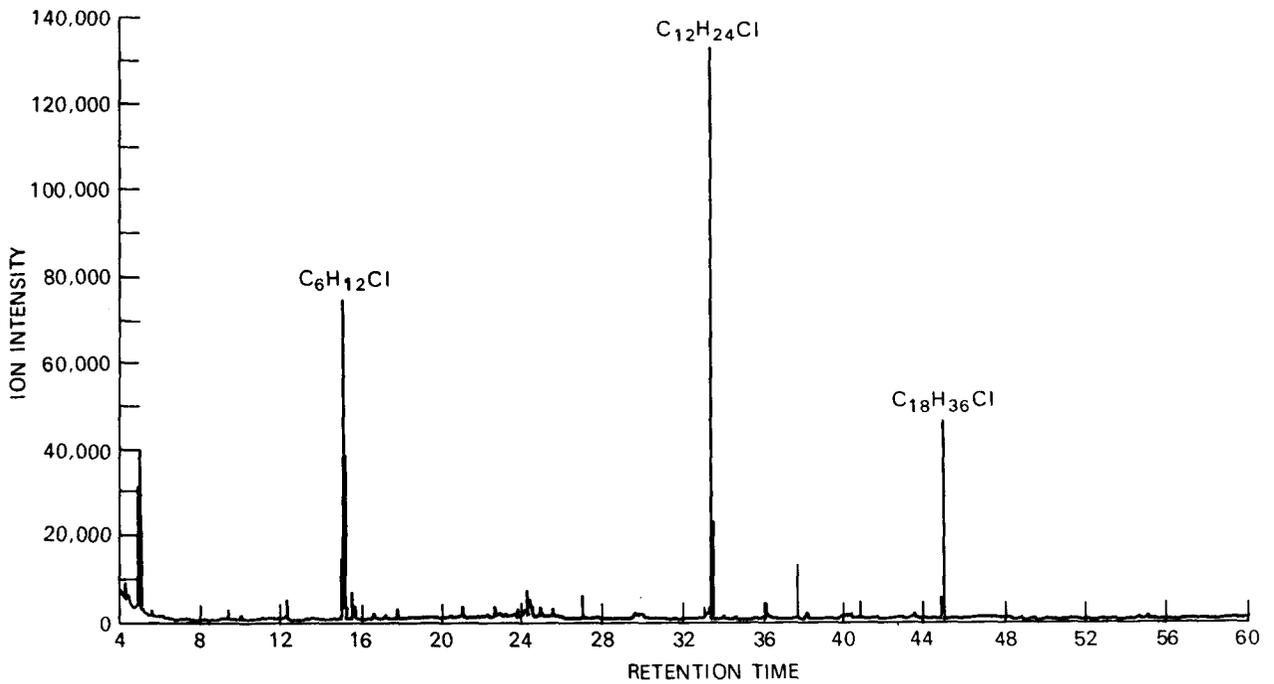


Figure 36.--Total ion chromatogram for gas chromatography/mass spectrometry analysis of closed-loop stripping extract from well FSW 242-77.

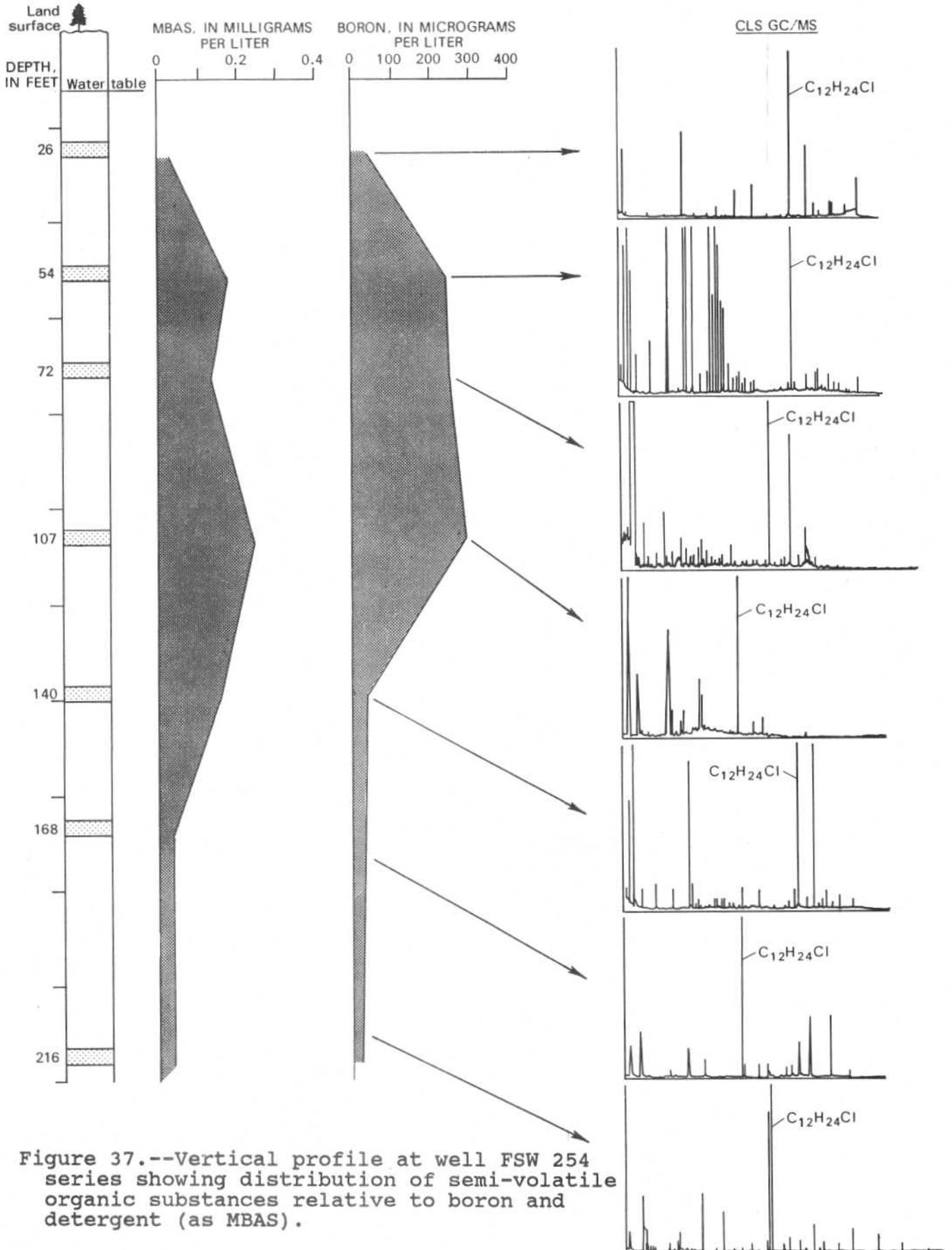


Figure 37.--Vertical profile at well FSW 254 series showing distribution of semi-volatile organic substances relative to boron and detergent (as MBAS).

Table 12. Semi-volatile organic compounds tentatively identified by mass spectra library fits from GC/MS analysis of closed-loop stripping extract, well FSW 254-26.

<u>COMPOUND</u>	<u>CONCENTRATION ng/L</u>
1. Octanal	7
2. Nonanal	19
3. Decanal	22
4. 1-(1,1-dimethylethyl-1,3-propanediyl ester propanoic acid	52

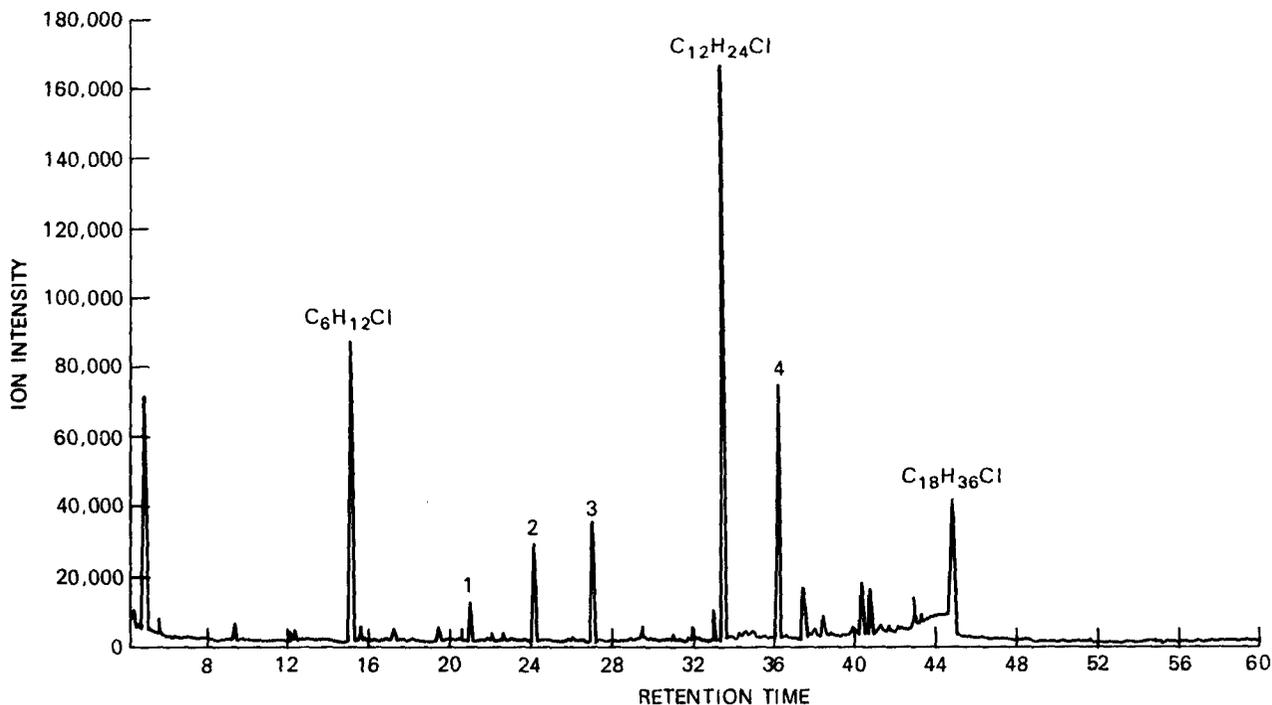


Figure 38.--Total ion chromatogram for gas chromatography/mass spectrometry analysis of closed-loop stripping extract from well FSW 254-26.

Table 13. Semi-volatile organic compounds tentatively identified by mass spectra library fits from GC/MS analysis of closed-loop stripping extract, well FSW 254-54.

<u>COMPOUND</u>	<u>CONCENTRATION ng/L</u>
1. Trichloroethene	185
2. 2,2,4-trimethyl-1-pentene	48
3. 2,3,4-trimethyl-2-pentene	33
4. Methylbenzene	64
5. Tetrachloroethene	1640
6. Dimethylbenzene (+ isomers)	470
7. Methyl ethylbenzene (+ isomers)	270
8. Propylbenzene	18
9. Trimethylbenzene (+ isomers)	450
10. Dichlorobenzene isomers	50
11. Tetramethylbenzene isomers	63
12. Nonanal	11
13. 2,3-dihydro-5-methyl-1H-indene	13
14. Decanal	10
15. 2,6-bis-di-t-butyl-p-benzoquinone	113
16. Hexadecane	11
17. Heptadecane	10
18. Octadecane	12

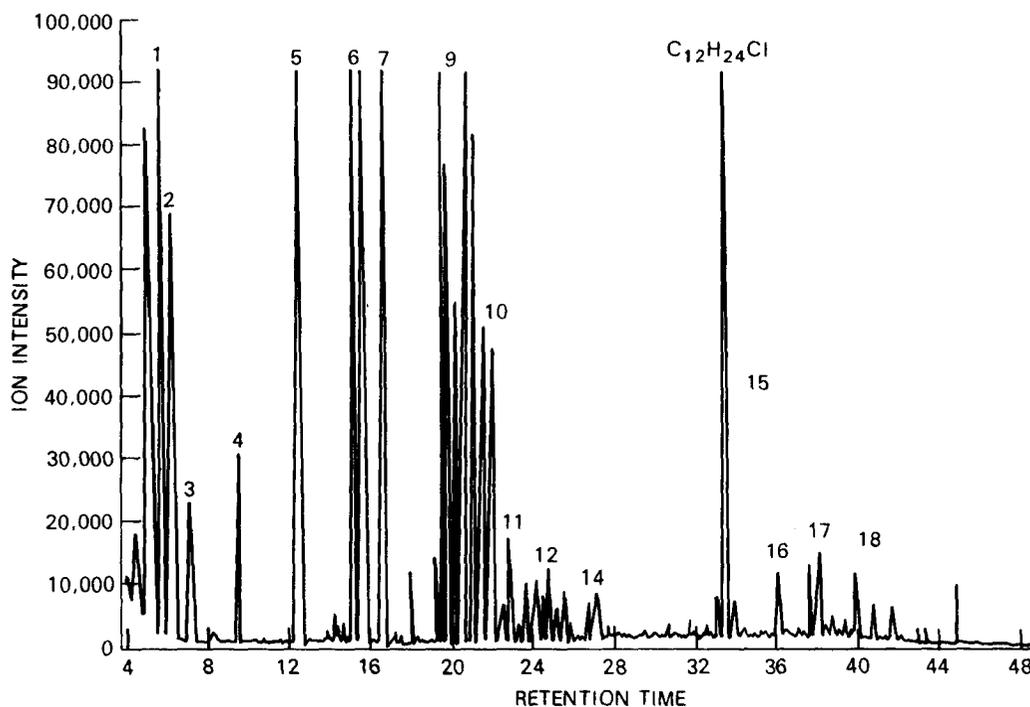


Figure 39.--Total ion chromatogram for gas chromatography/mass spectrometry analysis of closed-loop stripping extract from well FSW 254-54.

Table 14. Semi-volatile organic compounds tentatively identified by mass spectra library fits from GC/MS analysis of closed-loop stripping extract for well FSW 254-140.

<u>COMPOUND</u>	<u>CONCENTRATION ng/L</u>
1. Trichloroethene	1219
2. 2,3-dimethyl-2-butanol	14
3. Methylbenzene	24
4. Tetrachloroethene	22
5. Ethylbenzene	10
6. Dimethylbenzene isomers	33
7. Trimethylbenzene isomers	20
8. 2,2,4,4-tetramethyl-3-pentanone	10
9. Octanal	7
10. Nonanal	15
11. Decanal	15
12. 2,6-bis-di-t-butyl-p-benzoquinone	70
13. 3-methyl-1-butanolbenzoate	13
14. Farnesol	11
15. Dibutyl phthalate	11

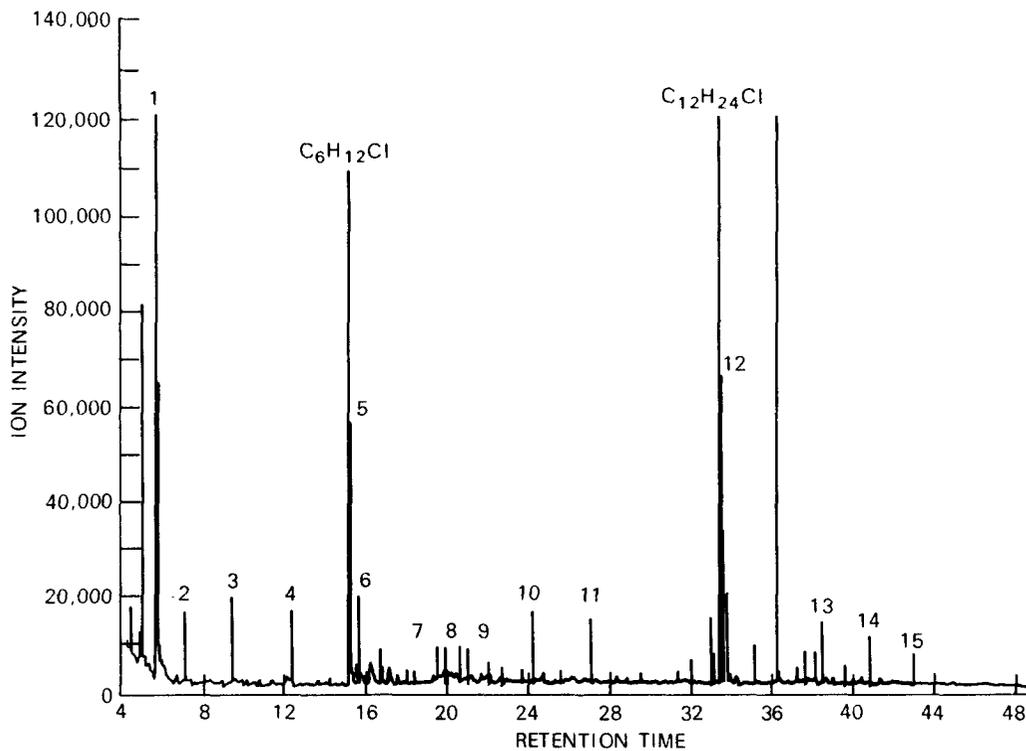


Figure 40.--Total ion chromatogram for gas chromatography/mass spectrometry analysis of closed-loop stripping extract from well FSW 254-140.

compounds present and their concentrations. In fact, single point values can easily lead to misinterpretations.

Samples analyzed by the purge and trap GC/MS method give considerably higher concentrations than those analyzed by CLS GC/MS for tri- and tetrachloroethene where concentrations of these compounds exceed 10 to 20 µg/L (Thurman and others, 1984). However, results for samples with low concentrations (less than 10 µg/L) give comparable values for the two methods if differences in sorbate amount and sample size are considered. The differences for the high-level samples are probably due to overloading of the 1.5 mg charcoal trap; thus, a portion of the contaminants may be recirculated without being trapped.

CONCLUSIONS

Closed-loop stripping (CLS) for the concentration of semi-volatile trace-level organic compounds from water, combined with gas chromatography/mass spectrometry (GC/MS) analysis, can be used successfully to establish the distribution of contaminants in ground water. To make a study more cost-effective, gas chromatography can be combined with other detectors, such as flame ionization or electron capture, to identify areas that are contaminated. Selected samples can then be analyzed by GC/MS for specific-compound identification. By picking appropriate indicator compounds that are amenable to CLS GC/MS analysis for a particular source of pollution, the occurrence of low-level contamination and the distribution of contaminants can be readily determined.

In the case of the OAB contaminant plume, three compounds serve as good tracers of sewage effluent: (1) trichloroethene; (2) tetrachloroethene; and (3) dichlorobenzene. These compounds were present in almost all contaminated ground-water samples analyzed. Chlorinated ethene compounds are widespread environmental contaminants; trichloroethene is the most frequently cited organic contaminant in ground water (Council on Environmental Quality, 1981). The distribution of the above three compounds corresponded closely with the distribution of inorganic and gross organic constituents within the plume. In addition, over 40 organic compounds were tentatively identified. They include chlorinated benzenes, alkylated benzenes, saturated and unsaturated aliphatic hydrocarbons, chlorinated aliphatic hydrocarbons, phthalates, alkylated phenols, and aldehydes.

Several discrete plumes of different classes of semi-volatile compounds were identified within the plume that was defined from inorganic measurements. The existence of these subplumes can be the result of several factors including different retardation factors for the various compounds; variations in the source input in time, space, and concentration;

and influence of geologic structure on the direction and rate of flow.

