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Natural Restoration of a Sewage Plume in a Sand and Gravel Aquifer, Cape Cod, Massachusetts

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ABSTRACT

Land disposal of treated sewage to infiltration beds at the Massachusetts Military Reservation on Cape Cod for 60 years has formed a plume of contaminated ground water in the sand and gravel aquifer that is more than 3.5 miles long. Sewage disposal ended in December 1995, and no action has been taken to restore the ground-water quality near the disposal site. In the first 30 months after disposal ended, the trailing edge of the conservative constituents in the plume, such as boron, moved more than 800 feet downgradient from the abandoned beds. Concentrations of dissolved oxygen remained at or near zero near the disposal beds, however, even though uncontaminated ground water that contains dissolved oxygen had been flowing into the sewage-contaminated zone from upgradient areas for 30 months. Biodegradation of organic matter associated with the sewage-contaminated sediments is probably the primary cause of the continuing suboxic to anoxic conditions. Nitrate concentrations in the center of the sewage-contaminated zone decreased to below detectable levels as nitrate moved away from the abandoned beds along with the ground-water flow or was converted to nitrogen gas by denitrification. As nitrate levels decreased to zero, the geochemical environment beneath the beds became more reducing, and dissolved-iron concentrations increased because insoluble ferric iron oxide coatings on the sediments were reduced to soluble ferrous iron. Ammonium had been expected to be oxidized to nitrate as oxygen re-entered the sewage-contaminated zone. Ammonium concentrations decreased, however, as ammonium desorbed from the sediments by cation exchange and was transported away from the disposal site in the reducing geochemical environment. pH did not change significantly because of the buffering effects of sorption on the sediment surfaces and anaerobic biodegradation. As a result, the concentrations of sorbed trace metals, such as zinc and copper, did not change significantly after disposal ended. Phosphorus concentrations remained elevated in the sewage-contaminated zone because of slow desorption from the sediments. Results of geochemical modeling of the natural restoration process indicate that restoration of ground-water quality to pre-contamination conditions will be slow because of the persistent oxygen demand in the sewage-contaminated zone.

INTRODUCTION

The cleanup of contaminated aquifers has proven to be a difficult technical challenge (National Research Council, 1994). The heterogeneity of geologic materials, sorption of contaminants to sediments, and slow degradation rates complicate efforts to implement engineered remedial solutions. Thus, natural restoration, also referred to as natural attenuation, has received increased attention as a remedial option (U.S. Environmental Protection Agency, 1997). This option relies on natural physical, chemical, and biological processes to restore the quality of ground water to acceptable levels.

Interest in natural restoration has created the need for increased understanding of the restoration process. Research on contaminant plumes has focused primarily on the processes that cause contaminants to attenuate and disperse as they migrate from source areas. Less attention has been paid to the processes that restore ground-water quality after a source has been removed. Many field investigations have shown that disposal of substances, such as sewage, that contain degradable organic materials creates a subsurface environment characterized by distinct geochemical zones (Lovley and others, 1989). Little is known, however, about how these environments evolve and affect contaminant fate and transport after the source is removed.

Treated sewage was disposed of for about 60 years to a sand and gravel aquifer at the Massachusetts Military Reservation (MMR) on western Cape Cod (fig. 1). The disposal created an extensive plume of sewage-contaminated ground water (LeBlanc, 1984; Hess and others, 1996; Savoie and LeBlanc, 1998). The plume has been studied since 1983 as part of the U.S. Geological Survey (USGS) Toxic Substances Hydrology Program (LeBlanc, 1996; Morganwalp, 1994).

On December 13, 1995, the MMR ended disposal of treated sewage at the site. Wastewater from the base is now treated at a newly built treatment facility, and effluent from the plant is pumped about 8 miles north to a disposal site near the Cape Cod Canal. The abandoned treatment plant was demolished in 1996-97, and surface pipes that carried the effluent to the disposal beds were removed. No further action, such as soil removal, was taken at the abandoned beds, which still receive natural recharge from precipitation.

The abrupt cessation of disposal without additional actions to remediate the aquifer at the disposal site provided a unique opportunity to observe the geochemical evolution of the plume as natural processes restore the water quality. This paper describes observations of ground-water quality made during the first 30 months after the disposal ended and interprets the changes in water quality that occurred. Other papers in this volume, by Kent and others (1999), Smith and others (1999), Barber and Keefe (1999), Campo and Hess (1999), and Stollenwerk and Parkhurst (1999), describe specific aspects of the natural restoration process.