The plume of tri- and tetrachloroethene contamination was determined by two analytical methods: closed-loop stripping (CLS) combined with GC/MS analysis, and purge and trap combined with GC/MS analysis. The CLS concentration technique allows the determination of organic compounds at the 1 to 10 ng/L level, whereas the purge and trap method has a higher detection limit of 1 to 5 µg/L. The plume defined from the CLS data had an areal extent that was considerably larger than the plume defined by purge and trap data. Thus, with the lower detection limit of the CLS method, the apparent dimensions of the plume increased significantly. This has important implications when field data are used to estimate the rate of transport for individual organic compounds in the aquifer.

In general, total recovery of the semi-volatile compounds concentrated by the CLS method amounts to only a small fraction (less than 0.1 percent) of the total dissolved carbon. Thus, it should be noted that the method is restricted in its application and cannot be used to determine the total organic contamination load. However, the compounds isolated by CLS are an important group of pollutants that are refractory and quite mobile in the ground-water environment. These compounds can be used to establish whether or not water has been contaminated by other trace-level organics.

Closed-loop stripping methodology may also be used to characterize trace-level naturally occurring organic compounds in ground water. This is an area of research that deserves more attention both to develop an understanding of the specific compounds that comprise natural dissolved organic carbon and to determine baseline data to be used in evaluating the impact of ground-water contamination.

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CHAPTER E

Microbial processes may play a key role in determining the fate of some contaminants in ground-water systems. In this paper, chemical and biological evidence are presented which show that bacteria significantly affect the distributions of organic carbon and inorganic nitrogen in the plume. Future microbiological research will focus on the zones in the plume where evidence of microbial activity was found.

EVIDENCE OF MICROBIAL PROCESSES IN SEWAGE-CONTAMINATED GROUND WATER

by Marnie L. Ceazan, David M. Updegraff, and E. Michael Thurman

Abstract

This study investigates the importance of microbial degradation of organic compounds and the transformation of inorganic compounds in the sewage plume at Otis Air Base, Massachusetts.

The number of plate-count bacteria in the water was determined by plating the ground-water samples on nutrient agar and dilute soil-extract (DSEA). The number of colony-forming units (CFU) on both nutrient agar and dilute soil-extract agar showed the same spatial distributions, but dilute soil-extract agar yielded higher numbers of colony-forming units than nutrient agar. An increase in bacterial count occurred in the contaminated zone. Evidence exists that microbially mediated denitrification, dissimilatory nitrate reduction, and nitrification could be occurring in the plume.

INTRODUCTION

Ground water contaminated by sewage effluent can be a significant problem (Burden, 1982; Jensen, 1981). Biological alteration by microorganisms may be an important factor in determining the effects of wastewater on ground-water quality (Rittman and others, 1980; Davis and others, 1981). The region of the Earth's crust considered as true soil has been studied extensively and is recognized as a zone of high biological activity; therefore, it was long thought that soils protected ground water from entry by pollutants. Early studies indicated that microbial numbers decreased sharply with depth (Waksman, 1916). Leenheer and others (1974) showed that the concentration of organic matter in pristine aquifers is typically about 1 mg/L; therefore, organic nutrients were considered to be too limited to support appreciable levels of microbial growth in ground water. Methods for sampling ground water aseptically are difficult and expensive; thus, relatively little published information is available on the microbiology of ground-water systems.

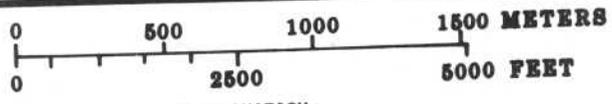
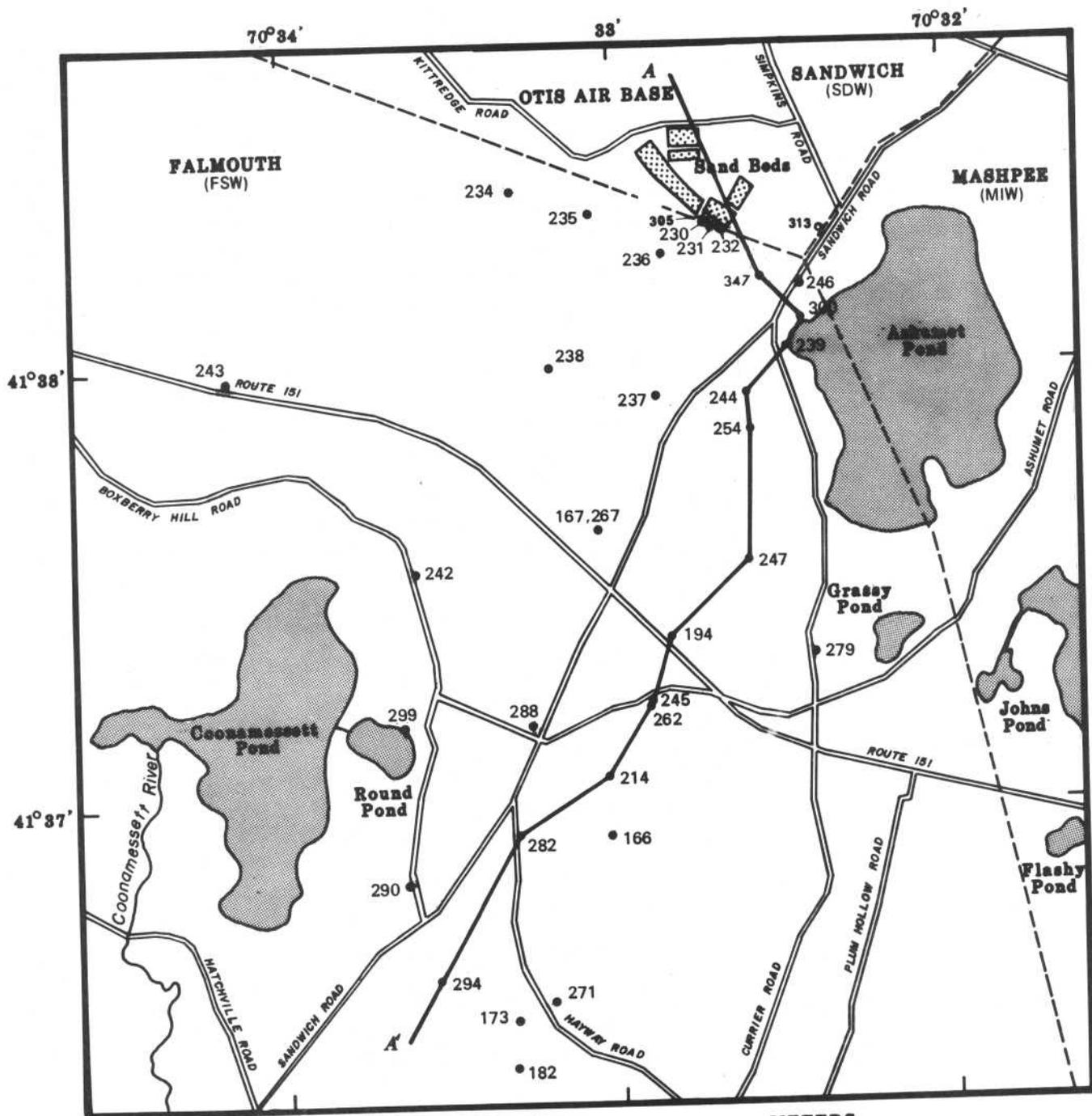
Interest in subsurface biological activity has been increasing because of widespread ground-water pollution by potentially hazardous organic compounds (Burmaster, 1982). Recently, several studies have suggested that microbes can be present at great depths in the subsurface. McNabb and Dunlap (1975) suggest that most subsurface environments are suitable as microbial habitats. As an example, nitrate-reducing bacteria were found at depths up to 12 feet in a study by Whitelaw and Rees (1980).

This paper describes the results of a study to determine if microorganisms potentially play a major role in determining the fate of contaminants in a sewage plume in ground water.¹ The objectives of the study were: (1) To conduct a broad reconnaissance of microbial numbers and chemical composition of the ground water in the aquifer that contains the plume; and (2) to obtain evidence that microorganisms affect distributions of selected contaminants such as ammonium (NH_4^+), nitrate (NO_3^-), and organic compounds. Subsurface biology was assessed by enumerating bacteria in water samples using standard plating techniques. Plate-count populations were then compared to nitrate, ammonium, orthophosphate (PO_4^{3-}), and dissolved organic carbon (DOC) distributions in the plume. In addition,⁴ samples were analyzed for coliform bacteria.

EXPERIMENTAL PROCEDURES

Water samples were collected during the summer of 1983 from observation wells (fig. 41) screened at different depths in the aquifer. Specific conductance, dissolved oxygen, pH, and temperature were measured at the time of collection, and samples were refrigerated at 4 °C. Bacteriological analyses and analyses for ammonium and nitrate were done within 2 days of collection. Other analyses were done later. The results of these water analyses are listed in table 15.

¹A description of the site, including its geologic and hydrologic setting, is given in Chapter A of this volume.



- EXPLANATION
- 313 ○ SDW WELL AND WELL NUMBER
 - 242 ● FSW WELL AND WELL NUMBER
 - A—A' LINE OF SECTION -- As shown in figures 42-45

Figure 41.--Location of observation wells.

Table 15.--Water sample analyses, Cape Cod, Massachusetts
July-August, 1983

[A dash indicates no analysis was available]

Well number	pH	Specific conductivity (umhos)	Dissolved oxygen ³ (mg/L)	Temperature (°C)
FSW				
166-67	5.8	100	0.8	9.5
167-55	6.0	48	10.8	9.0
173-69	5.9	122	--	10.0
182-69	5.7	80	--	9.0
194-57	5.6	145	4.4	11.5
214-60	5.6	83	--	13.5
230-48	5.4	115	--	10.5
231-57	--	145	--	12.0
232-58	5.9	153	--	12.0
234-99	6.4	122	--	12.5
235-94	--	81	--	11.0
236-106	4.9	126	--	10.0
237-88	6.4	128	--	14.0
238-106	5.2	95	--	10.0
239-64	6.6	190	.0	13.0
242-77	5.4	51	--	10.0
243-45	6.2	38	--	9.0
244-90	6.6	230	--	11.0
245-25	4.7	200	--	10.0
246-35	5.6	152	--	12.0
247-70	5.4	120	2.6	--

³The dissolved oxygen data were collected in 1979 (LeBlanc, 1982).

Table 15.--Water sample analyses, Cape Cod, Massachusetts
July-August, 1983--Continued

[A dash indicates no analysis was available]

Well number	pH	Specific conductivity (umhos)	Dissolved oxygen ³ (mg/L)	Temperature (°C)
FSW				
254-216	6.9	59	.1	10.0
254-168	6.4	115	.0	10.0
254-140	6.3	175	--	10.5
254-107	6.2	235	.0	10.5
254-72	6.7	225	.0	11.0
254-54	6.3	220	.0	10.5
254-26	4.9	70	8.1	10.0
262-159	6.7	125	--	10.0
262-85	5.9	255	.0	11.0
262-69	5.7	200	.0	11.0
262-41	5.0	90	8.0	10.0
267-155	6.7	122	--	9.0
267-136	6.0	95	8.2	9.0
267-111	5.9	120	.0	9.0
267-88	5.5	195	.0	9.0
271-165	6.9	125	--	9.0
271-141	6.9	132	--	9.0
271-85	5.0	150	--	10.0
271-41	5.2	55	--	10.0
279-86	--	76	4.3	11.0
279-61	--	73	7.3	11.0

³The dissolved oxygen data were collected in 1979 (LeBlanc, 1982).

Table 15.--Water sample analyses, Cape Cod, Massachusetts
July-August 1983--Continued

[A dash indicates no analysis was available]

Well number	pH	Specific conductivity (umhos)	Dissolved oxygen ³ (mg/L)	Temperature (°C)
FSW				
282-123	5.9	143	.8	9.0
282-94	5.7	208	.1	9.0
282-70	5.4	215	.2	10.0
282-49	6.0	100	11.4	9.0
288-97	6.3	142	.0	9.0
290-91	5.9	90	.3	10.0
294-89	6.0	139	.4	9.5
299-20	5.2	76	--	10.0
300-30	6.5	410	.0	11.5
300-10	5.2	138	5.9	13.0
347-67	6.3	302	.0	10.0
SDW				
305-32	6.2	122	--	9.5
313-60	--	100	10.0	10.0

³The dissolved oxygen data were collected in 1979 (LeBlanc, 1982).

Table 15.--Water sample analyses, Cape Cod, Massachusetts
July-August, 1983--Continued.

[A dash indicates no analysis was available]

Well number	NO ₃ (mg/L as N)	NO ₂ (mg/L as N)	NH ₄ ⁺ (mg/L as N)	Dissolved organic carbon (mg/L)
FSW				
166-67	0.92	<0.06	<0.10	1.3
167-55	<.06	<.06	<.10	1.0
173-69	2.2	<.06	<.10	1.0
182-69	1.6	<.06	<.10	1.0
194-57	1.7	<.06	1.6	2.3
214-60	2.3	<.06	.11	1.4
230-48	3.4	<.06	<.10	2.0
231-57	6.4	<.06	<.10	3.0
232-58	4.6	<.06	<.10	3.2
234-99	2.2	<.06	<.10	.9
235-94	1.3	<.06	<.10	.9
236-106	1.1	<.06	<.10	1.1
237-88	2.6	<.06	3.8	1.1
238-106	2.0	<.06	<.10	<1.0
239-64	<.06	<.06	7.0	1.9
242-77	.21	<.06	<.10	.9
243-45	.29	<.06	<.10	.8
244-90	<.06	<.06	10.7	1.8
245-25	1.2	<.06	<.10	1.0
246-35	5.0	<.06	<.10	2.0
247-70	1.4	<.06	.60	1.0
254-216	<.06	<.06	<.10	1.0

Table 15.--Water sample analyses, Cape Cod, Massachusetts
July-August, 1983--Continued.

[A dash indicates no analysis was available]

Well number	NO ₃ ⁻ (mg/L as N)	NO ₂ ⁻ (mg/L as N)	NH ₄ ⁺ (mg/L as N)	Dissolved organic carbon (mg/L)
FSW				
254-168	<0.06	<0.06	<0.10	1.1
254-140	.31	<.06	<.10	1.9
254-107	1.0	<.06	<.10	2.3
254-72	.08	<.06	9.1	2.8
254-54	.57	<.06	7.6	3.2
254-26	.80	<.06	.15	1.2
262-159	.32	<.06	<.10	2.0
262-85	.32	<.06	<.10	3.7
262-69	2.9	<.06	2.1	2.8
262-41	1.4	<.06	<.10	1.0
267-155	.19	<.06	<.10	2.0
267-136	1.8	<.06	<.10	1.0
267-111	3.7	<.06	<.10	1.0
267-88	3.5	<.06	7.6	1.2
271-165	<.06	<.06	<.10	1.0
271-141	.56	<.06	<.10	2.0
271-85	.98	<.06	<.10	2.0
271-41	.07	<.06	<.10	1.0
279-86	.42	<.06	<.10	1.0
279-61	.25	<.06	<.10	<1.0
282-123	.28	<.06	<.10	3.1

Table 15.--Water sample analyses, Cape Cod, Massachusetts
July-August, 1983--Continued.

[A dash indicates no analysis was available]

Well number	NO ₃ (mg/L as N)	NO ₂ (mg/L as N)	NH ₄ ⁺ (mg/L as N)	Dissolved organic carbon (mg/L)
FSW				
282-94	0.78	<0.06	<0.10	4.0
282-70	1.36	<.06	<.10	4.2
282-49	<.06	<.06	<.10	1.9
288-97	3.8	<.06	2.3	2.2
290-91	2.1	<.06	<.10	1.0
294-89	1.4	<.06	<.10	3.1
299-20	3.1	<.06	<.10	2.0
300-30	14	<.06	5.3	3.5
300-10	.26	<.06	<.10	1.0
347-67	<.06	<.06	2.1	4.0
SDW				
305-32	3.8	<.06	<.10	3.0
313-60	.90	<.06	<.10	1.0

Table 15.--Water sample analyses, Cape Cod, Massachusetts
July-August, 1983--Continued.

[A dash indicates no analysis was available]

Well number	DSEA counts (CFU/mL)	NA counts (CFU/mL)	MPN (coliform)
FSW			
166-67	7	540	0*
167-55	1,490	370	0
173-69	35	--	--
182-69	5	--	0
194-57	24	--	0
214-60	11	--	0
230-48	1,570	540	0
231-57	332	--	--
232-58	910	280	0
234-99	26	--	0
235-94	27	--	0
236-106	219	90	0
237-88	90	80	0
238-106	259	65	0
239-64	800	288	0
242-77	27	--	0
243-45	--	--	--
244-90	640	176	0
245-25	7	--	0
246-35	17	11	0
247-70	46	--	--

*0 = negative, *+ = positive*, D = doubtful

Table 15.--Water sample analyses, Cape Cod, Massachusetts
July-August, 1983--Continued.

[A dash indicates no analysis was available]

Well number	DSEA counts (CFU/mL)	NA counts (CFU/mL)	MPN (coliform)
FSW			
254-216	1,500	550	0
254-168	1,130	390	0
254-140	1,500	700	0
254-107	5,670	3,000	0
254-72	22,680	22,580	0*
254-54	5,100	3,480	0
254-26	470	240	0
262-159	5,600	--	--
262-85	7,100	1,950	+*
262-69	570	318	0
262-41	15	5	0
267-155	1,020	560	0
267-136	1,150	68	0
267-111	40	16	0
267-88	180	77	0
271-165	3,400	1,420	0
271-141	11	12	0
271-85	1,150	50	0
271-41	10	6	0
279-86	80	69	0
279-61	50	13	0

*0 = negative, *+ = positive*, D = doubtful

Table 15.--Water sample analyses, Cape Cod, Massachusetts
July-August, 1983--Continued.

[A dash indicates no analysis was available]

Well number	DSEA counts (CFU/mL)	NA counts (CFU/mL)	MPN (coliform)
FSW			
282-123	120	80	0
282-94	4,500	2,700	0
282-70	1,060	490	0
282-49	--	--	0
288-97	1,400	1,140	0
290-91	11	5	0
294-89	18,140	2,390	0
299-20	80	--	0
300-30	300	57	0
300-10	17	13	0
347-67	160	70	0
SDW			
305-32	--	350	0
313-60	50	17	0

*0 = negative, *+ = positive*, D = doubtful

Analysis of Inorganic Constituents

Specific conductance was measured with a conductivity meter, and dissolved oxygen² was assayed with a Yellow Springs Instrument Company dissolved oxygen meter. Temperature was measured with an ordinary mercury thermometer and pH was measured with a glass electrode pH meter.

Nitrate analysis was done at a laboratory on site using the colorimetric cadmium-reduction method (American Public Health Association, 1981). Nitrate is reduced to nitrite in the presence of cadmium. Nitrite is then diazotized with sulfanilamide, and coupled with N-(1 naphthyl)-ethylenediamine, to form a highly colored dye. The concentration of this dye is measured colorimetrically at 540 nm. Correction for any nitrite present in the sample is made by analyzing without the reduction step.

Water samples were analyzed for ammonium by colorimetric analysis. The method was adapted from the automated method used by the U.S. Geological Survey National Water Quality Laboratory, Arvada, Colorado (Skougstad and others, 1979). Inorganic ammonium reacts with sodium salicylate and sodium nitroferricyanide in an alkaline medium to form a colored compound, the absorbance of which is directly proportional to the ammonium concentration.

Samples were analyzed for phosphate by the same laboratory by an automated colorimetric method (Skougstad and others, 1979). Orthophosphate ion reacts with ammonium molybdate in acidic solution to form phosphomolybdic acid. When phosphomolybdic acid is reduced with ascorbic acid, an intensely colored blue complex is formed that is measured by a colorimeter at 660 nm.