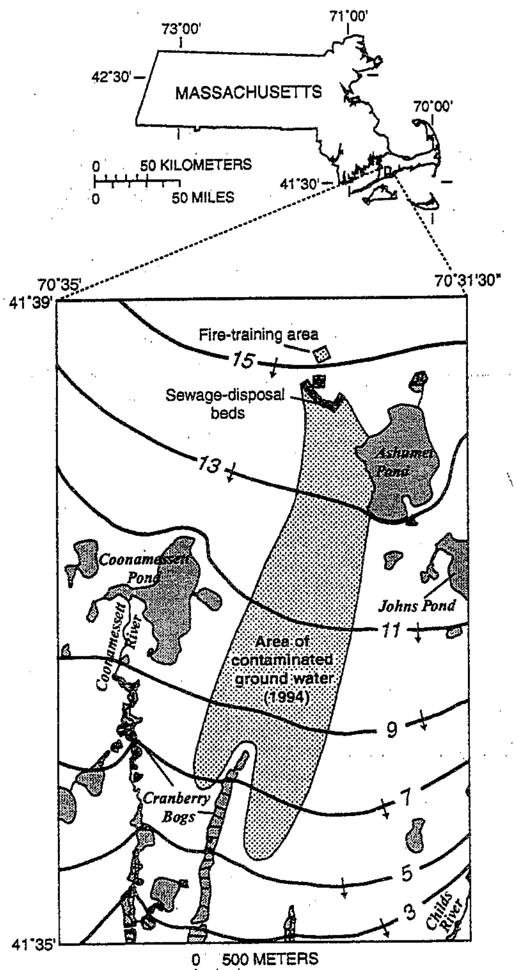

Figure 1. Location of the sewage-disposal beds, area of contaminated ground water, fire-training area, and water-table contours, western Cape Cod, Massachusetts.

DESCRIPTION OF THE SEWAGE PLUME

The disposal of secondarily treated sewage to infiltration beds on the MMR (fig. 2) for about 60 years created a plume of contaminated ground water that extended more than 3.5 miles from the disposal site in 1994. The plume was about 4,000 feet wide and about 80 feet thick. Downgradient accretion of recharge from precipitation formed an uncontaminated zone above the plume that increased in thickness with distance downgradient from the disposal site.

Hydrogeologic Setting

The treated sewage recharged the permeable, unconfined sand and gravel aquifer

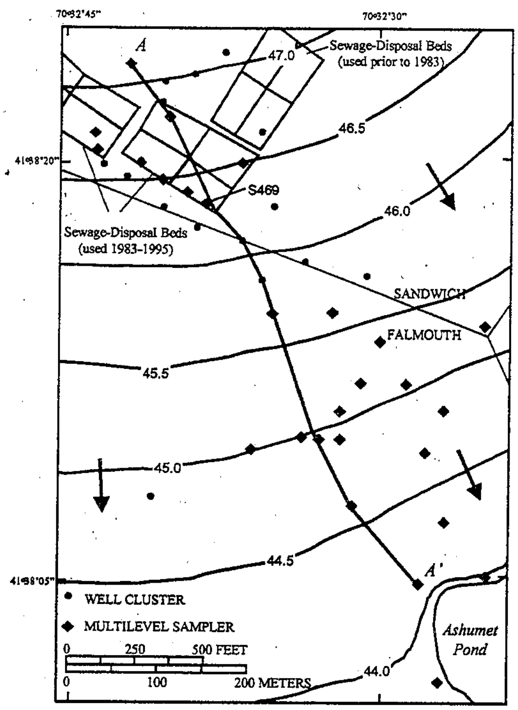

Figure 2. Location of the sewage-disposal beds, well clusters, multilevel samplers, vertical section A-A', water-table contours, and inferred direction of ground-water flow, western Cape Cod, Massachusetts. Water-table contours are in feet above sea level in January 1994.

that underlies western Cape Cod. The aquifer receives about 26 inches per year of natural recharge from precipitation (Masterson and others, 1998). At the sewage-disposal site, the aquifer is about 350 feet thick and has a hydraulic conductivity of 150 to 380 ft/d (feet per day). The depth to water varies as a function of land-surface altitude and is about 20 feet beneath the disposal beds. The water table slopes southward near the disposal site with an average hydraulic gradient of 0.0015 (fig. 2). The porosity is 35 to 40 percent, and the average ground-water velocity is 1 to 2 ft/d (LeBlanc, 1984; LeBlanc and others, 1991; Bohlke and others, 1999).

Disposal of Treated Sewage

The secondarily treated sewage was discharged to the infiltration beds from about 1936 until December 13, 1995. The rate of discharge varied over time with population at the MMR from 0.1 to 1.8 Mgal/d (million gallons per day) and was 0.1 to 0.5 Mgal/d in the 1990's prior to cessation of sewage disposal. During 1983-95, the treated sewage was applied to eight infiltration beds located along the Sandwich-Falmouth town boundary (fig. 2). The disposal history prior to 1983 is not well known, although it is known that treated sewage was discharged to four beds located at the northeastern corner of the plant for at least several years prior to 1983 (fig. 2).

The rate of sewage disposal to the beds during 1983-95 was about 30 times greater than the natural recharge rate from precipitation to the beds. The resulting water-table mound caused significant vertical flow beneath the beds. At the downgradient edge of the beds, the sewage-contaminated zone was about 80 feet thick. Ground water flowing from upgradient areas was diverted beneath and to the sides of the sewage plume, as shown schematically in figure 3A.

The treated wastewater contained generally elevated levels of dissolved substances, including nitrate, ammonium, phosphorus, and trace metals (Savoie and LeBlanc, 1998). During 1994-95, the treated wastewater was characterized by a specific conductance of about 500 µS/cm (microsiemens per centimeter), dissolved-oxygen concentrations of about 9 mg/L (milligrams per liter), dissolved-organic-carbon concentrations of about 17 mg/L, and nearly neutral pH (about 6.5). In contrast, uncontaminated ground water at the site contains low levels of dissolved substances (LeBlanc, 1984) and is characterized by a specific conductance of less than 100 µS/cm, dissolved-oxygen concentrations of 6 to 12 mg/L, less than 1 mg/L dissolved organic carbon, and acidic pH (less than 5.7).

Geochemistry of the Plume

Biodegradation of organic matter in the zone of contaminated ground water resulted in the creation of distinct geochemical zones (Hess and others, 1996). The zones were characterized by steep geochemical and microbiological gradients (Smith and others, 1991a). The plume had a core that contained little or no dissolved oxygen, and elevated concentrations of dissolved iron and manganese, which are indicative of a reducing

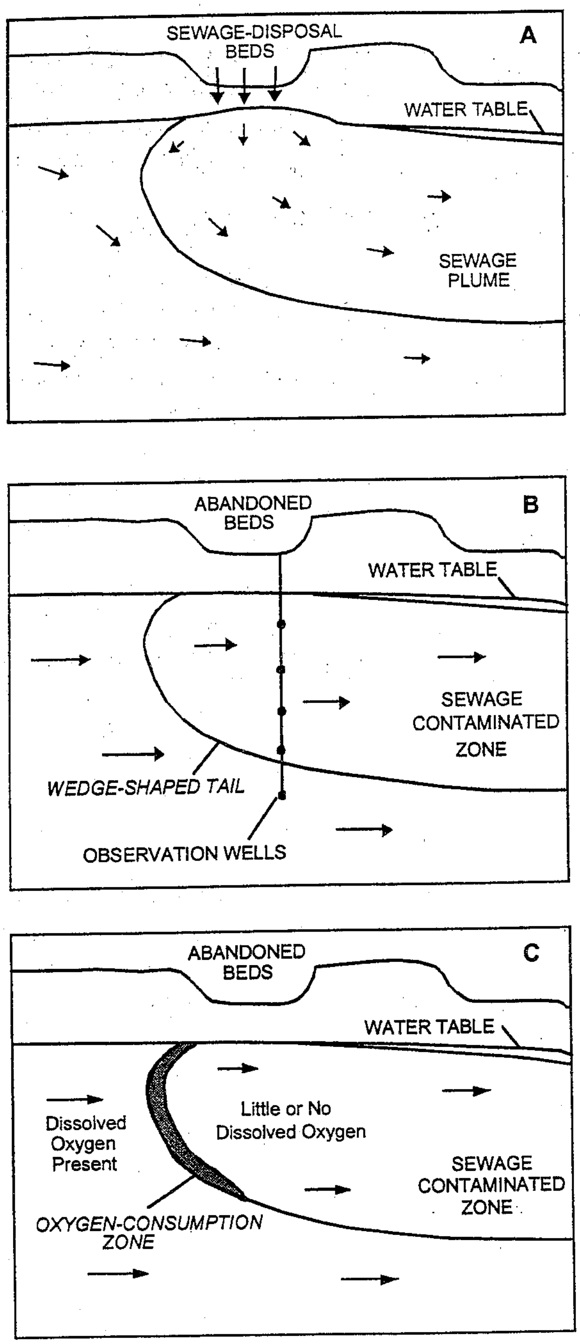

Figure 3. Schematic vertical sections through the sewage-contaminated zone (A) before and (B) after sewage disposal was stopped and (C) the hypothesized oxygen-consumption zone at the trailing edge of the plume.

geochemical environment (Kent and others, 1994). Nitrate was absent in the anoxic core because of denitrification, and transport of ammonium and phosphorus was retarded by sorption to the sediments (Ceazan and others, 1989; Smith and others, 1991b; Walter and others, 1996). Hess and others (1996) document the spatial and temporal variability of concentrations of boron, dissolved oxygen, and phosphorus near the beds that reflects historical variations in sewage-disposal patterns and rates at the site.