Dissolved Organic Carbon

Dissolved organic carbon (DOC) analyses were done by Huffman Laboratory (Arvada, Colorado) using a 5020 Coulometrics total carbon apparatus. After filtration through a Selas 0.45 μm silver membrane filter, the sample is acidified to pH 2 with hydrochloric acid, and purged to remove inorganic carbon. A 0.2-mL aliquot of sample is injected into the carbon analyzer where carbon is completely oxidized to carbon dioxide in an oxygen atmosphere at 1,000°C. The combustion gases are swept into a Coulometrics carbon dioxide coulometer, and the carbon dioxide in the gas stream is measured.

Enumeration of Viable Cells

Plate counts were made on nutrient agar and dilute soil-extract agar by the pour-plate method (Ghiorse and Balkwill, 1981). Dilute soil-extract agar (DSEA) is prepared by autoclaving 500 g of sandy-loam surface soil in 500 mL of distilled water for one hour at 121°C. The resulting extract is filtered. The filtrate is diluted tenfold with distilled water, and is amended with 1.5 percent Bactoagar. Media are sterilized by autoclaving at 121°C for 20 minutes.

²The use of trade names is for descriptive purposes only, and does not constitute endorsement by the U.S. Geological Survey.

Because of the large number of samples and time limitations, plate counts were not replicated, but, in every case three serial dilutions were done, and there seemed to be satisfactory agreement between dilutions. Volumes of 1-mL, 0.1-mL, and 0.01-mL water samples were added to pour plates of Difco nutrient agar and DSEA agar. These plates were incubated for one week at 22 to 24°C. After the incubation period, the number of colony-forming units per milliliter (CFU/mL) were counted. Coliform bacteria were determined with the MPN (most probable number) presumptive coliform test (American Public Health Association, 1981) using three tubes of lauryl tryptose broth for each dilution. Confirmational tests were not performed.

EVIDENCE OF MICROBIAL PROCESSES

Temperature, pH, and Specific Conductance

The temperature of samples of ground water collected from wells ranged from 9.0 to 13.5°C, and pH ranged from 5.3 to 7.1 pH units. Uncontaminated ground water has a specific conductance of 40-80 µmhos, whereas the treated sewage has a specific conductance of 400 µmhos. Specific conductance has been used previously by LeBlanc (1982) to delineate the plume. Conductivity is a useful indicator of the extent of the plume because the specific conductance of the treated sewage is much higher than that of uncontaminated ground water.

A vertical section of the specific conductance data along the axis of the plume is shown on figure 42. The area of conductivity greater than 200 µmhos extends at least 11,000 feet downgradient and is 85 feet thick 3,000 feet downgradient from the sand beds. The area of highest specific conductance is immediately adjacent to the sand beds.

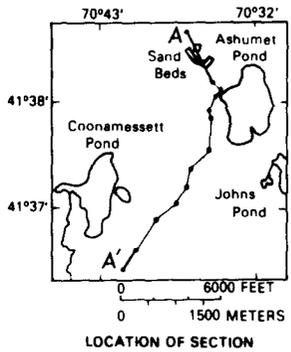
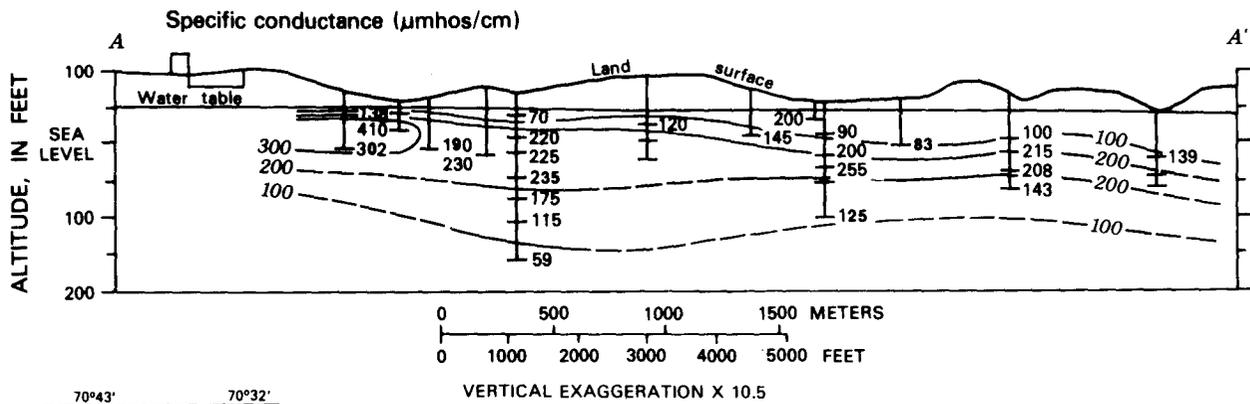
Dissolved Oxygen

The distribution of dissolved oxygen in ground water is shown in figure 43. Data from 1979 (LeBlanc, 1982) were used because the dissolved oxygen data for 1983 are questionable due to mechanical problems with the dissolved oxygen meter. Within 5,000 feet of the sand beds, dissolved oxygen is present in a thin boundary zone (about 25 feet thick) along the top of the plume. Dissolved oxygen in this zone is derived from recharge through the sandy soils that are low in organic matter content (LeBlanc, 1982). Dissolved oxygen is not present in the center of the plume within 5,000 feet of the sand beds.

At about 6,000 feet downgradient from the sand beds, dissolved oxygen is found in the center of the plume. The presence of dissolved oxygen at this location is caused by mixing of the contaminated and uncontaminated ground water, and possibly by insufficient oxygen demand. No dissolved oxygen was found below the plume in the deeper part of the aquifer.

Nitrate, Ammonia, and Phosphate

Domestic sewage contains many organic and inorganic nitrogen compounds derived from human wastes and food wastes. Nitrogen in organic compounds is readily converted to ammonium by bacterial processes. The inorganic species are predominantly ammonium and nitrate. The nitrate concentration in the effluent is 12 mg/L and is about twice as high as the ammonium concentration in the effluent (6.4 mg/L).



EXPLANATION

-  SITE OF SEWAGE PLANT AND SAND BEDS
-  WELL SITE -- horizontal lines indicate points sampled. Number is specific conductance in micromhos per centimeter at 25 Celsius.
-  --200-- LINE OF EQUAL SPECIFIC CONDUCTANCE -- Shown in micromhos per centimeter. Dashed where inferred.

Figure 42.--Vertical distribution of specific conductance in ground water, July-August 1983.

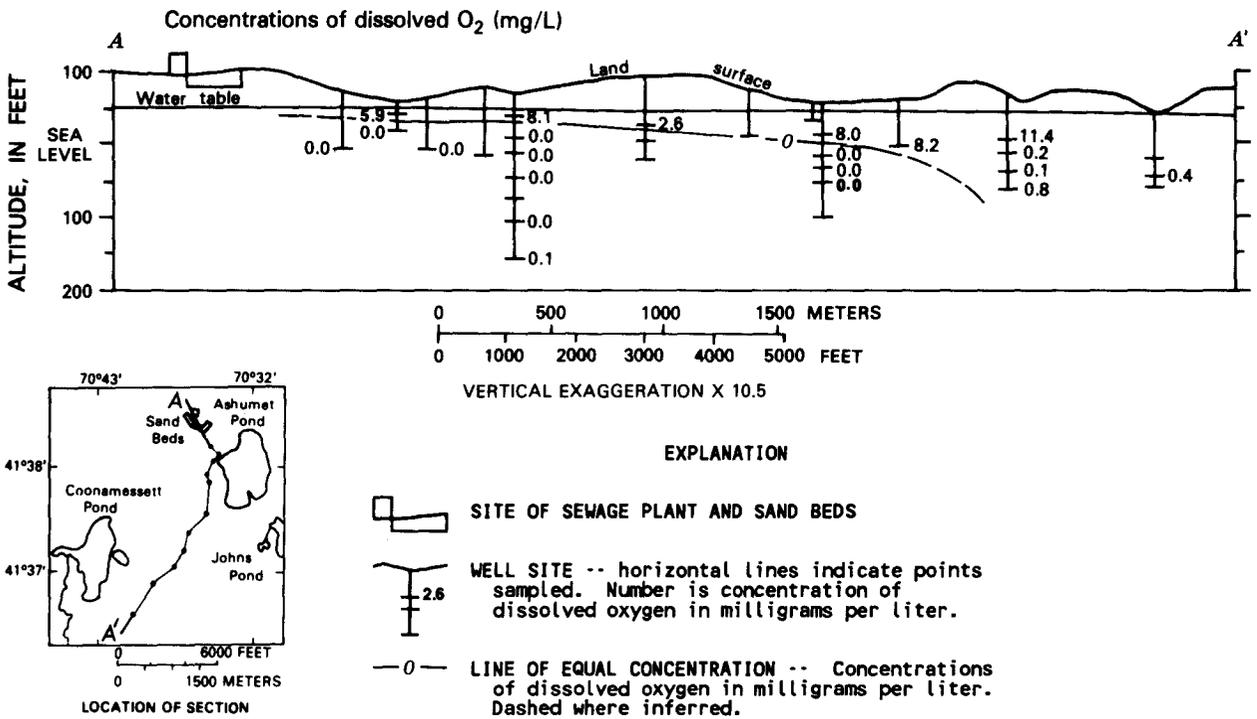


Figure 43.--Vertical distribution of dissolved oxygen in ground water, May 1978 through May 1979 (from LeBlanc, 1982).

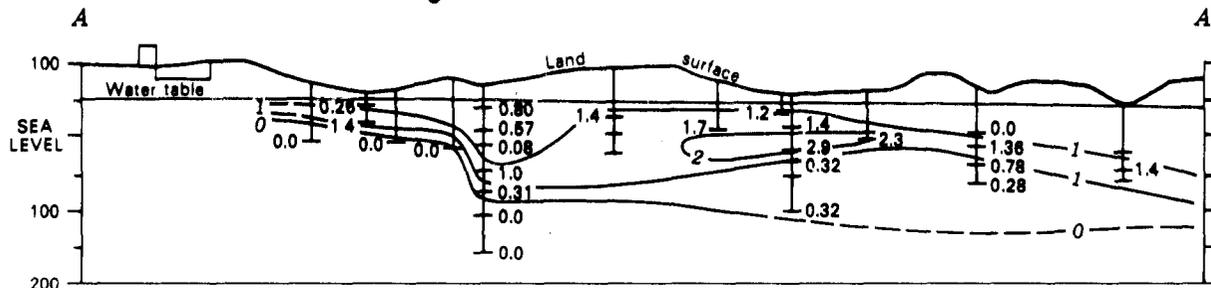
As can be seen in figure 44, the ammonium plume (indicated by the area with concentrations greater than 2 mg/L) extends 8,000 feet downgradient of the sand beds. The highest ammonium concentrations are 1,000 to 3,000 feet from the sand beds. The area where nitrate concentrations are greater than 1 mg/L extends at least 11,000 feet from the sand beds. Higher nitrate concentrations (greater than 2 mg/L) are found about 6,000 feet downgradient. The distribution of nitrate in 1983 is similar to the distribution in 1978-79 (LeBlanc, 1982).

Although the nitrate concentration in the effluent is 12 mg/L, the concentration of nitrate in the center of the plume is only 2.9 mg/L. Studies have shown that nitrate is readily reduced in anaerobic soils and sediment (Smith and others, 1982). Two types of bacterially mediated nitrate reduction can occur: (1) Nitrate assimilation, which involves uptake of nitrate by the cells, reduction to ammonium and incorporation into microbial cellular material; and (2) nitrate respiration, which is a dissimilatory process whereby nitrate functions as the terminal electron acceptor in the absence of oxygen. Nitrate respiration consists of two possible mechanisms: (1) Denitrification, which is the reduction of nitrate to molecular nitrogen; and (2) dissimilatory nitrate reduction, which is the reduction of nitrate to ammonium. The loss of nitrate as the effluent enters the aquifer may result from denitrification because the product is a gaseous species. Also, it is evident from figure 44 that the zone of high ammonium concentration is generally coincident with the zone of low nitrate concentration; therefore, dissimilatory nitrate reduction, in which ammonium is being produced, is another possible nitrate sink.

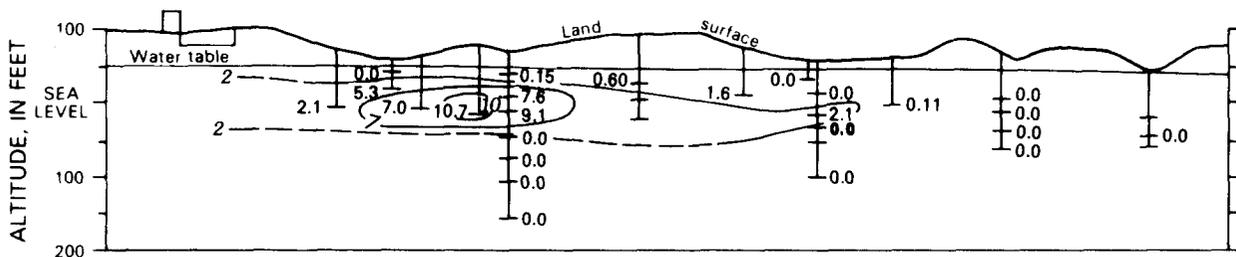
Within 6,000 feet of the sand beds, the predominant nitrogen species in the plume is ammonium. At 6,000 feet from the source of contamination, the predominant chemical species of inorganic nitrogen changes from ammonium to nitrate. LeBlanc (1982) suggested that the observed ammonium-nitrate distributions could be explained by nitrification. The process of nitrification is the oxidation of ammonium to nitrate by the nitrifying bacteria Nitrosomonas and Nitrobacter. These organisms generally grow autotrophically, although it has been shown that some species of Nitrobacter grow heterotrophically (Kalthoff and others, 1979; Smith and others, 1982; Bock, 1976). Autotrophic organisms are not inhibited by the low carbon content of ground water, and previous studies have shown that nitrifiers are indigenous to ground water (Behnke, 1975). Dissolved oxygen is a requirement for nitrifying bacteria. At about 6,000 feet downgradient from the sand beds, dissolved oxygen is present in the center of the plume; corresponding decreases in ammonium and increases in nitrate in this area indicate that nitrification may be occurring here. Nitrate, but no ammonium is present beyond 8,000 feet from the sand beds.

Most phosphorus in secondarily treated sewage is in the form of orthophosphate. The average concentration of orthophosphate in treated sewage is 7 mg/L; yet, orthophosphate has not moved more than 1,000 feet from the sand beds (fig. 44). One explanation for this is that phosphate may precipitate as the minerals hydroxyapatite ($K_{sp}=10^{-57.8}$) and fluoroapatite ($K_{sp}=10^{-60.4}$). Calcium (0.4 to 17.0 mg/L) and fluoride (0.01 to 0.27 mg/L) are both present in the plume; thus, phosphate may be removed near the infiltration beds. Alternatively, phosphate may be removed by bacterial uptake.

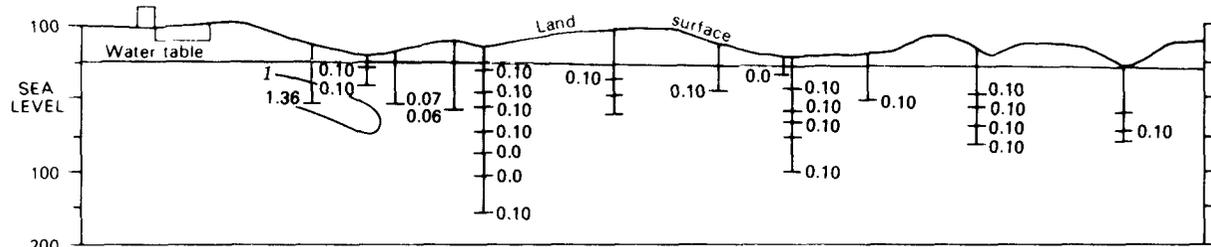
Concentrations of NO_3^- (mg/L as N)



Concentrations of NH_4^+ (mg/L as N)



Concentrations of $(\text{PO}_4)^{3-}$ (mg/L as P)



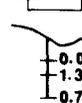
0 500 1000 1500 METERS
0 1000 2000 3000 4000 5000 FEET

VERTICAL EXAGGERATION X 10.5

EXPLANATION



SITE OF SEWAGE PLANT AND SAND BEDS



WELL SITE -- Horizontal lines indicate points sampled. Number is concentration in milligrams per liter.



LINE OF EQUAL CONCENTRATION -- Concentrations of nitrate, ammonia, and phosphate in milligrams per liter. Dashed where inferred.

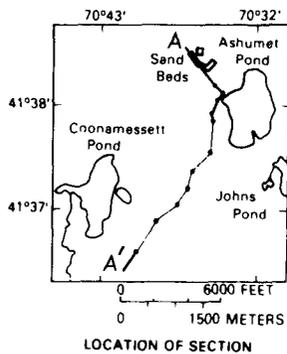


Figure 44.--Vertical distribution of nitrate, ammonia, and phosphate in ground water, July-August, 1983.

Plate Counts

The counts on nutrient agar and dilute soil-extract agar (DSEA) give similar spatial profiles of the plume (fig. 45). The plate counts show areas of elevated bacterial counts (greater than 4,000 CFU/mL for DSEA and greater than 2,000 CFU/mL for nutrient agar) that extend at least 11,000 feet downgradient from the sand beds. These profiles indicate a positive response of the microbial population to the chemical plume as delineated by conductivity, nitrate, and DOC.

Nutrient agar is a rich organic medium while DSEA has lower levels of organic nutrients. In general, DSEA medium yielded higher cell counts and smaller colonies than nutrient agar. Similar results have been found in other aquifer systems (Ghiorse and Balkwill, 1981; Wilson and others, 1983). Wilson and his coauthors concluded that DSEA medium was preferred over rich organic media because higher numbers of plate count bacteria were obtained with DSEA. In a ground-water system where organisms are adapted to oligotrophic conditions, it is not surprising that DSEA was the preferred medium.

It is important to understand that plate counts are not total cell counts. Because of the existence of aggregates of cells, several cells may produce just one colony. Also, some microorganisms from the subsurface may not grow on nutrient agar or DSEA.

Dissolved Organic Carbon

The shape and extent of the dissolved organic carbon (DOC) plume is similar to the conductance plume. Two locations of high DOC were found (fig. 45). One area is in the immediate vicinity of the sand beds; the other area is 8,000 to 9,000 feet downgradient from the sand beds, where 50 percent of the DOC is in the form of nonbiodegradable detergents (Thurman and others, 1984). The detergent plume does not correlate with the plate counts, and it is not biodegradable.

The DOC in the effluent is 12 mg/L; however, within 1,000 feet of the sand beds, the DOC is quickly depleted to 1-2 mg/L. Microbes in the subsurface are likely a major mechanism for the removal of organic matter. The relationships between depth, distance from the sand beds, DOC, and bacterial populations for the well clusters FSW 254, FSW 262, and FSW 282 are shown in table 16. In general, depth profiles of bacterial plate counts display a pattern similar to depth profiles of DOC. In addition, a strong similarity exists between DOC distribution and bacterial counts along a horizontal transect away from the sand beds (fig. 45), which suggests that microbial processes are involved in the removal of organic matter in this ground-water system. A corresponding increase in alkalinity within 1,000 to 2,000 feet of the infiltration beds also suggests that microbial processes are mineralizing organic carbon to carbon dioxide (Thurman and others, 1984).