Predicted Changes After Sewage Disposal Ended

Hess and others (1996) predicted that ground-water-flow patterns would change after the sewage disposal ended, and that uncontaminated ground water would flow into the sewage-contaminated zone. The reintroduction of dissolved oxygen into the sewage-contaminated zone was expected to cause ammonium to oxidize to nitrate and ferrous iron to oxidize to ferric iron as the anoxic zone became smaller and eventually disappeared. The lower pH of the uncontaminated ground water was expected to cause desorption of contaminants, such as zinc and copper, that were bound to the sediments. These geochemical changes were expected to cause concentrations of some contaminants to increase temporarily in parts of the sewage-contaminated zone following the cessation of disposal.

STUDY METHODS

Ground-water samples were collected synoptically to observe the spatial distributions of constituents at specific times before and after disposal ended. Water-table altitudes were measured to estimate ground-water-flow directions.

Collection and Analysis of Water Samples

Water samples were collected periodically from observation wells and multilevel samplers (MLS) to observe water-quality changes during the natural restoration of the sewage plume. The wells are typically constructed of 2-inch-diameter polyvinyl chloride (PVC) pipe and 2-foot-long screens, and are arranged in clusters of two to eight wells screened at different depths. The

MLS include 15 individual 0.25-inch polyethylene sampling tubes bundled together and open to the aquifer at different depths. The methods used to collect water samples from the wells and MLS are described in Savoie and LeBlanc (1998).

The sampling sites are located near the abandoned disposal beds and in an area between the beds and Ashumet Pond (fig. 2). The sites near the beds include 68 wells and 14 MLS located mostly in the beds loaded during 1983-95 (fig. 2). Water-quality changes following cessation were expected to occur first at these sites, so the sampling points are closely spaced vertically and horizontally. Several sites were located upgradient from the recently loaded beds so that inflowing ground water could be sampled.

The sampling sites between the disposal beds and Ashumet Pond include 48 wells and 29 MLS located in the direction of ground-water flow from the beds (fig. 2). Water-quality changes were expected to propagate into this heavily instrumented area within about 1 year of cessation of disposal of sewage. Several of the well clusters and MLS are located along a transect (A-A' in figure 2) that is aligned with the direction of flow.

The full set of wells and MLS (fig. 2) was sampled in spring 1996, 1997, and 1998. A subset of the sites, including those near the beds and along transect A-A', was also sampled each year in the fall. Selected wells and MLS in and near the sewage beds were sampled biweekly to bimonthly with decreasing frequency from September 1995 until about February 1997. Samples were collected most frequently during the 6 months following the end of sewage disposal.

Ground-water samples were analyzed in the field for specific conductance, pH, dissolved oxygen, and turbidity. Samples were analyzed at USGS National Research Program laboratories in Boulder, Colorado, and Menlo Park, California, for dissolved species, including dissolved organic carbon (DOC), nitrate, ammonium, trace metals, phosphorus, and other selected cations and anions.

Measurement of Ground-Water Levels

Water-table altitudes were measured periodically in a network of 29 observation wells near the sewage-disposal beds and Ashumet Pond. The well locations (not shown in this report) and the three-point triangulation method used to estimate the slope of the water table are described by McCobb and others (1999).

NATURAL RESTORATION OF THE SEWAGE PLUME

The sampling described in the previous section documents the natural restoration process observed to date. In this paper, the observations are summarized by means of profiles showing water quality at MLS S469 at the downgradient edge of the disposal beds, and vertical sections showing water quality along section A-A' aligned with the direction of flow (fig. 2). Section A-A' passes through the center of the plume and intersects the anoxic zone downgradient from the disposal beds.

Water Levels and Ground-Water-Flow Direction

Water levels in the observation-well network near the disposal site were measured a few hours prior to cessation of disposal on December 13, 1995, and about 7 days after disposal ended. Water levels declined as much as 0.2 feet during this time, with the maximum decline measured at the center of the beds (Hess and others, 1996). Ground water from upgradient areas that previously had been displaced by the treated sewage could now pass unperturbed hydrologically through the sewage-contaminated zone (fig. 3B). This interpretation is supported by the detection of trace concentrations of volatile organic compounds in shallow wells in the beds during 1996-98 that are believed to originate from an abandoned fire-training area (fig. 1) located upgradient from the sewage-disposal site (Campo and Hess, 1999).