Coliforms

Coliform bacteria (specifically fecal coliform) inhabit the intestines of warm-blooded animals, and are typically present in sewage; therefore, these bacteria serve as indicators of potential fecal pollution. Previous studies have shown that coliforms are not transported in ground water. Vecchioli and others (1972) found that coliforms generally were not transported very far from an injection well because of filtration. A study on the movement of coliforms from a septic tank effluent (Reneau and Pettry, 1975) indicated that total and fecal coliforms decreased significantly with horizontal

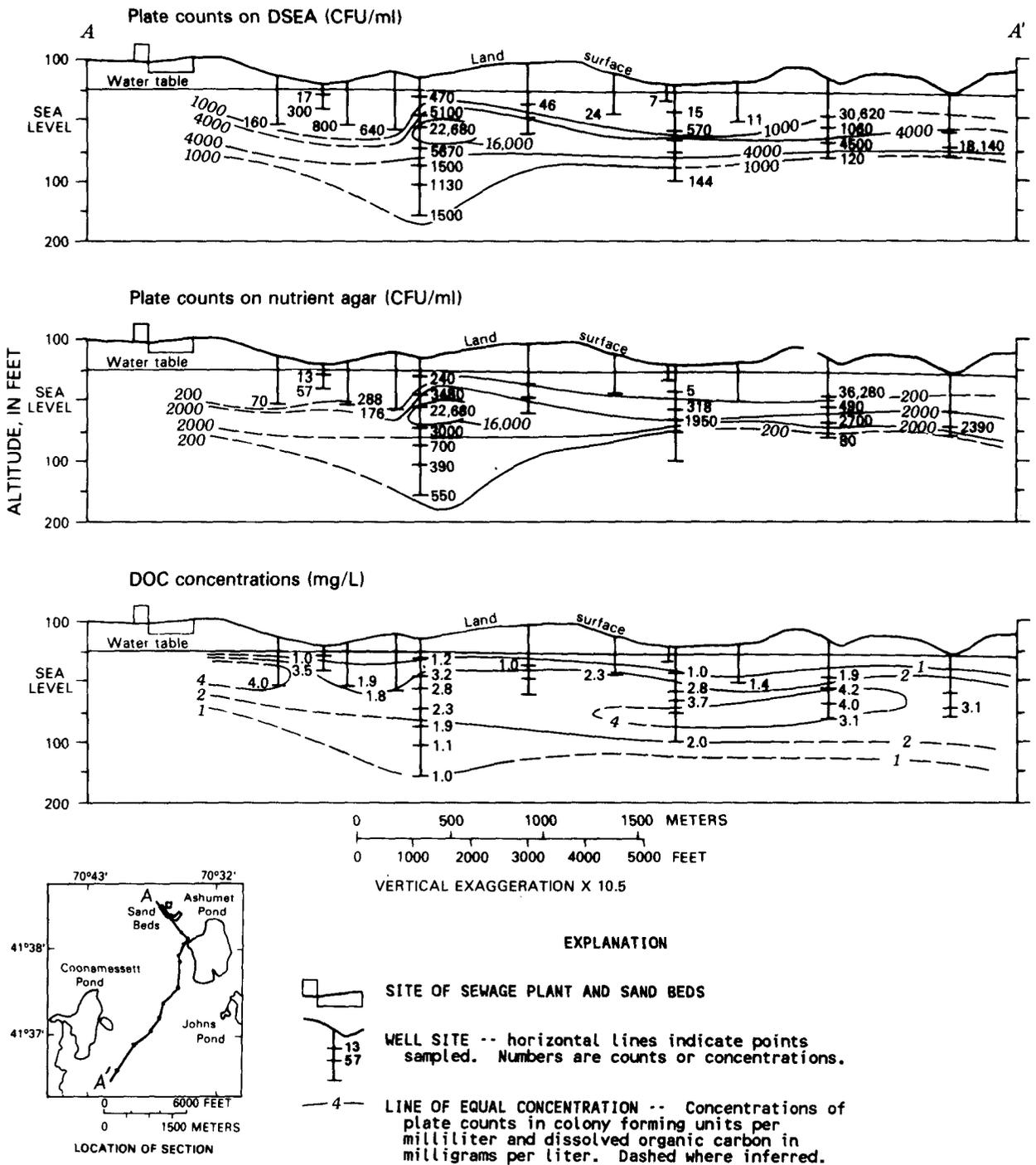


Figure 45.--Vertical distribution of plate counts and dissolved organic carbon in ground water, July-August 1983.

Table 16--Dissolved organic carbon concentrations and bacterial counts
in ground water, July-August 1983.

[a dash indicates no analysis was available]

Well number	Depth from surface	Distance from beds (ft)	DOC (mg/L)	DSEA plate counts (CFU/mL)
FSW 254-216	216	3000	1.0	1500
254-168	168	3000	1.1	1130
254-140	140	3000	1.9	1500
254-107	107	3000	2.3	5670
254-72	72	3000	2.8	22680
254-54	54	3000	3.2	5100
254-26	26	3000	1.2	470
262-159	159	7000	2.0	144
262-109	109	7000	4.0	5600
262-85	85	7000	3.7	7100
262-69	69	7000	2.8	570
262-41	41	7000	1.0	15
282-123	123	9000	3.1	120
282-94	94	9000	4.0	4500
282-70	70	9000	4.2	1060
282-49	49	9000	1.9	----

distance and depth. More recently, however, Rahe and others (1978) found movement rates of 1500 cm/hour for Escherichia coli in soils under conditions of saturated flow. The same study indicated that Escherichia coli survived for at least 96 hours in the soils, and could be used as tracers for subsurface water flow.

In this study, no coliform bacteria could be detected, except in wells FSW 254-107 and FSW 262-85 (see figure 41 for location of wells). Neither of these wells is in the vicinity of the sand beds; therefore, coliforms from the sewage do not appear to be transported. The reason that coliform bacteria were detected in two of the wells is unknown, and these wells should be resampled next field season.

SUMMARY AND CONCLUSIONS

During the summer of 1983, a broad reconnaissance of microbial numbers and chemical composition in the plume of sewage-contaminated ground water was conducted at Otis Air Base, Cape Cod, Massachusetts. Water analyses reveal that microbial processes may play a major role in determining the fate of contaminants in the ground water. Smith and Duff (1984) have conducted a study of denitrification in the plume. Other pertinent processes, such as nitrification and bacterial uptake of organics, should be investigated.

The major conclusions of this study are:

1. Nitrate is present in high concentrations in the sewage effluent, but is depleted in the zone of contamination within 1000 feet of the sand beds. This implies that a nitrate sink exists within the aquifer which may be a result of denitrification, nitrogen assimilation to organic nitrogen, and reduction of nitrate to ammonium.
2. Ammonium is present in high concentrations a short distance downgradient of the sand beds and is depleted or absent further downgradient where nitrate levels are elevated and oxygen is present. This implies that ammonium is being oxidized to nitrate, perhaps by microbial nitrification.
3. Colony counts on nutrient agar and dilute soil-extract agar give comparable spatial distributions.
4. Dilute soil-extract agar is a better medium than nutrient agar for bacterial enumeration from subsurface environments.
5. The removal of dissolved organic carbon in the plume appears to be due, in part, to microbial degradation.

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CHAPTER F

The previous paper by Ceazan, Updegraff, and Thurman presented evidence that bacteria are degrading and transforming contaminants in the plume. In this paper, the size, distribution, and general level of activity of the bacterial population is evaluated at several locations in the aquifer. This information is needed to determine the rates and conditions under which these microbes degrade and transform contaminants.

MICROBIAL DISTRIBUTION AND HETEROTROPHIC UPTAKE IN A SEWAGE PLUME

by Ronald W. Harvey, Richard L. Smith, and Leah George

ABSTRACT

The bacterial abundance, distribution, and heterotrophic uptake in ground water contaminated by treated sewage at Otis Air Base, Massachusetts, was determined from ground water and sediment-core samples. Numbers of free-living bacteria in contaminated ground water declined steadily with increasing distance from the infiltration sand beds where the treated sewage recharges the aquifer. The numbers decline from $1.94 \pm 0.20 \times 10^6$ mL⁻¹ (per milliliter) at 0.21 km (kilometers) from the beds to $0.25 \pm 0.02 \times 10^6$ mL⁻¹ at 0.97 km from the beds. Bacterial abundances in ground water sampled from a cluster of wells located 0.31 km from the beds correlated strongly with specific conductance and increased sharply from $0.04 \pm 0.003 \times 10^6$ mL⁻¹ at depth of 6 m (meters) to $1.58 \pm 0.12 \times 10^6$ mL⁻¹ at a depth of 14 m, then declined at depths of 20 m and 31 m to $1.29 \pm 0.12 \times 10^6$ mL⁻¹ and $0.96 \pm 0.12 \times 10^6$ mL⁻¹, respectively. A majority of the bacteria in contaminated and uncontaminated zones of the aquifer were bound to surfaces of particulates with diameters of less than 60 micrometers. Glucose-uptake rates, assayed at in situ and 5 μ M (micromolar) concentrations, declined steadily in ground water sampled along a transect that extends from 0.64 to 1.80 km. A preparative wet-sieving technique for use in processing core samples for bacterial enumeration was found to yield higher counts than a previously used preparative settling technique.

INTRODUCTION

Microbial degradation of organic contaminants in ground water has been a subject of considerable recent interest, but little is known about sizes, distributions, and activities of bacterial populations in freshwater aquifers. Much of our present information derives from studies performed on well water samples. However, a majority of the bacterial population in the saturated zone of the terrestrial subsurface may be associated

with solid surfaces and would not be accounted for in such investigations. Also, few definitive studies have dealt with the response of ground-water bacteria to significant organic contamination.

A study was made to examine partitioning of aquifer bacteria between solid surfaces and solution. This information may be useful in predicting the fate of organic contaminants in ground water. Another objective was to examine the relationship between bacterial numbers and uptake rates for glucose in contaminated ground water as a function of distance from the source of contamination. The hypothesis is that localized organic contamination of oligotrophic ground water should result in a zone in which size and activity of the bacterial population is dependent, in part, upon concentrations of readily-degraded organics and, hence, distance from the source of contamination. In this report, we describe the effect of ground-water contamination upon bacterial abundances, distribution, solid/solution partitioning, and glucose uptake rates in a plume formed by land disposal of treated sewage on Cape Cod, Massachusetts¹. We also evaluate a preparative technique used in conjunction with acridine-orange epifluorescence to enumerate particle-bound bacteria in aquifer core material.

The authors thank D.R. LeBlanc, W. Nichols, and others with the New England District for their help and technical assistance.

EXPERIMENTAL PROCEDURES

Collection of Samples

Water samples for microbial assays were obtained from a network of screened, PVC (polyvinyl-chloride) observation wells that are 3.8 or 5.0 cm in diameter. The wells, which have PVC screens with slots 250 μm wide, are located along the path of the plume (fig.46). At three sites located 0.21, 0.31 and 2.9 km from the infiltration beds, clusters of wells screened at a different depth were sampled to obtain depth profiles of the plume. A stainless-steel submersible pump (model SP-81, Keck Geophysical Instruments, Inc. Okemos, Michigan) connected to Teflon tubing was used to sample ground water from the wells. Samples were taken in sterile glass and plastic bottles after three to five well volumes had been pumped and specific conductance and pH had stabilized. Plastic gloves were worn during the sampling procedure to reduce sample contamination from skin-associated flora. Samples used for total bacterial counts were fixed immediately with glutaraldehyde (0.2 percent weight per volume final concentration); all samples were kept on ice during transport and stored at 4°C in the laboratory. Where possible, samples were processed within 48 hours.

Six core samples of aquifer sediments were collected at depths ranging from 12 to 32 m below land surface at distances of 0.21 and 2.93 km from the source of contamination. This was

¹A description of the site, including its geologic and hydrologic setting, is given in chapter A of this volume.

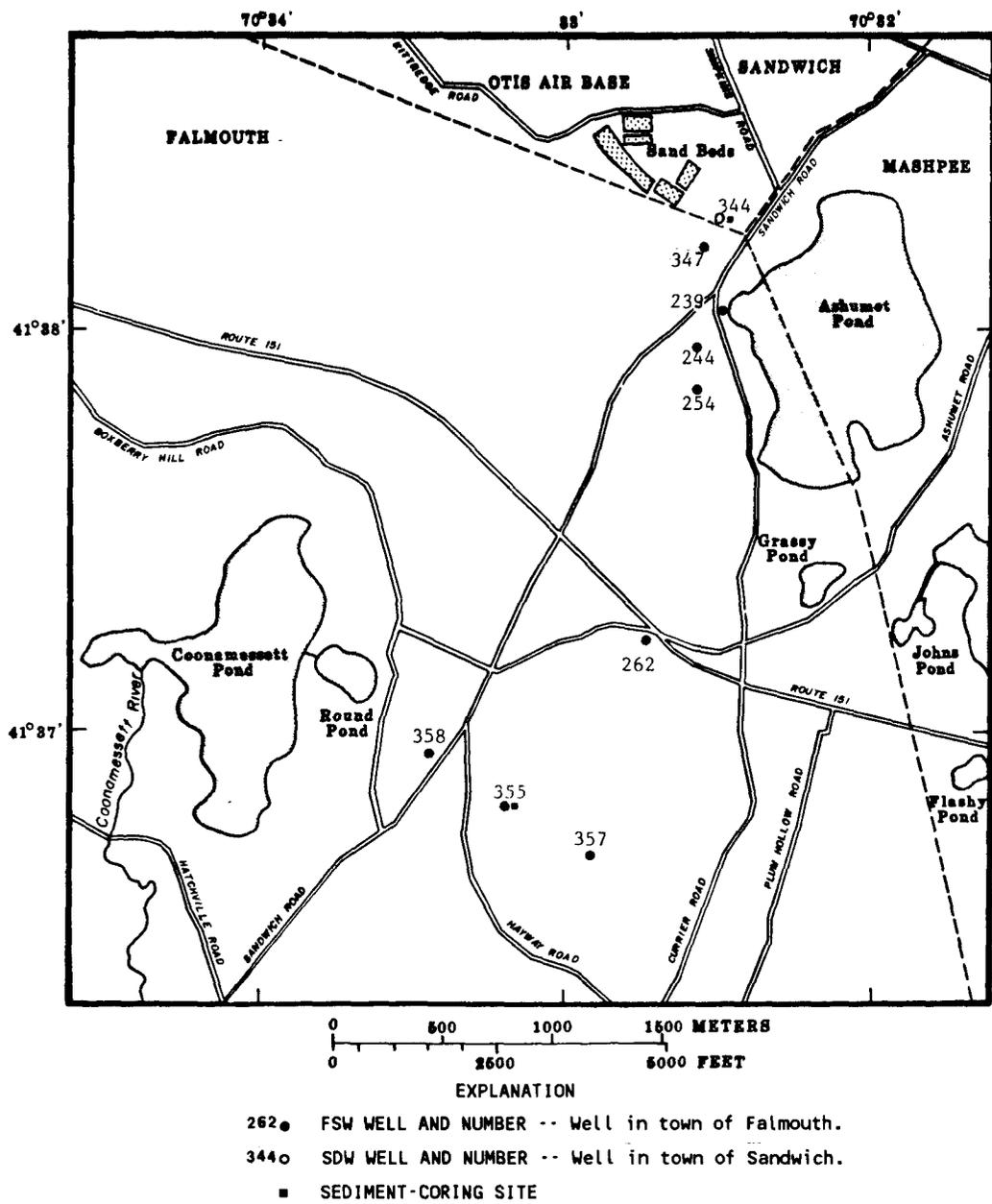


Figure 46.--Study area and data-collection sites.

accomplished by means of a split-spoon sampling device lowered down the hollow barrel of an auger drilling rig and driven 0.3 to 0.6 m below the bottom of the augers. Approximately 1 kg of solid aquifer material was stored in sterile 500 mL bottles and kept on ice until processed. Data obtained from core samples were compared to that obtained from ground water sampled from adjacent wells at equivalent depths.

Enumeration of Bacteria

Free-living bacteria in well-water samples were enumerated using an acridine-orange direct counting (AODC) procedure (Hobbie and others, 1977). Since quantities of abiotic suspended particulates in sampled well water were low, between 1 and 40 ml of undiluted sample could be used for each acridine-orange preparation. The amount of sample used depended upon bacterial abundance. Particle-bound bacteria, which constituted less than 5 percent of the total sample population, were not enumerated. A Leitz Dialux 20 microscope, fitted for epifluorescence (HBO 100w Hg lamp, H-2 barrier/exciter filter system with K480 quenching filter, 100x (1.32NA) NPL Fluotar iris objective) was used to enumerate bacteria at a total magnification of 1000x.

Enumerations of adherent bacteria in core samples were made for four particle-size fractions. Core subsamples of approximately 100 g were weighed and aseptically wet-sieved through a sequential series of mesh filters having progressively smaller mesh openings: 105 μ m (polypropylene), 60 μ m (nylon), and 20 μ m (nylon) (Spectrum Medical Industries, Inc.). Sieved particulates were collected in sterile 400 mL Pyrex beakers containing approximately 100mL of water. Particles retained on each mesh filter were voided of remaining interstitial water using a gentle rinse and collected in 250 mL polypropylene bottles, which were then filled with filter-sterilized water. All preparative operations were performed using a laminar flow hood (greater than 99.9 % efficiency at 0.3 μ m), surgical gloves, sterile apparatus, and filter-sterilized (0.2 μ m), Milli-Q purified water (18 megaohm resistivity). Levels of contamination introduced in sample processing were accounted for with a control blank, which was prepared by NaOH-washing (0.1N) of a subsample prior to the preparative procedure.

Well-stirred, 250-mL suspensions of size-fractionated particulates in the three smaller size fractions were sampled by Eppendorf pipet and assayed for solids content and population density of adherent bacteria (Ruble and Dornseif, 1978). For the largest size fractions, which consisted of sand grains with diameters greater than 105 μ m, adherent bacteria were enumerated on individual grains embedded in 0.1 percent agar under 500x magnification. Calculated concentrations of adherent bacteria were expressed both as numbers per unit dry weight of size-fractionated and total sediment samples and as numbers per unit volume of aquifer material. Porosities used in these calculations were estimated from amounts of water which could be added to dry, weighed core material occupying a known volume. The wet-sieving procedure was compared to a preparative settling technique described in an earlier subsurface microbial study

(Wilson and others, 1983). In the latter study, a 2-minute settling procedure was used to void core-material suspensions of the largest sand grains, which interfere in the enumeration procedure.

Tritiated-glucose uptake by ground-water bacteria was measured in four well water samples obtained along an 0.6 km-long transect within the plume. Four 50 mL aliquots of each sample were placed in plastic 50 mL syringes which were then sealed with rubber-stoppered injection hubs. One syringe was injected with NaOH (0.1N final concentration) and served as a killed control. A second syringe was amended with glucose (5 μ M final concentration). All syringes were injected with similar quantities of 3 H-glucose (New England Nuclear, 14.5 Ci/mmol, 3.6 uCi total), shaken, and incubated at 12°C. The third and fourth syringes were assumed to contain near in-situ concentrations of glucose, since final concentrations of added 3 H-glucose were 5 nM. A 10 mL subsample from each syringe was filtered through a Gelman metricel filter (0.2 μ m pore size, 25 mm diameter) after 0, 5, 10, 22, and 48 hours of incubation. The filters were then clarified in 10 mL of aquasol, dark-adapted, and assayed for 3 H activity by liquid scintillation counting using the internal standard addition (3 H-toluene) method for quench-factor correction.