Conservative, Nonreactive Chemical Constituents

The water-quality observations indicate that the inflow of uncontaminated ground water from upgradient areas has begun to flush conservative, nonreactive chemical constituents away from the disposal site. Decreases in concentrations are evident in several water-quality profiles at MLS S469 (fig. 4). Specific conductance and boron concentrations in November 1995 show that the plume at the downgradient edge of the beds was about 80 feet thick during the plant operation. Specific conductance and boron concentrations had decreased in the bottom half of the plume by May 1996, 6 months after disposal ended, and were near background levels at all depths by June 1998 (figs. 4A and 4B).

The apparent cleanup from the bottom up shown in figure 4 may be evidence that the sewage plume had a wedge-shaped trailing edge (fig. 3B). The field data were too sparse to delineate this shape, but the northward flow of some treated sewage for a short distance because of the water-table mound and the accretion of treated sewage along the several-hundred-foot-long flowpath across the beds both could have contributed to development of a wedge-shaped tail.

The flushing of the conservative, nonreactive constituents is also evident in the longitudinal sections showing boron concentrations in June 1996 and June 1998 (fig. 5). By June 1998, 30 months after cessation of disposal, the trailing edge of elevated boron concentrations was more than 800 feet downgradient from the edge of the disposal beds. This observed rate of movement, about 1 ft/d, is consistent with the estimated average ground-water velocity of 1 to 2 ft/d.

Dissolved Oxygen and Dissolved Organic Carbon

Hess and others (1996) predicted that concentrations of dissolved oxygen in the plume would increase as uncontaminated ground water flowed into the sewage-contaminated zone from upgradient areas. Dissolved-oxygen concentrations in the plume did not change significantly, however, during the first 30 months after disposal ended (figs. 4 and 6). Concentrations beneath the disposal beds were less than 0.2 mg/L (referred to as suboxic conditions) in June 1998 and were zero (referred to as anoxic conditions) in some zones (fig. 4C). Although dissolved-oxygen concentrations at the bottom of the plume increased from June 1996 to June 1998, the zone of low dissolved-oxygen levels at the downgradient edge of the disposal beds was still 70 feet thick in June 1998 (fig. 4C).

The persistence of low dissolved-oxygen levels near the disposal beds indicates that oxygen continues to be consumed in the sewage-contaminated zone beneath the beds by biodegradation of organic matter or other chemical reactions. The oxygen may be consumed in a narrow zone where oxygen-containing ground water from upgradient areas enters the area contaminated by the treated sewage (fig. 3C). This zone may move slowly downgradient as the oxygen demand is depleted.

The concentrations of dissolved organic carbon (DOC) decreased significantly near the disposal beds after disposal ended (Barber and Keefe, 1999). By June 1998, the trailing edge of decreasing DOC concentrations was more than 800 feet downgradient from the edge of the beds. Readily mobile DOC is being flushed away from the beds by the uncontaminated ground water; however, DOC levels beneath the beds remained above background levels 30 months after cessation (Barber and Keefe, 1999). Organic matter stored on the sediments in the sewage-contaminated zone may be slowly biodegrading, a process that could maintain the suboxic and anoxic conditions near the disposal beds for many years.

Ammonium, Nitrate, and Dissolved Iron

Ammonium concentrations in the sewage-contaminated zone decreased during the first 30 months after disposal ended (Smith and others, 1999). Prior to cessation, some of the ammonium in the treated sewage was converted to nitrate by nitrification as it entered the aquifer beneath the disposal beds. Nitrification occurred because the treated sewage contained as much as 9 mg/L

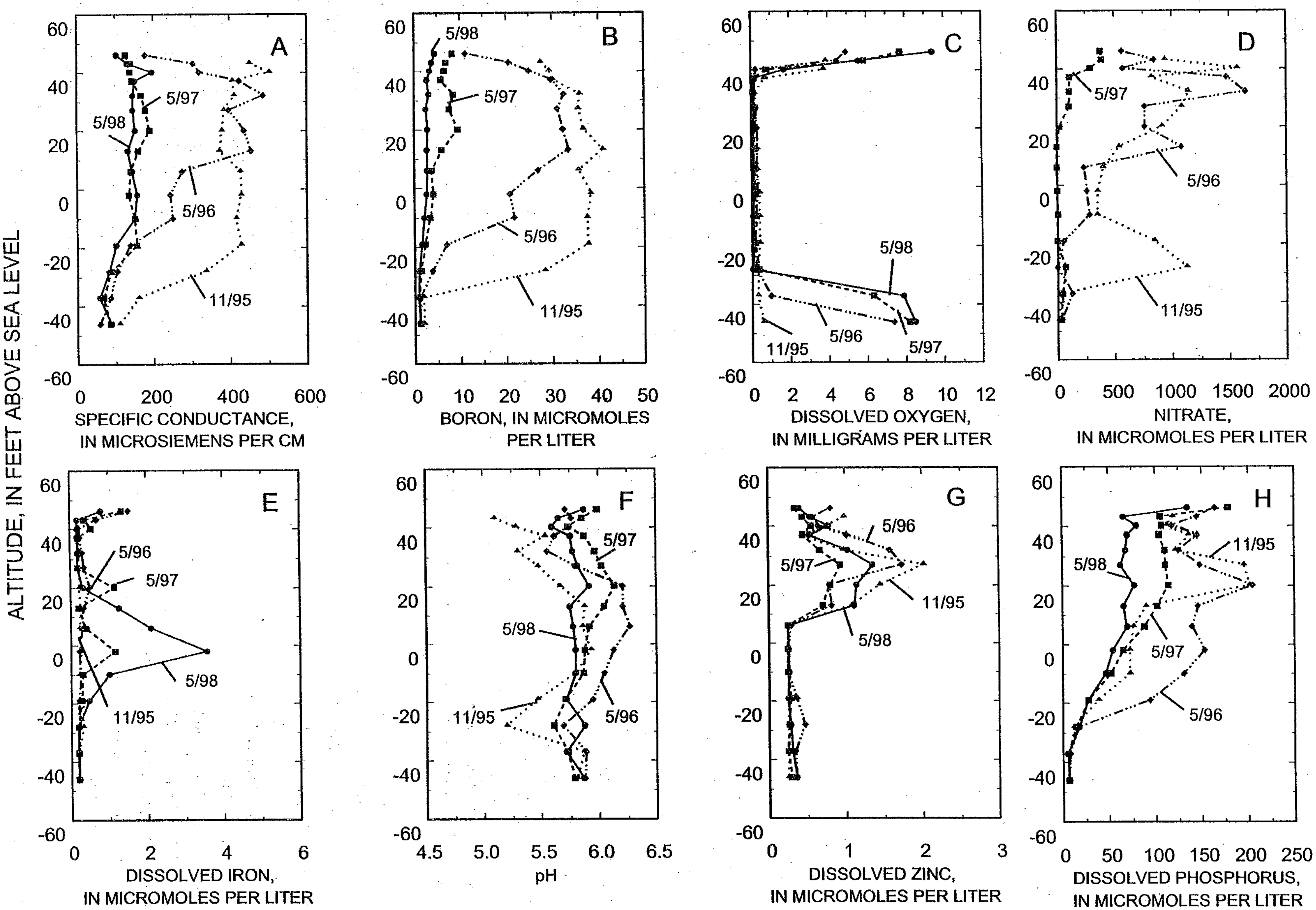

Figure 4. Vertical profiles of specific conductance, boron, dissolved oxygen, nitrate, iron, pH, zinc, and phosphorus at multilevel sampler S469, western Cape Cod, Massachusetts, 1995-98. Location of sampler shown in figure 2.