MICROBIAL DISTRIBUTION AND HETEROTROPHIC UPTAKE

Microbial Distribution

Concentrations of ground-water bacteria along the path of the plume are depicted as a function of distance from the infiltration beds in figure 47. Bacterial numbers in ground water sampled from the middle of the plume declined sharply from $1.94 \pm 0.20 \times 10^6$ mL⁻¹ at 0.21 km from the beds to $0.25 \pm 0.02 \times 10^6$ mL⁻¹ at 0.93 km. However, bacterial counts in contaminated ground water from the three more distant sampling locations ($0.21 \pm 0.02 \times 10^6$ mL⁻¹, average) were significantly higher than counts for uncontaminated ground water ($0.04 \pm 0.005 \times 10^6$ mL⁻¹) sampled in the same region but from a shallower depth.

Bacterial numbers in the well water as a function of the depth of the well screen at two sites located 0.21 and 0.31 Km from the beds are shown in figure 48. At both sites, bacterial abundance was lowest in samples taken from the shallowest well, increased at the next depth, and decreased in the two deepest wells. At the site located 0.31 km from the beds, bacterial concentrations increased from $0.04 \pm 0.003 \times 10^6$ mL⁻¹ at 6m below land surface to $1.58 \pm 0.12 \times 10^6$ mL⁻¹ at 14 m, a 40-fold increase within 8 m. Specific conductance increased over four fold in these same samples from 68 μ mhos to 300 μ mhos. Numbers of free-living bacteria at both sites correlated strongly with specific conductance. The coefficients of determinations (r^2) at the two sites were 0.91 and 0.96 ($p < 0.05$).

Counts of surface-attached bacteria per unit volume of aquifer for six core samples taken in the saturated zone are listed in table 17. Counts of free-living bacteria in water collected from wells screened at the same depth as the cores are

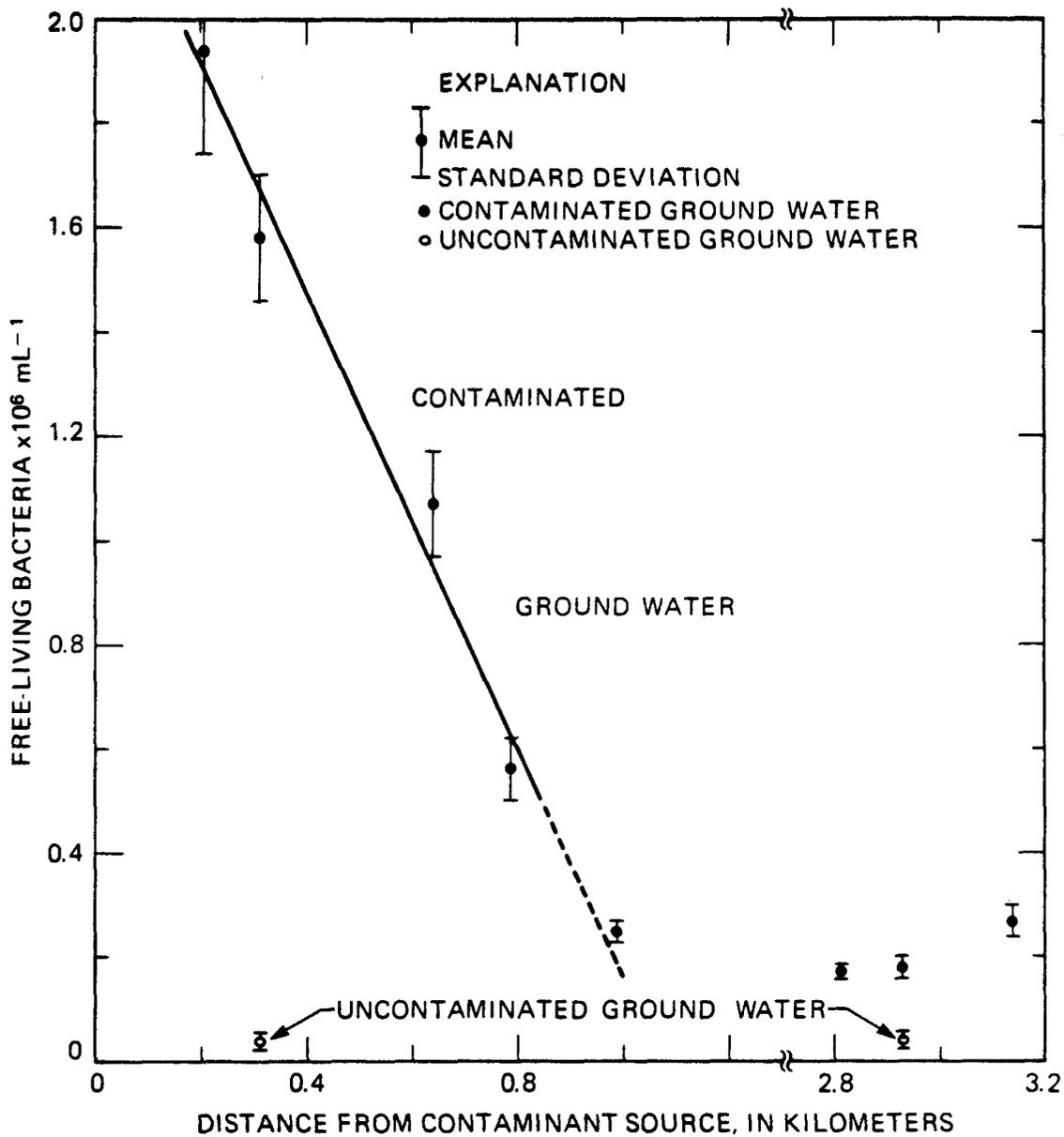


Figure 47. Numbers of free-living bacteria in ground water versus distance from sewage disposal beds. Straight line indicates the best fit using linear regression ($r^2=0.98$ at $p \leq 0.05$).

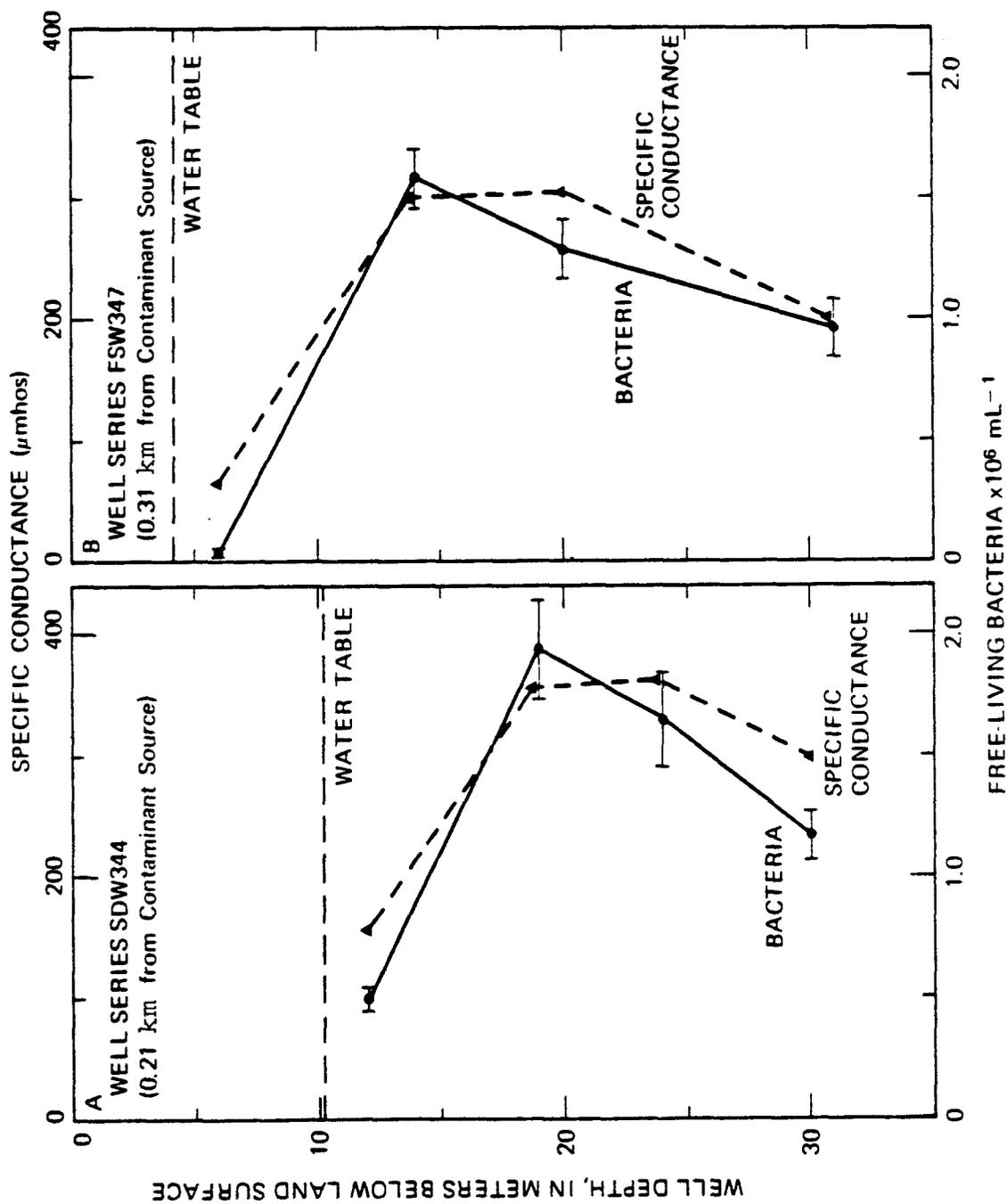


Figure 48. Numbers of free-living bacteria and specific conductance versus depth below land surface for two clusters of observation wells located 0.21 km (A) and 0.31 km (B) from the sewage disposal area. Difference in water-table depth between the two well clusters is due to topographical variation.

Table 17. Bacterial numbers and distribution in contaminated and uncontaminated zones

Distance to contaminant source (km)	Sample depth (m)	Ground water specific con- ductance (μ hos)	Bacteria (per cm ³ aquifer material)		
			Free-living ¹	Particle-bound ²	(percent bound)
0.21	12	158	1.87±0.19×10 ⁵	1.84±0.22×10 ⁷	(98.9)
0.21	19	355	6.42±0.66×10 ⁵	1.94±0.29×10 ⁷	(96.8)
0.21	25	365	5.38±0.62×10 ⁵	4.04±0.38×10 ⁷	(98.7)
0.21	31	300	3.98±0.34×10 ⁵	2.29±0.18×10 ⁷	(98.3)
2.93	24	70	1.59±0.19×10 ⁴	3.09±0.46×10 ⁷	(100)
2.93	32	265	6.98±0.74×10 ⁴	2.43±0.17×10 ⁷	(99.7)

¹Determined from well water bacterial abundance and porosity data.

²Determined from porosity data and abundances of adherent bacteria in core samples taken adjacent to screens of sampled wells.

Table 18. Average distribution of aquifer solid material and adherent bacteria among four size fractions and portions lost after 2 minutes of settling during a preparative procedure used in enumeration of soils bacteria

Size fraction (μ m)	Relative distribution ¹		Lost during 2 minutes settling ¹	
	Particulates (percent)	Adherent bacteria (percent)	Particulates (percent of size class)	Adherent bacteria (percent of total population)
<20	0.97±0.65	67.3±7.61	38.8±6.8	26.1±5.45
20-60	0.95±0.66	22.8±5.75	92.5±2.6	21.1±5.35
60-105	1.03±0.65	9.85±3.93	99.1±1.1	9.76±3.90
>105	97.1±1.89	0±0	100±0	0
Totals:	100	100	--	57.0±8.58

¹Average and standard error computed for six core samples taken from contaminated and uncontaminated zones in the Cape Cod aquifer.

also shown in table 17. The free-living counts in the water samples were multiplied by the measured porosity of the corresponding cores to convert them to counts per unit volume of aquifer. A majority of the bacteria in all samples were attached to particulates. Portions of the total sample population associated with solid surfaces ranged from 98 percent at 0.21 km from the beds and 19 m below land surface to 100 percent at 2.93 km and 24 m. Population densities of adherent bacteria ranged from $1.84 \pm 0.22 \times 10^7 \text{ cm}^{-3}$ to $6.06 \pm 0.57 \times 10^7 \text{ cm}^{-3}$ of aquifer material, whereas population densities of free-living bacteria varied from $1.59 \pm 0.19 \times 10^5 \text{ cm}^{-3}$ to $6.42 \pm 0.66 \times 10^5 \text{ cm}^{-3}$. Variations in abundances of adherent bacteria at 0.21 km correlated with changes in specific conductance, as did numbers of free-living bacteria in adjacent well samples (fig. 48). However, no significant differences were found between abundances of adherent bacteria for the two sites where cores were collected.

Average distributions of the adherent bacterial population among particle-size fractions in the six core samples are listed in table 18. A majority of the adherent bacteria (67 ± 7 percent) were associated with particles smaller than 20 μm diameter, which constituted only about 1 percent of the total particulate mass of the sample. In contrast the largest particulate size-fraction constituted a majority (97 ± 2 percent) of the total particulate mass, but harbored an insignificant portion of the adherent bacterial population.

Portions of particulates and adherent bacteria that would settle out from well-mixed suspensions during 2 minutes of quiescent settling are also given in table 18. Most of the particulate mass in the three largest size fractions and greater than 38 percent of the particles less than 20 μm in diameter settled out of solution within 2 minutes. The total quantity of particulate matter settling out during this procedure corresponded to a loss of 57 ± 9 percent of the adherent bacterial population from suspension. Much of the population loss was accounted for in the size fractions with diameters less than 60 μm .

Heterotrophic Uptake

Uptake rates of glucose in four ground-water samples taken between 0.64 and 1.8 km from the sand beds are illustrated in figure 49. Significant increases in uptake at both in-situ and 5 μM glucose concentrations were observed as distance from the source of contamination decreased. Uptake rates in glucose-amended (5 μM) samples were 10.6 and 35.9 $\text{nM} \cdot \text{day}^{-1}$, for contaminated ground water from wells located 1.80 and 0.64 km from the beds, respectively. Uptake rates were more comparable when corrected for differences in the sizes of the bacterial populations. Specific uptake rates in amended samples collected from wells at 1.80 and 0.64 km were 3.36×10^{-17} and 2.47×10^{-17} Moles $\cdot \text{bacterium}^{-1} \text{ day}^{-1}$, respectively.

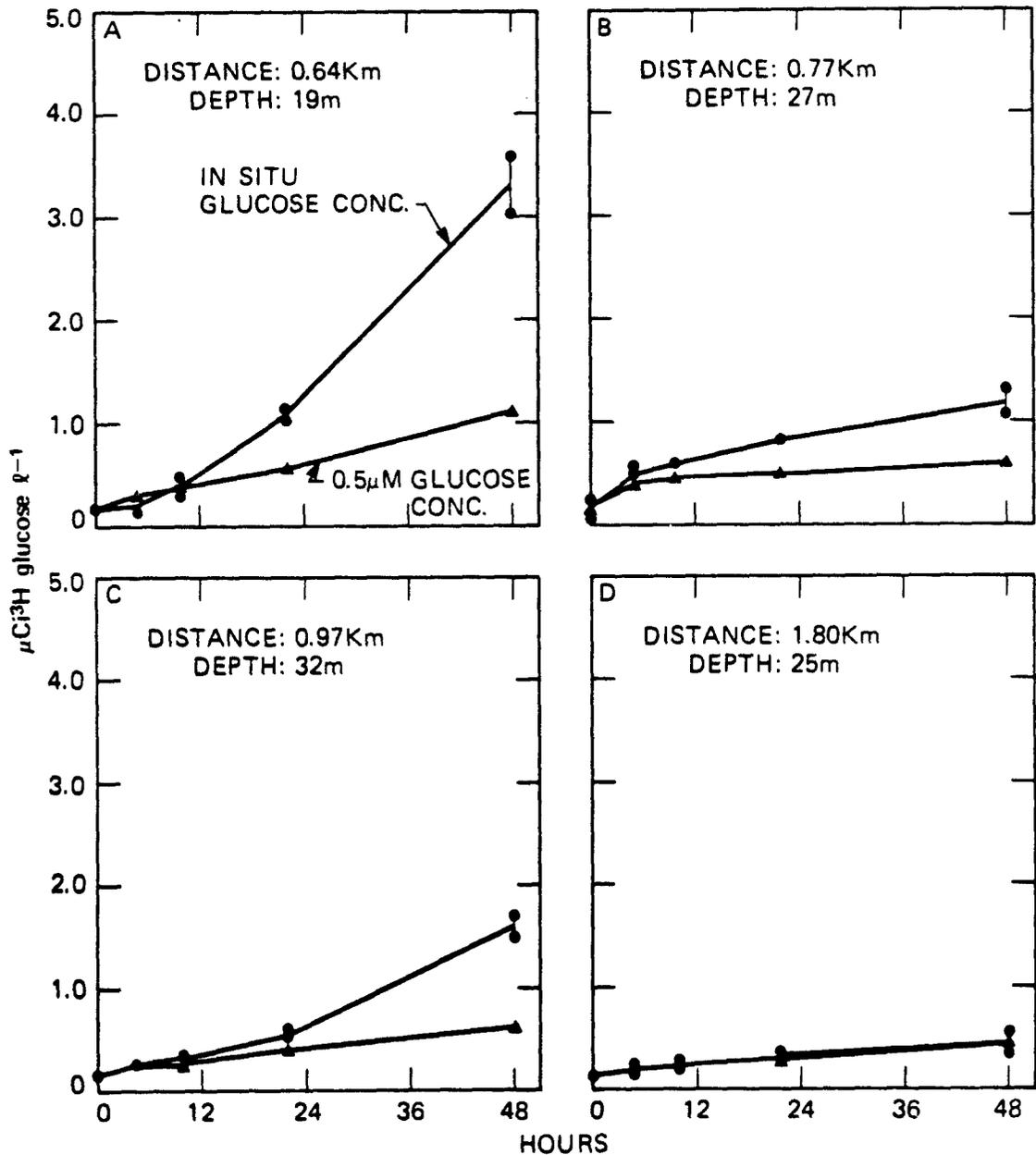


Figure 49. Uptake of ^3H -glucose versus time for four contaminated ground-water samples taken along the path of the plume at distances of 0.64 and 1.80 kilometers from the sewage-disposal area. Uptake of glucose in killed controls (not shown) was not significant.

RELATION OF BACTERIA TO PROXIMITY TO CONTAMINATION SOURCE

The strong correlation between abundance of free-living ground-water bacteria and proximity to the source of contamination (fig. 47) within 1 km of the infiltration beds suggests an influence from contaminant organics. This is also corroborated by data on glucose uptake rates, which were generally higher for contaminated ground-water samples taken closer to the source of contamination. However, much of the observed differences in glucose uptake rates among glucose-amended samples may be explained by differences in the sizes of the bacterial populations. Since ^3H -glucose autoradiography was not performed, uptake rates could not be expressed in terms of numbers of bacteria involved in active uptake of glucose. Nevertheless, these data suggest that bacterial populations in the plume closer to the infiltration beds may utilize readily-degraded organic compounds at higher rates than populations further downgradient.

The lack of correlation between numbers of free-living bacteria in contaminated ground water farther than 1.0 km from the beds and proximity to the infiltration beds (fig. 47) may reflect the more refractory nature of dissolved organic material (DOM) in this portion of the plume. Much of the DOM assayed in contaminated ground water sampled from the more distant observation wells consisted largely of highly-refractory detergents (Thurman and others, 1984). Since bacterial abundances in these samples are still significantly higher than those observed in uncontaminated samples from the same region, the plume may still have a measureable effect upon microbial biomass at distances of 2 to 3 km from sewage disposal site.