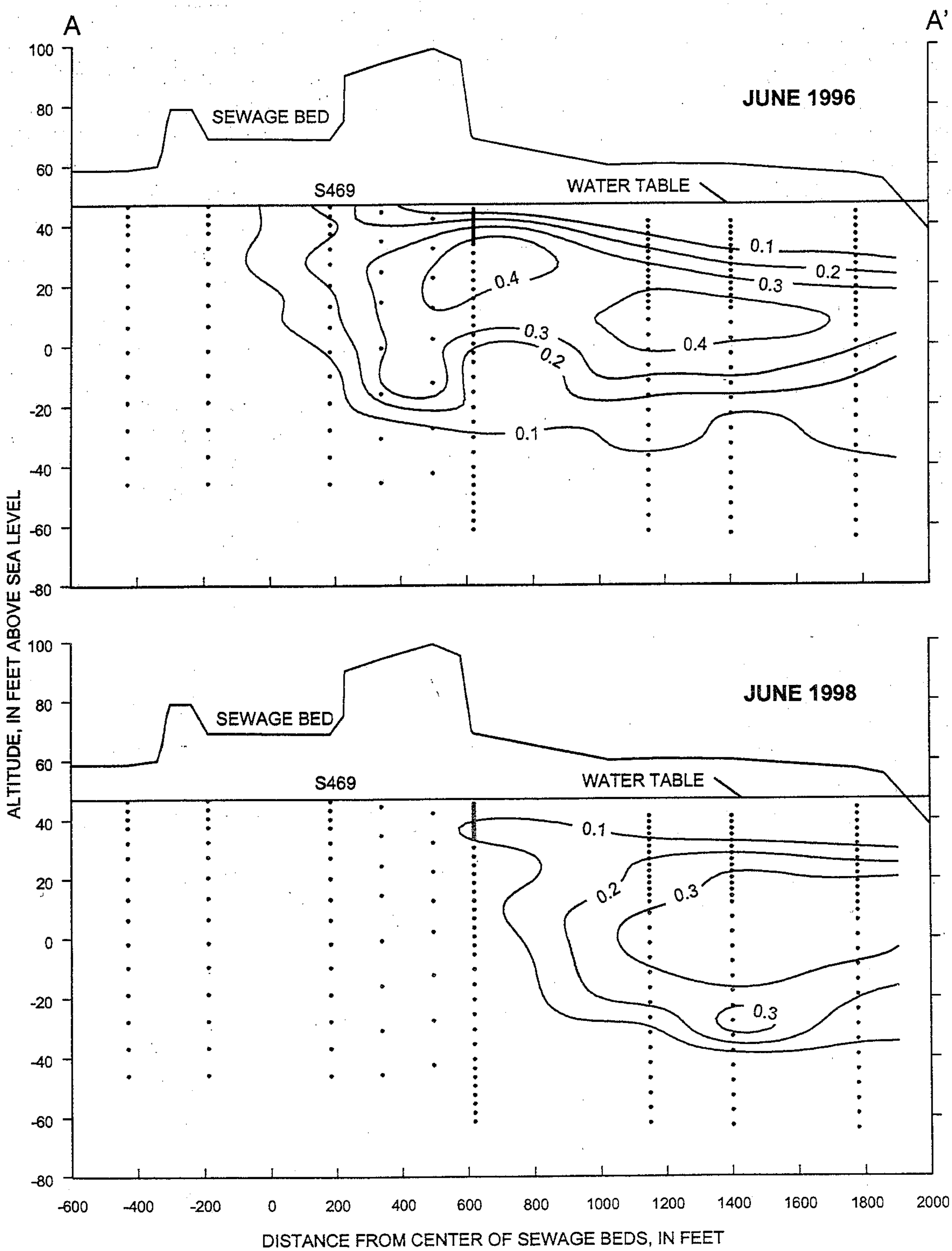

Figure 5. Longitudinal sections showing the distribution of boron concentrations between the sewage-disposal beds and Ashumet Pond, western Cape Cod, Massachusetts, June 1996 and June 1998. Lines of equal concentration in milligrams per liter. Dots show positions of well screens and multilevel-sampler ports. Location of section line shown in figure 2.