The variation in specific conductance and bacterial abundance in ground water sampled in the two depth profiles (fig. 48) illustrates the three-dimensional nature of the plume. The linear relationship between specific conductance and abundance of free-living bacteria appears to be an indirect one. Since specific conductance of the treated sewage (400 μmhos) is 4 to 5 times higher than the specific conductance of uncontaminated ground water (50 to 80 μmhos), observed variations in specific conductance within vertical transects through the plume reflect the degree of dilution with uncontaminated ground water. Therefore, specific conductance indirectly reflects dilution of other contaminants which do influence bacterial abundance. The free-living bacterial counts of $0.04 \pm 0.003 \times 10^6 \text{ mL}^{-1}$ observed in the uncontaminated ground-water sample (specific conductance equals 68 μmhos), collected from a well 0.21 km from the beds and 6 m deep, were similar to those found in another uncontaminated sample (specific conductance equals 70 μmhos ; free-living bacterial counts equal $0.04 \pm 0.005 \times 10^6 \text{ mL}^{-1}$) from a well 2.93 km from the beds and 24 m deep. These data suggest that bacterial abundance in uncontaminated ground water of this region may be as low as 10^4 - 10^5 mL^{-1} . Reported bacterial abundances for other uncontaminated ground water range from 1.1×10^3 to $2.0 \times 10^6 \text{ mL}^{-1}$ (Olson and others, 1981; Ladd and others, 1982). These data were reported for samples taken at depths of 1200 m and 1.5 m, respectively, and thus may represent extreme values of population densities.

The microbial population in contaminated and uncontaminated areas of the saturated zone (table 18) appears to be dominated by adherent bacteria. Bacterial distributions between ground water

and particulate surfaces have not been reported for freshwater aquifers. However, large fractions of total bacterial populations associated with particulate surfaces in other particle-laden environments have been well documented (Harvey and Young, 1980a and 1980b; Harvey and others, 1983; Rublee and others, 1983) and seem reasonable for the terrestrial subsurface. Expressed in terms of particulate dry weight, the range of adherent bacteria reported here ($1.1 \pm 0.1 \times 10^7 \text{ g}^{-1}$ (counts per gram) to $3.4 \pm 0.3 \times 10^7 \text{ g}^{-1}$) are somewhat higher than the range reported for six uncontaminated cores taken from the unsaturated and saturated subsurface at depths of 1.2 to 5.0 m in Oklahoma ($3.4 \pm 2.6 \times 10^6 \text{ g}^{-1}$ to $9.8 \pm 1.3 \times 10^6 \text{ cells g}^{-1}$) (Wilson and others, 1983). These differences may, in part, reflect differences in enumeration techniques, since a settling procedure was used to separate out the larger sized particles in the latter study. Numbers of bacteria reported in the two studies for the saturated zone are three to four orders of magnitude lower than those reported for estuarine surface sediments (Rublee, 1982; Dale, 1974), likely reflecting substantial differences in available nutrients and environmental conditions.

It appears that most bacteria in the aquifer are associated with fine silt particles less than 20 μm in diameter (table 18). Furthermore, microscopic observations indicate a large number of bacterial clusters within the smaller particle-size fractions. This suggests a high degree of heterogeneity on a microscopic scale. The possibility exists that small colonies of bacteria associated with the silt-sized particle fraction may break down a significant quantity of the contaminant organics degraded in the aquifer, although more definitive study is clearly needed.

A substantial loss of particles smaller than 105 μm in diameter from solution during 2 minutes of settling suggests that a preparative settling procedure for enumeration of soils bacteria may not account for a substantial portion of the adherent bacterial population (table 18). Much of that loss occurs during the settling out of silt particles. It appears that wet sieving would likely yield more representative bacterial counts for subsurface samples. Since the procedure definitively separates out particulates greater than 105 μm in diameter, counts made of adherent bacteria in a variety of core material may be more comparable. The advantages would appear to outweigh the added investment of time and equipment required by the wet-sieving technique.

SUMMARY

The presence of organic contaminants in the ground water of Cape Cod significantly affects abundance and uptake potential of the free-living bacterial population. Numbers of free-living bacteria in well water samples varied with distance from the contaminant source and correlated with both specific conductance and glucose uptake rates. A majority of the bacteria in sampled portions of the aquifer appear to be associated with solid surfaces, as has been observed in other particle-laden systems. Although there is considerable heterogeneity in abundance of adherent bacteria on a microscopic scale, surprisingly little

variation in abundance of adherent bacteria was observed among core samples. Clearly, more work is needed to better characterize the population of particle-bound bacteria in the aquifer and to delineate its role in the degradation of organic contaminants. Such studies would greatly benefit from improvements in sampling techniques for obtaining intact aquifer material from a variety of depths in the terrestrial subsurface.

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CHAPTER G

A major goal of research on toxic wastes in ground water is to determine the rates of microbial degradation and transformation of contaminants. This paper presents a preliminary study of one process, denitrification, which may play a significant role in the removal of nitrogen from ground water in the plume. Determination of the rates of denitrification and other nitrogen-transforming processes may be a first step toward simulation of nonconservative solute transport.

PRELIMINARY STUDY OF DENITRIFICATION IN A PLUME OF SEWAGE-CONTAMINATED GROUND WATER

by

Richard L. Smith and John H. Duff

ABSTRACT

High concentrations of nitrate (1 mM) were present in secondarily treated sewage entering sand infiltration beds at the Otis Air Base, Massachusetts, sewage-treatment plant, as opposed to undetectable concentrations of nitrate and oxygen in the underlying ground water. This suggested that a zone of denitrification had been established within the contaminated aquifer. Well water and core samples taken from the zone of contamination were assayed for denitrification potential using the acetylene blockage technique. Sewage effluent and slurried core material demonstrated endogenous denitrifying activity, whereas corresponding well water samples did not. Addition of nitrate (1 mmole/L) had no effect upon denitrification rates but glucose + nitrate amendments (1 mmole/L of each) stimulated activity in both water and core samples. In general, the highest rates of activity were evident in samples taken nearest the sand beds; samples taken from outside the contamination plume did not produce N₂O under any conditions tested. These results establish that denitrification can occur in subsurface systems and thereby serve as a mechanism to remove nitrate from contaminated ground water.

INTRODUCTION

The quality of ground water and the processes that affect the quality of ground water are topics of vast economic importance due to the widespread usage of subsurface aquifers for commercial and domestic purposes. Ground-water quality can be affected by physical-chemical interactions between soluble and particulate components of the aquifer material, by biological activities, and by anthropogenic influences. While each of these three components can have a direct bearing upon the others, in many cases the ultimate quality of ground water may be controlled by the activities of microorganisms within the ground-water system (McNabb and Dunlap, 1975).

Among the substances entering ground-water systems from anthropogenic origin, nitrate is very prominent. It is highly soluble and mobile and represents a health hazard at relatively low concentrations (Foster and others, 1982). Contamination of ground-water supplies by nitrate is an increasingly common phenomenon in both rural and urban areas as a result of natural and chemical fertilizer application and leaching of human and animal wastes (Foster and others, 1982; Gormly and Spalding, 1979; Katz and others, 1980; Porter, 1980; Robertson, 1979; Saffigna and Keeney, 1977; and Spalding and others, 1978). In agricultural regions, nitrate contamination can occur in widespread areas due to combined fertilization and irrigation practices (Saffigna and Keeney, 1977; Spalding and others, 1978).

Once it enters a ground-water supply, nitrate will likely remain in the ground water unless it is removed or transformed by biological activity. Reduction of nitrate to N_2 (denitrification) or to NH_4^+ (dissimilatory nitrate reduction) are energy-generating processes carried out by microorganisms and, as such, are the processes most likely to affect nitrate concentrations in ground water. These are anaerobic processes and hence would predominate only in O_2 -free aquifers, but they also can occur in anaerobic microniches in habitats that are considered aerobic (Brock, 1979). Indirect evidence, such as NO_3^- and N_2 concentrations (Vogel and others, 1981; Robertson, 1979), $^{15}N/^{14}N$ ratios (Gormly and Spalding, 1979) and isolation of denitrifying bacteria (Willis and others, 1975; Whitelaw and Rees, 1980), suggest that

denitrification does occur in ground water. However, very little is actually known about denitrification rates in these habitats, even though such measurements are necessary to understand the dynamics and the controls of the process. The potential for nitrate reduction to ammonia has been virtually ignored in studies of aquifers and indeed is poorly understood in other habitats. However, this process can account for 7 to 30 percent of the nitrate reduced in lake sediments, 20 to 70 percent in marine sediments, and 60 to 70 percent in sewage sludge (J. M. Tiedje, Michigan State Univ., oral communication, 1982) and therefore must be considered as a potential nitrate sink in ground water as well. Thus, although these two processes represent potential detoxification mechanisms for ground-water supplies, the occurrence and extent of these activities in either contaminated or pristine aquifers is currently unknown.

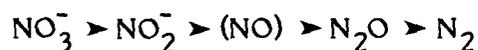
The U.S. Geological Survey's ground-water contamination study site at Cape Cod, Massachusetts,¹ represents a suitable location to study inorganic nitrogen transformations in ground-water systems. High concentrations of nitrate (1 mM) are present in the treated sewage percolating into the ground water, yet immediately downgradient from the infiltration beds the ground water contains no detectable nitrate or oxygen and high levels (0.6 to 0.7 mM) of ammonia (Ceazan and others, 1984). These trends suggest that a nitrate sink exists within the aquifer; denitrification and dissimilatory nitrate reduction are the most likely explanations for the nitrate disappearance. This paper describes the preliminary results of a study to test the hypothesis that a zone of denitrification and (or) dissimilatory nitrate reduction is established in an aquifer in response to increased quantities of nitrate and organic carbon and thereby serves as a mechanism to remove nitrate from ground water.

We thank W. Nichols and C. Banks for technical field assistance and E. M. Thurman and R. Oremland for manuscript review. We also thank D. LeBlanc for coordinating the field work and for offering many helpful suggestions.

¹A description of the site, including its geologic and hydrologic setting, is given in Chapter A of this volume.

OVERVIEW OF DENITRIFICATION

Denitrification is an anaerobic process in which nitrate substitutes for the oxygen utilized in aerobic respiration. Nitrate acts as the terminal electron acceptor and is reduced in a stepwise fashion to dinitrogen gas:



Although the pathway involves gaseous intermediates (NO and N₂O), neither accumulate to a significant extent. Accurate estimates of denitrification activity by measuring the amount of N₂ produced are difficult to obtain due to the significant potential for interference by atmospheric N₂ (Knowles, 1982). However, the enzyme that catalyzes the terminal reduction of N₂O to N₂, nitrous oxide reductase, is inhibited by acetylene. This phenomenon is utilized in a relatively simple and sensitive assay for denitrification known as the acetylene block technique (Balderston and others, 1976; Yoshinari and others, 1977; Knowles, 1982). Provided a sufficient acetylene concentration is present, the inhibition by acetylene is complete and results in the stoichiometric production of N₂O. Nitrous oxide is assayed by a sensitive gas chromatographic method that employs an electron capture detector (Kaspar and Tiedje, 1980). This technique has been utilized to estimate rates of denitrification in soils, sediments (both freshwater and marine), lake waters, digested sewage sludge and benthic stream communities (Kaspar and others, 1981; Knowles, 1982; Triska and Oremland, 1981).

EXPERIMENTAL PROCEDURES

Sample Collection

The study area consists of a sand and gravel aquifer located in Cape Cod, Massachusetts, which has been contaminated with secondary sewage effluent from the sewage treatment facility at Otis Air Base (fig. 50). The nature of the aquifer, the types of monitoring wells, and the contamination plume have been described in the preceding chapters. Observation wells

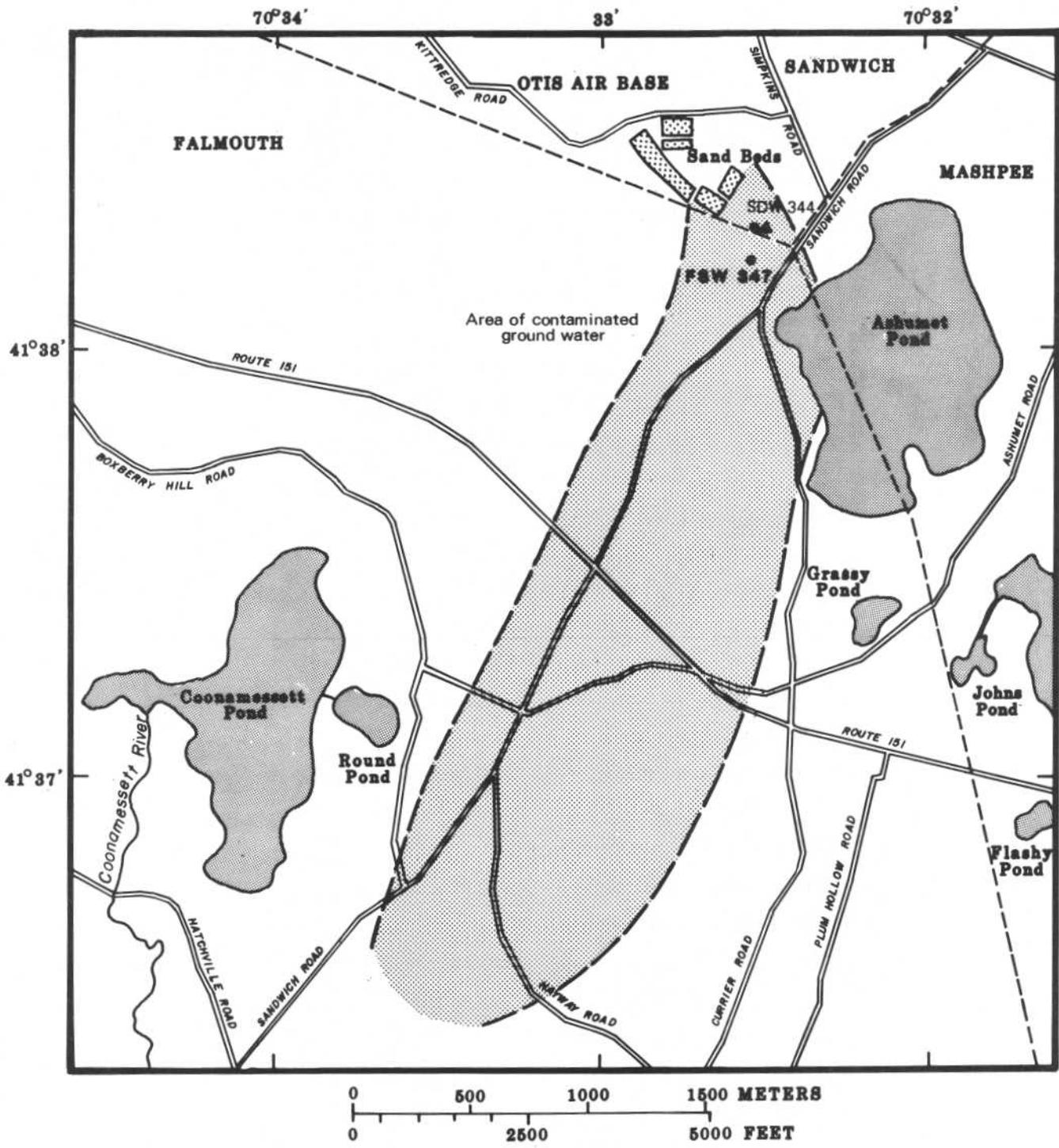


Figure 50. Ground-water study area in Cape Cod, Massachusetts. Dashed lines delineate the path of the contaminant plume (as determined by specific conductance) caused by infiltration of treated sewage into the aquifer. Triangle indicates site where core sample was taken. Circles indicate sampled observation wells.

were sampled with a Keck² submersible pump after suitable evacuation of the water contained within the well casing (Thurman and others, 1984). Specific conductance and dissolved oxygen were assayed as described by Ceazan and others (1984), dissolved methane as described by Oremland and Des Marais (1983), and ammonia and nitrate by a Hach water analysis kit. Water samples were collected in 1-liter acid-washed glass bottles that were completely filled and capped to avoid an air headspace. Secondarily treated sewage effluent was sampled at the Otis Air Base sewage-treatment plant from a flow channel leading onto an active infiltration sandbed. Aquifer sediments were sampled with an auger drilling rig immediately adjacent to well cluster SDW 344. Split-spoon cores (2 feet in length) were taken at selected depths (59-61, 78-80, and 98-100 feet below land surface) and the core material transferred to widemouth acid-washed glass jars. These jars were completely filled with sample material. All samples were stored on ice and transported to the U.S. Geological Survey laboratory in Menlo Park, California. Denitrification assays were initiated 2 to 3 days after sampling.

Denitrification Assay

Three 100 mL aliquots of each water sample were transferred to 150 mL serum bottles that were being flushed with O₂-free N₂. A fourth bottle received a 100 mL aliquot that had been filter sterilized with a 0.2 micron Gelman Acrodisc filter. The bottles were sealed with recessed butyl rubber stoppers and flushed with N₂ for an additional minute. A similar series of bottles was prepared for each core sample. Approximately 50 g (wet weight) of core material was transferred to pretared bottles. The solids were slurried with 50 mL of water sample taken from the well of corresponding depth. The bottles were flushed with O₂-free N₂ and reweighed. Control slurries were killed by adding HgCl₂ (1 percent weight per unit volume). All bottles were incubated at 12°C with shaking. After a 10-minute preincubation, two non-control bottles from each group of four was amended with 1.0 mL of 100 mM NaNO₃. One of the two bottles also received 1.0 mL of 100 mM glucose. Acetylene (10 mL) was added to the

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

headspace of all the bottles and the bottles were shaken for 2 minutes prior to the removal of zero-time samples. Successive headspace gas samples (0.3 mL) were removed by glass syringe and analyzed for N₂O by ⁶³Ni-electron capture gas chromatography (Culbertson and others, 1981).

RESULTS AND DISCUSSION

The specific conductance of ground-water samples taken from clusters of wells located 600 feet and 750 feet from the infiltration beds was 250 μ mhos, or greater, with two exceptions (table 19). The exceptions were the shallowest well at each location. A comparison of these values with the specific conductance of the sewage effluent (390 μ mhos) and an uncontaminated ground-water sample (51 μ mhos) clearly indicates that these two well series represent depth profiles into the zone of contaminated ground water. The shallow wells are located near the upper periphery of the contamination zone, which in general is being displaced downward with increasing distance from the sandbeds by recharge from precipitation (LeBlanc, 1982).

The concentration of nitrate in the sewage effluent was high relative to the nitrate contained in uncontaminated ground water (table 19). However, the large nitrate inputs were not reflected in the nitrate profiles from either well series SDW 344 or FSW 347. Assuming that 1 mM represents an average long-term estimate of the sewage nitrate concentration, a mechanism for nitrate removal must exist in the ground-water system. Conversely, the ammonia concentration in several of the wells sampled was higher than that of the sewage effluent (table 19), indicating the potential for ammonia production within the aquifer as well.

At the location of well series SDW 344 and FSW 347 the contamination plume is anaerobic. Dissolved oxygen was detected only in water from well SDW 344-38, but at a concentration that was markedly lower than the dissolved oxygen content of uncontaminated ground water (table 19). The presence of dissolved methane corroborates the anaerobic nature of these ground-water samples since methane is produced by obligately anaerobic bacteria. Thus, the occurrence of a nitrate depletion, ammonia production,

Table 19. Chemistry of water samples taken from the contaminated ground-water study site.

Sample location or well number ^a	Distance from sewage beds (ft)	Specific conductance (μ mhos)	Dissolved oxygen ^c (mg/L)	Dissolved methane (nM)	Nitrate (mM)	Ammonia (mM)
Sewage effluent	0	390 ^b	5.0 ^b	---	1.0	0.1-0.4
SDW 344-38	600	158	2.5	6	---	----
-61	600	380	<0.2	540	0	0.7
-80	600	250	0.5	460	0	0.6
-100	600	350	<0.2	470	0	0.6
FSW 347-20	750	37	<0.2	0	0.06	0.02
-46	750	325	<0.2	12	0	0.6
-67	750	345	<0.2	110	0	0.2
-101	750	260	<0.2	22	0.003	0.2
FSW 242-51 ^d	6200	51	9.9	---	0.01	0

^aThe number after the dash is the depth (feet) of the well screen below the land surface.

^bData taken from LeBlanc (1982).

^cThe lower limit of detection of the oxygen electrode utilized was 0.2 mg/L.

^dWater from this well is assumed to represent uncontaminated ground water.

and anaerobic conditions suggest that these two locations within the contamination zone were potential sites for active denitrification and dissimilatory nitrate reduction.

Denitrifying activity in water samples from well SDW 344-100 was assayed with the acetylene blockage technique (fig. 51). No N_2O production was detected during 60-hour incubations with an unamended subsample (endogenous), a subsample amended with 1 mmole/L NO_3^- , or a filtered control. However, a subsample amended with 1 mmole/L glucose + 1 mmole/L nitrate did display significant N_2O production after a 35-hour time lag. This denitrification potential implies the presence of denitrifying bacteria in this well water sample. This population was either inactive (with respect to denitrification) or present in very low numbers in the unamended subsample, or both. The in situ nitrate concentration does not appear to be the limiting factor since the nitrate amendment did not stimulate denitrification. However, the response to the addition of glucose plus nitrate identified the availability of electron donors as a factor controlling denitrification. Indeed, the 35-hour time lag and the exponential increase in the rate of N_2O production in this subsample strongly imply active growth of a denitrifying population during the course of this assay.

A similar set of denitrification assays were run with water samples from the other wells in the FSW 347 and SDW 344 series. N_2O was not produced with any of the unamended subsamples, with the exception of well SDW 344-61. In that sample 0.1 nmoles N_2O /mL H_2O was produced after 60 hours. The addition of 1.0 mmole/L NO_3^- had no effect on any sample. Figure 52 presents the results of the glucose + nitrate amendment. In general, samples from the two deeper wells at SDW 344 and the middle wells at FSW 347 (FSW 347-46, FSW 347-67) demonstrated the greatest stimulation. N_2O production in water from well FSW 347-20, which is not within the zone of contamination (table 19), was not stimulated by the addition of glucose and nitrate. This result, plus the minimal stimulation in samples from wells FSW 347-101 and SDW 344-61, indicates that the response of the samples that were stimulated was not due to the introduction of contaminants by the sampling and handling procedures.

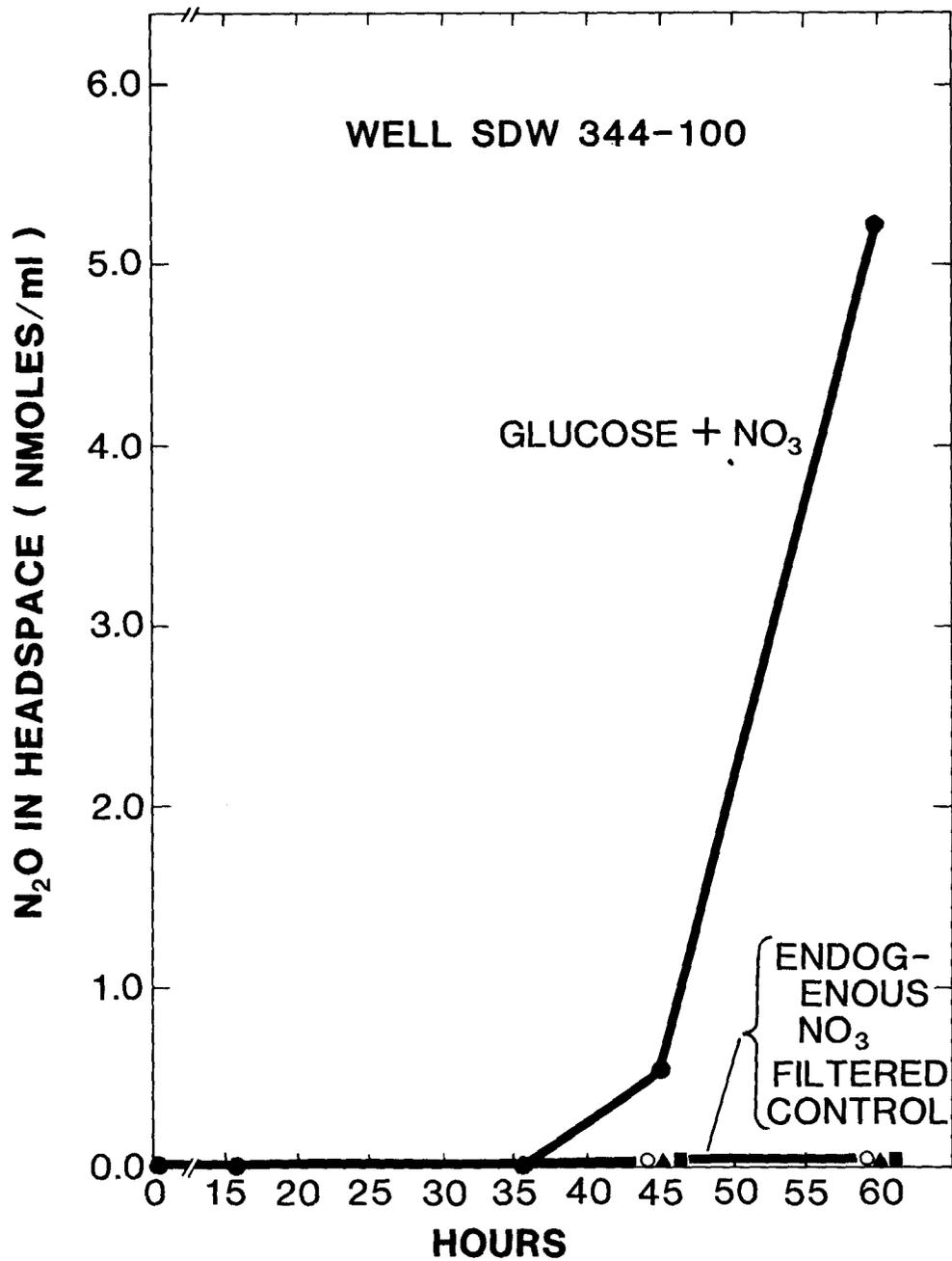


Figure 51. N₂O production in water from well SDW 344-100. Sample incubated at ambient nitrate concentration (○), amended with 1 mmole/L NO₃⁻ (▲), amended with 1 mmole/L NO₃⁻ + 1 mmole/L glucose (●), or filtered control (■).

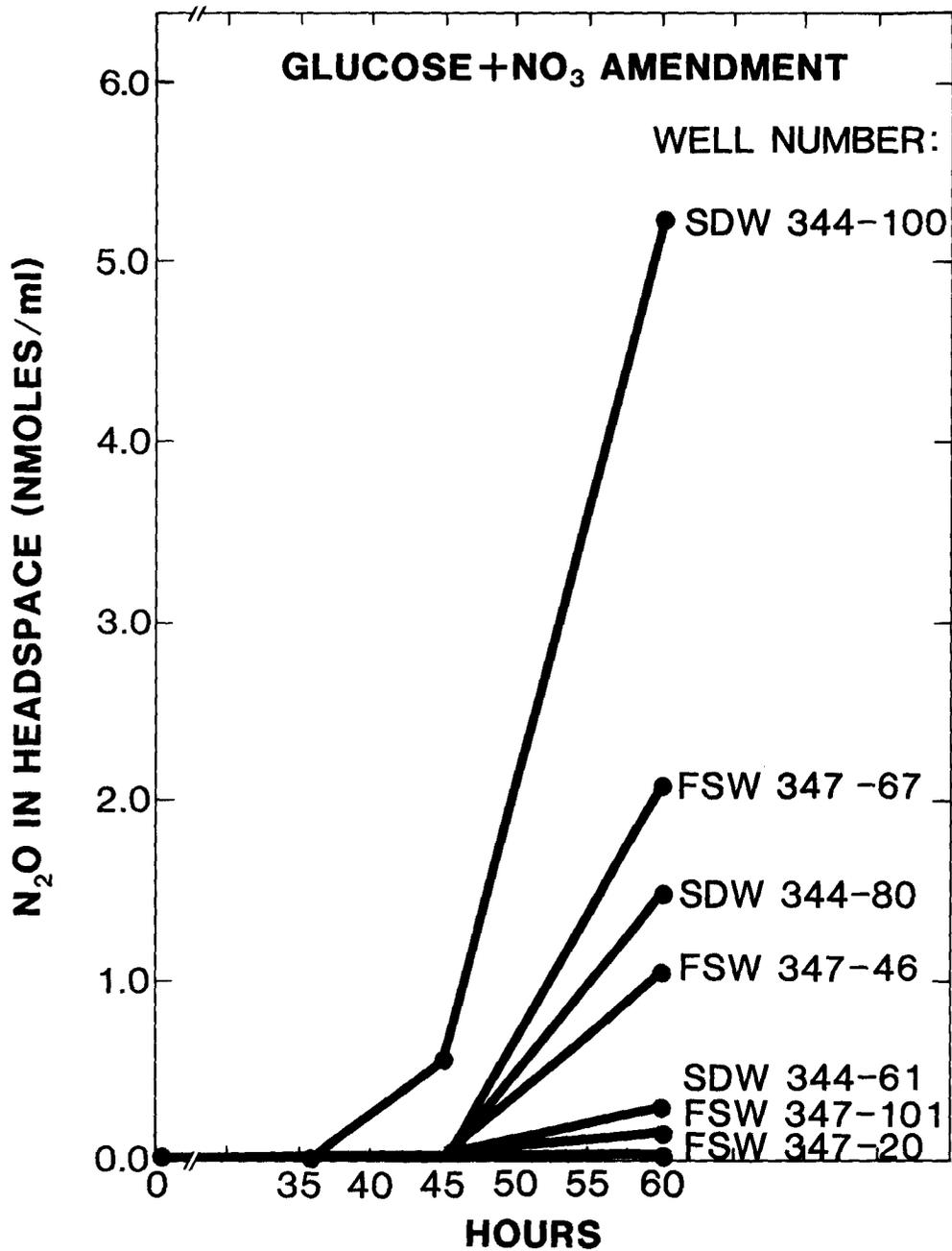


Figure 52. N₂O production in well-water samples when amended with 1 mmole/L NO₃⁻ + 1 mmole/L glucose.

A major hypothesis being tested at the Cape Cod contamination site is that a significant fraction of microbial biomass and microbially-mediated activity is associated with particulate surfaces rather than in a free-living state in the interstitial ground water (see Harvey and others, 1984). Hence, denitrifying activity was also assayed in core material taken opposite each well screen at SDW 344. Slurries prepared from core material taken from the 78-80 ft depth interval produced N_2O endogenously (fig. 53). The lack of N_2O production in the killed control ($HgCl_2$) indicated that the activity was biologically mediated. As with the well water samples, the addition of nitrate had no effect, whereas glucose + nitrate greatly enhanced the level of activity. In general, these trends were evident for each core (fig. 54 and 55). Nitrate stimulated N_2O production five-fold for the core material from 59 to 61 ft, which was the only exception (data not shown). Particularly significant was the fact that endogenous N_2O production was evident for each core sample, but not for the well water sample taken from the equivalent depth. These results suggest that core samples, and not well water samples, are required to adequately assess rates of denitrification in ground-water aquifers.

For comparative purposes, the sewage effluent entering the infiltration sand beds was also assayed for denitrification potential (fig. 56). Unlike the well water samples, the sewage effluent displayed a significant rate of endogenous activity, with no apparent time lag. Amendment with glucose + nitrate greatly stimulated the rate of N_2O production, also with little time lag. Thus, the sewage effluent must contain a sizeable population of microorganisms capable of denitrification, which is characteristic of waste treatment systems (Kaspar and others, 1981; Knowles, 1982). It should be noted however, that the sewage effluent is oxygenated (table 19), whereas the assay system is anaerobic. The actual rate of denitrification in the sewage effluent before it percolates into the sand bed is probably very low.

A summary of the denitrification rates for both water and core samples during the 60-hour incubation is presented in figures 57 and 58. Since the rate of N_2O production was not linear with time in most cases, the calculated rates are labeled as denitrification potentials. They do not

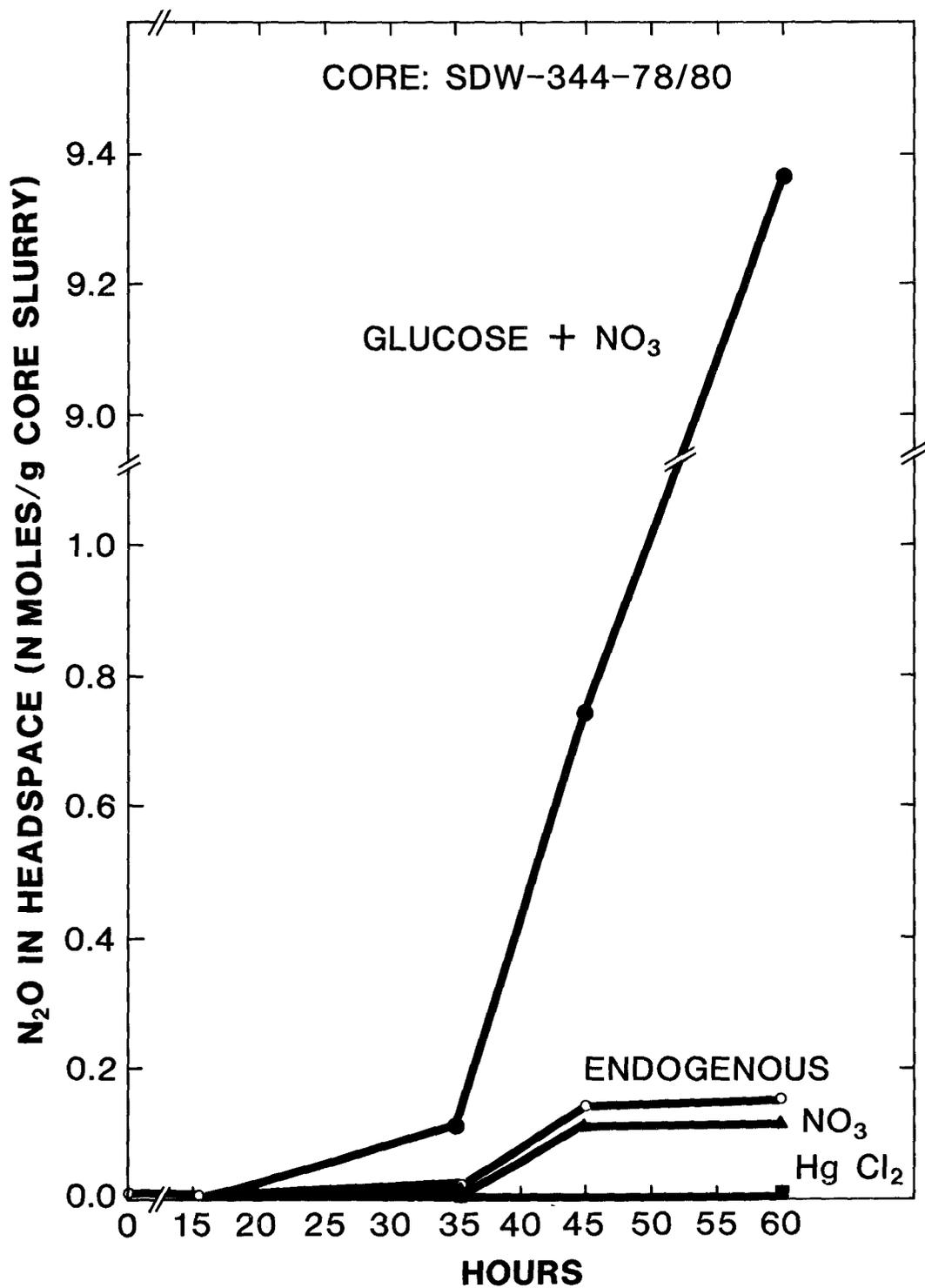


Figure 53. N₂O production in slurrified core material taken from the 78 to 80 ft depth interval immediately adjacent to well series SDW 344. Sample incubated at ambient nitrate concentration (○), amended with 1 mmole/L NO₃⁻ (▲), amended with 1 mmole/L NO₃⁻ + 1 mmole/L glucose (●), or amended with HgCl₂ (■).

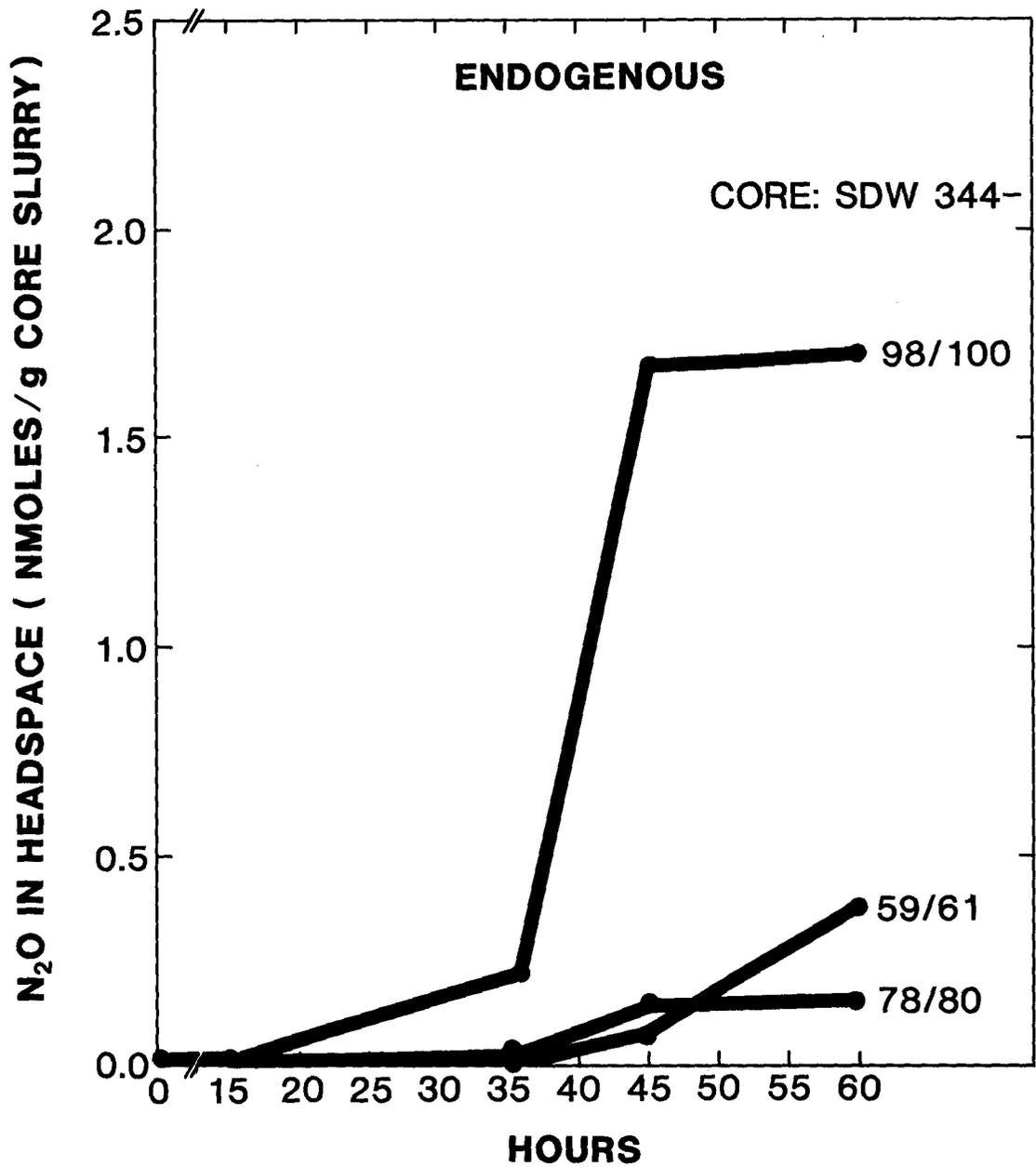


Figure 54. N_2O production in slurred core material from core SDW 344 when incubated at ambient nitrate concentration. Depth (ft) of the core from land surface as indicated.

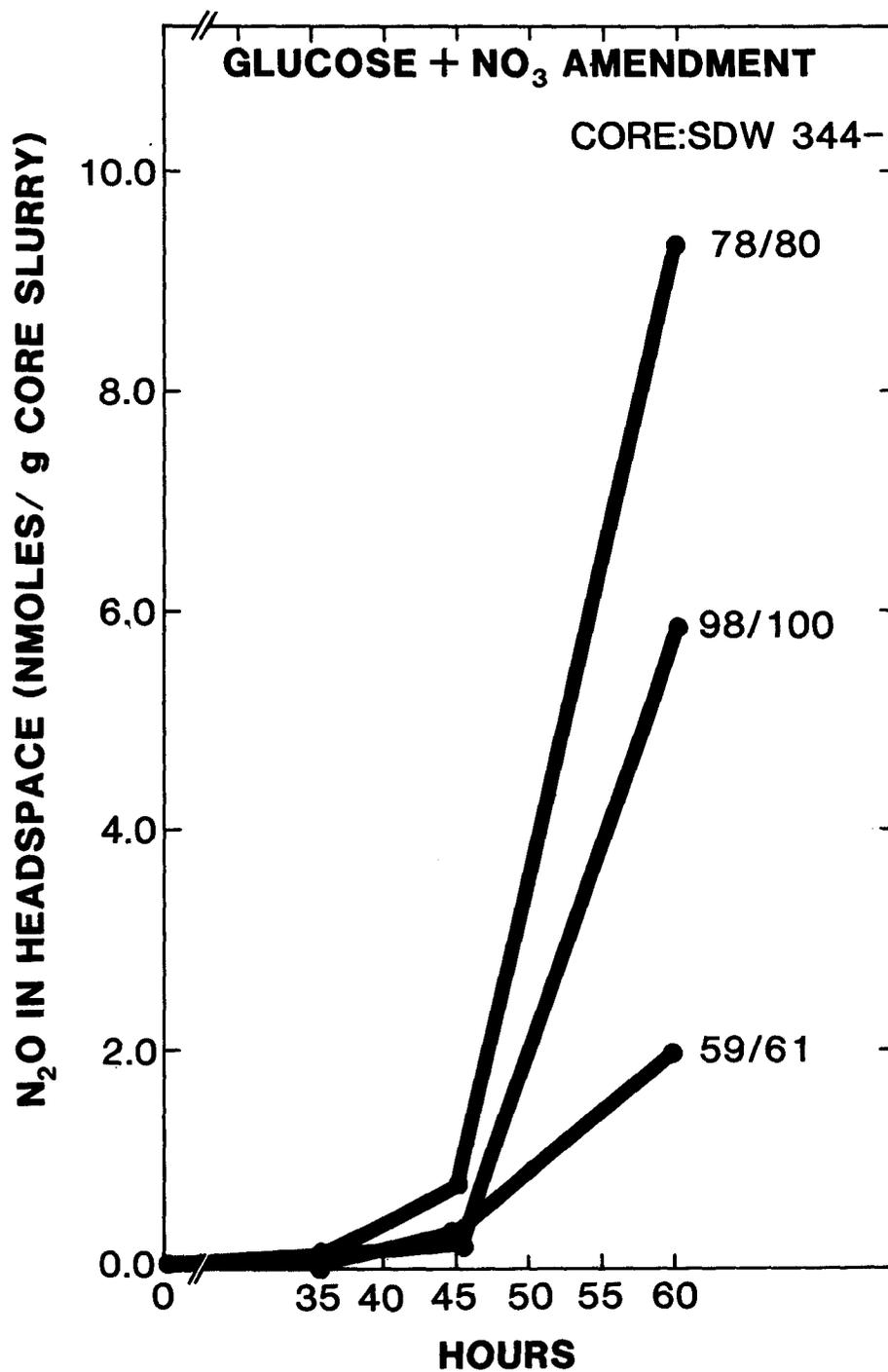


Figure 55. N₂O production in slurrified core material from core SDW 344 when amended with 1 mmole/L NO₃⁻ + 1 mmole/L glucose. Depth (ft) of the core from land surface as indicated.

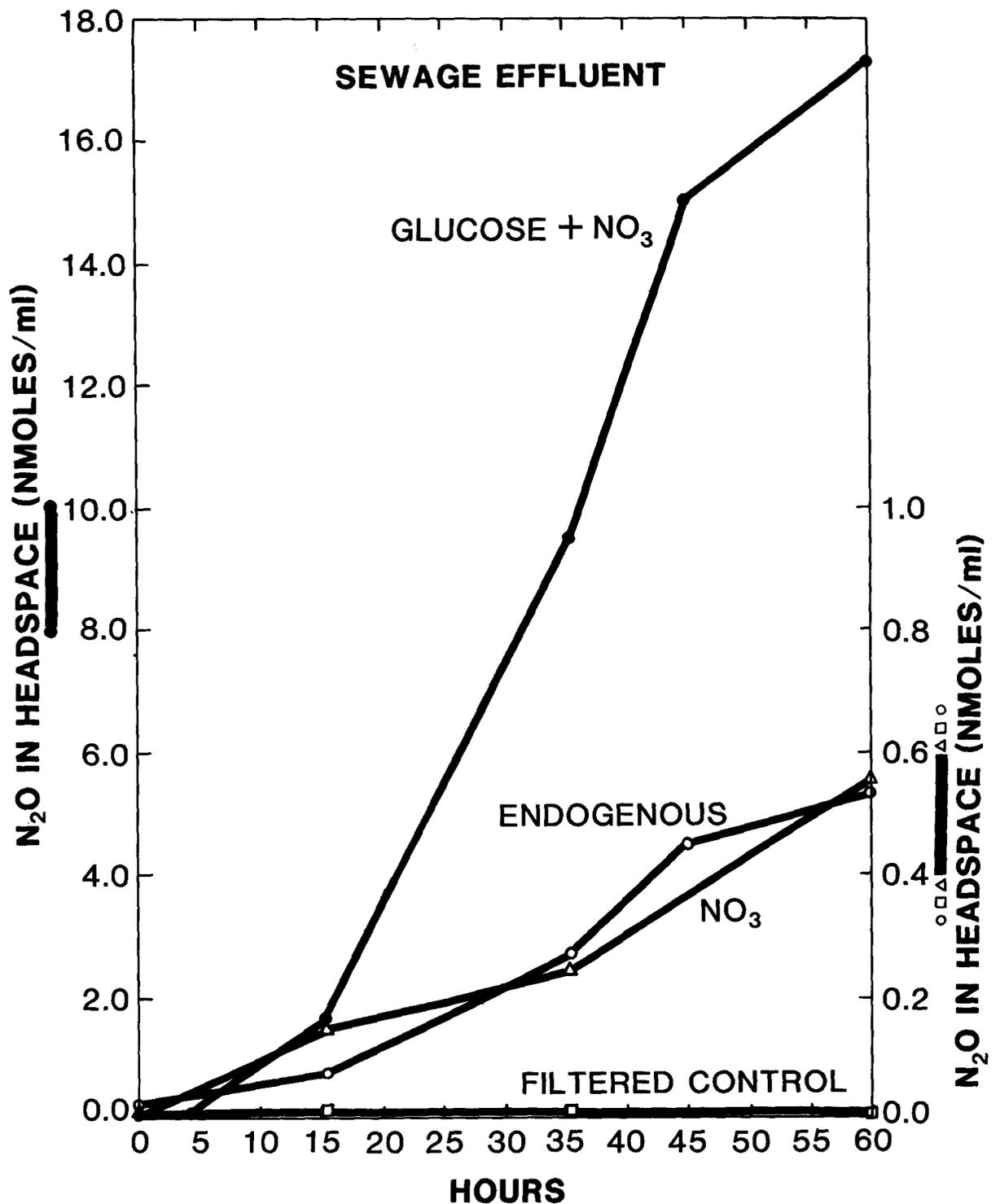


Figure 56. N_2O production by the sewage effluent entering an infiltration sand bed on December 8, 1983. Sample incubated at ambient nitrate concentration (o), amended with 1 mmole/L NO_3^- (Δ), amended with 1 mmole/L NO_3^- + 1 mmole/L glucose (\bullet), or filtered control (\square).

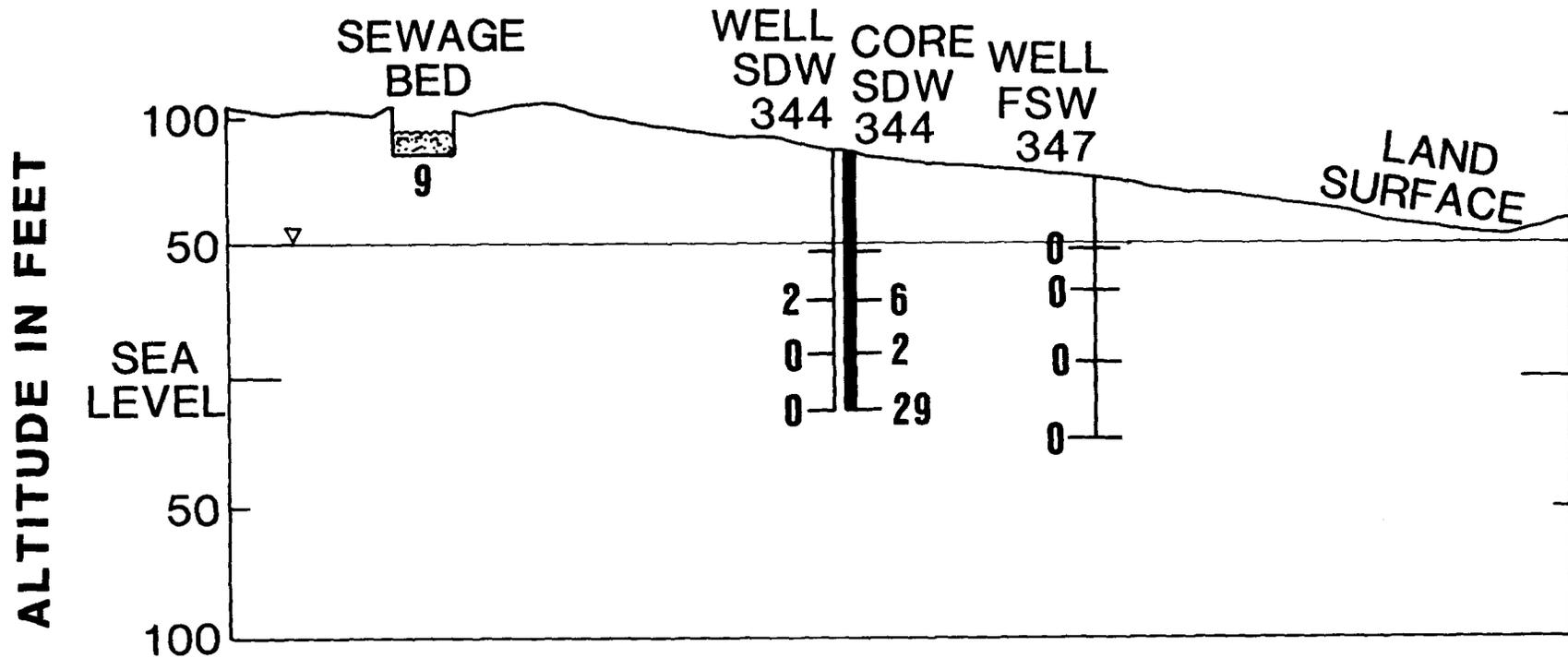


Figure 57. Vertical distribution of denitrification potential for samples incubated at ambient nitrate concentration. Rates were calculated from the 60-hour time point of time course assays. Rates are given in pmoles N_2O produced/ml H_2O /hr for water samples, and pmoles N_2O produced/g core slurry/hr for core samples. Horizontal axis not drawn to scale.

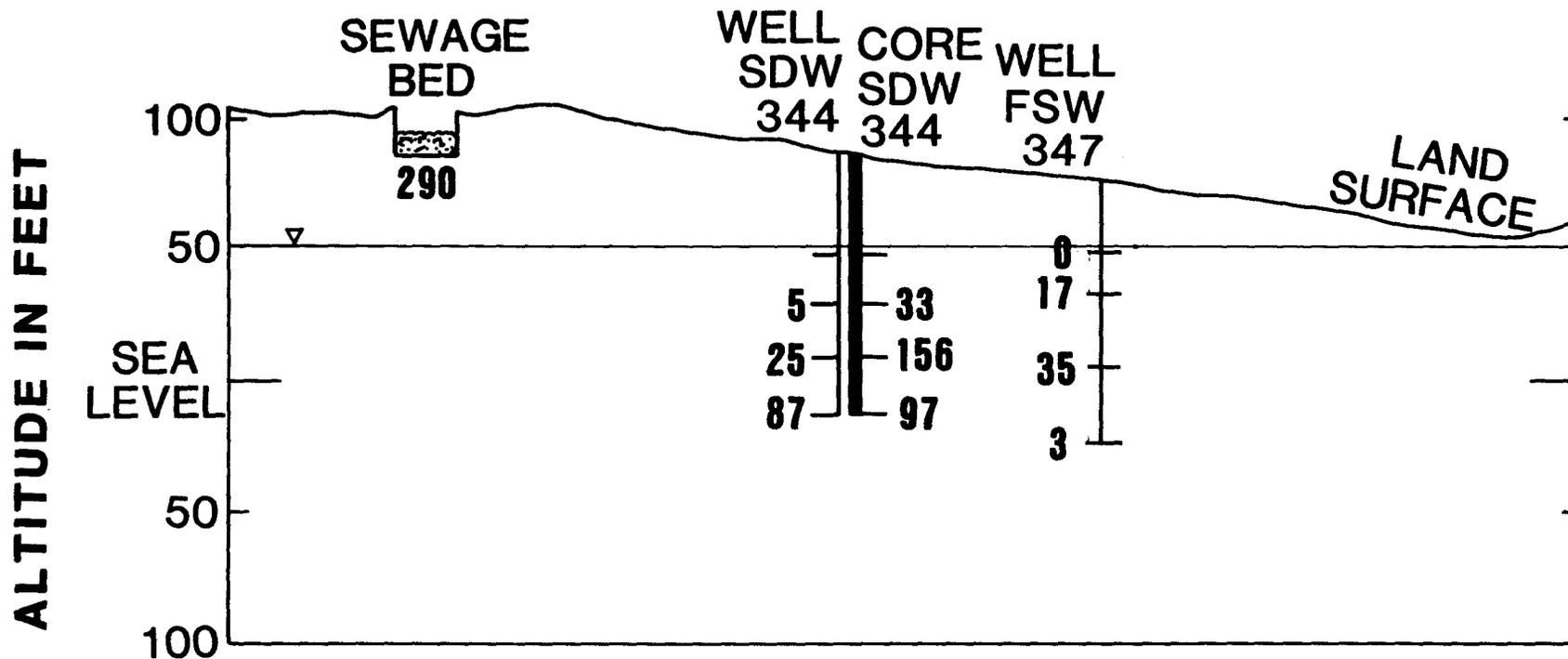


Figure 58. Vertical distribution of denitrification potential for samples amended with 1 mmole/L NO_3^- + 1 mmole/L glucose. Rates were calculated from the 60-hour time point of time course assays. Rates are given in pmoles N_2O produced/ml H_2O /hr for water samples or pmoles N_2O produced/g core slurry/hr for core samples. Horizontal axis not drawn to scale.

necessarily represent the actual rate in the ground-water system. However, these results demonstrate that denitrification can occur in ground-water systems and thereby serve as a mechanism for nitrate removal from ground water. The activity appears to be associated with solid surfaces within the aquifer. With one exception, no denitrification was evident in unamended well water samples (fig. 57). This has important ramifications for the sampling techniques employed in future studies involving microbial processes in ground water.

In general, denitrification in this environment seems to be carbon (electron donor) limited rather than nitrate limited. Additions of glucose stimulated denitrification in most water samples, all of the core samples, and even the sewage effluent (fig. 58), despite the relatively high levels of dissolved organic carbon present in the effluent (Thurman and others, 1984). On the other hand, denitrification was essentially non-existent in samples from wells FSW 347-20 and FSW 347-101 (fig. 56 and 57). Thus, the denitrifying activity demonstrated by most of the samples was not due to an indigenous population of denitrifying organisms present throughout the aquifer. Rather, a zone of denitrification has been established in response to the sewage contamination. This zone is not established solely by an elevated nitrate concentration. For example, well FSW 347-20 contained 0.06 mM NO_3^- and no dissolved oxygen (table 19). The results suggest that there is a requirement for sufficient electron donor availability as well. Indeed, once the denitrification zone becomes established, the nitrate concentration within that zone is actually lower than the nitrate concentration in the uncontaminated ground water (table 19).

This preliminary study raises several points which remain to be addressed. First, the potential for dissimilatory nitrate reduction to ammonia remains to be examined. This activity may be as significant as denitrification. Since the ammonia concentration in the well water is high, tracer techniques will have to be developed to assay this activity. Procedures for sampling core material also need to be developed to retain interstitial water and preclude potential sample contamination. In addition, denitrification assay techniques need to be refined to eliminate the time lag and obtain linear rates of N_2O production. Finally, it appears that the

maximum rates of denitrification are occurring much closer to the sand beds than originally anticipated. Given the potential denitrification rates in the sewage effluent, it is quite possible that most of the nitrate present in the effluent is actually reduced immediately beneath the sand beds. If such is the case, the system would be very efficient in its ability to remove the nitrate present in the sewage effluent.

SUMMARY AND CONCLUSIONS

- 1) High concentrations of nitrate present in sewage effluent and low concentrations of nitrate and oxygen in the sewage-contaminated ground water suggested that a zone of denitrification had been established within a contaminated aquifer at Otis Air Base, Cape Cod, Massachusetts.
- 2) Well water and core samples taken from the zone of contamination were assayed for denitrification potential using the acetylene blockage technique. The core material demonstrated endogenous denitrifying activity while the corresponding well water sample did not. This suggested that the denitrifying microorganisms were associated with particulate surfaces and would not be adequately quantified with well water samples.
- 3) Denitrification rates were stimulated by addition of glucose, but not by addition of nitrate, in both water and core samples, indicating that the activity was carbon-limited rather than nitrate-limited within this environment.
- 4) In general, the highest rates of denitrification occurred in samples taken from nearest the infiltration sand beds, while samples taken from outside the contamination plume did not produce N_2O .
- 5) These results establish that denitrification can occur in subsurface systems and thereby serve as a mechanism to remove nitrate from contaminated ground water.

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