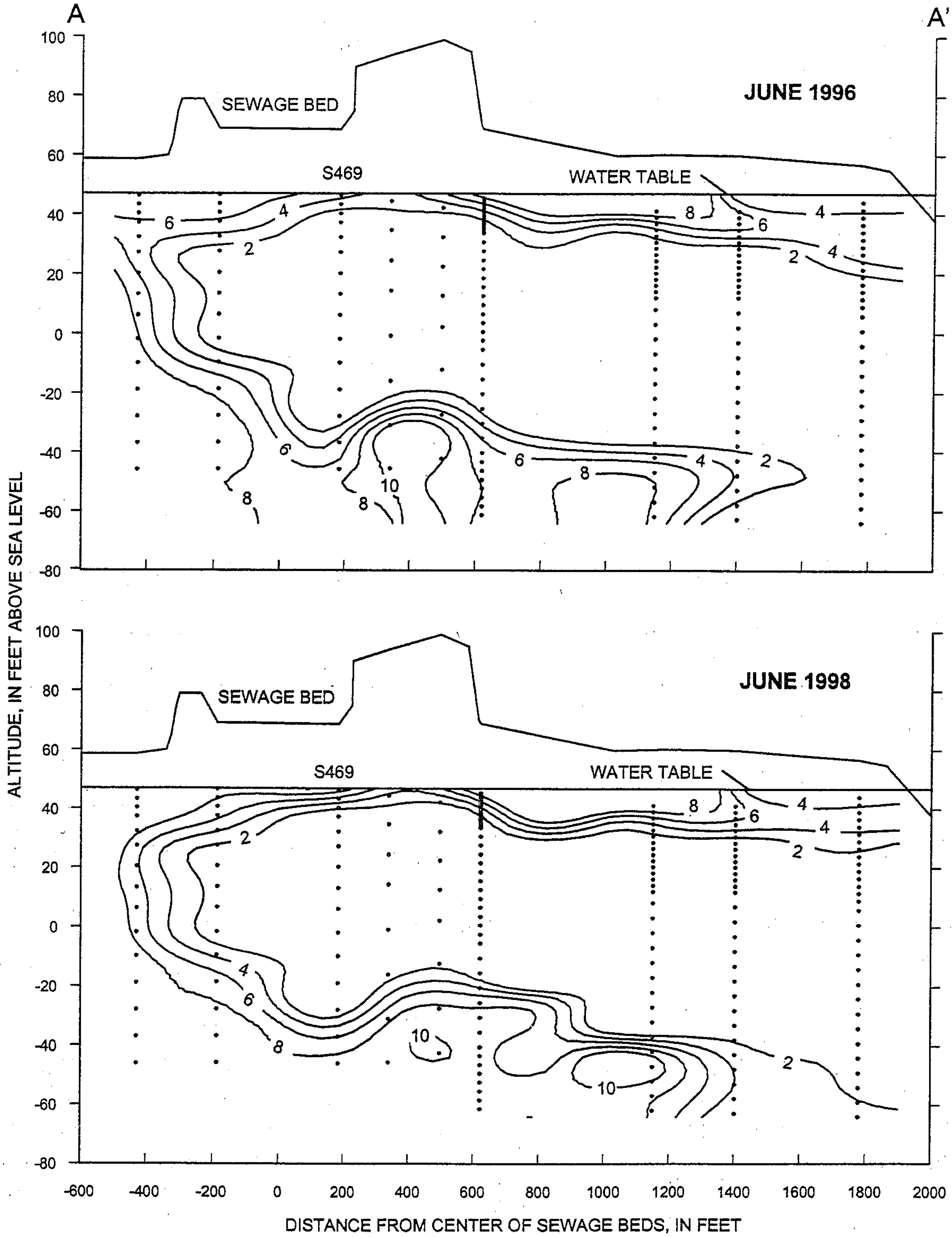

Figure 6. Longitudinal sections showing the distribution of dissolved-oxygen concentrations between the sewage-disposal beds and Ashumet Pond, western Cape Cod, Massachusetts, June 1996 and June 1998. Lines of equal concentration in milligrams per liter. Dots show positions of well screens and multilevel-sampler ports. Location of section line shown in figure 2.

dissolved oxygen. Ammonium that was not nitrified was transported downgradient from the beds at a slower rate than that of ground-water flow because of sorption by cation exchange on the sediments (Ceazan and others, 1989).

Hess and others (1996) predicted that the sorbed ammonium would be converted to nitrate as uncontaminated ground water entered the sewage-contaminated zone. The ammonium was desorbed and moved away from the beds, however, because nitrification of ammonium to nitrate was not occurring in the persistent suboxic and anoxic environments near the disposal beds (Smith and others, 1999).

Concentrations of nitrate were elevated at the top and bottom of the plume during sewage disposal, but were low in the center of the plume (fig. 4D) because of denitrification of nitrate to nitrogen gas in the suboxic environment (Smith and others, 1991a). Nitrate concentrations decreased significantly near the bottom of the plume at the beds within 5 months of cessation. By May 1997, nitrate concentrations had decreased to below detection limits through much of the sewage-contaminated zone at MLS S469 (fig. 4D). The presence of a thin zone of elevated concentrations of nitrate near the water table beneath the beds indicates that nitrate, possibly formed by continuing nitrification in the unsaturated zone, was being carried down to the water table by natural recharge. Smith and others (1999) concluded that nitrate beneath the abandoned disposal beds was being removed by transport downgradient and by denitrification because of the decreased nitrate input and the absence of dissolved oxygen. In suboxic zones surrounding the core of the plume, nitrate concentrations approached levels characteristic of uncontaminated ground water upgradient from the disposal site.

Concentrations of dissolved iron at the disposal beds were below detection limits prior to cessation of disposal (fig. 4E). The dissolved oxygen in the treated sewage was sufficient to maintain suboxic conditions in the plume within 400 feet of the downgradient edge of the beds. The core of the plume was anoxic farther downgradient, where dissolved oxygen and nitrate had been completely consumed by biodegradation of organic materials.

After nitrate in the center of the plume beneath the disposal beds had been depleted (fig. 4D), dissolved-iron concentrations steadily increased (fig. 4E), probably because insoluble ferric iron oxide on the sediments was reduced to soluble ferrous iron (Lovley and others, 1989). The appearance of dissolved iron and the depletion of nitrate and dissolved oxygen beneath the beds indicate that the geochemical environment in the sewage-contaminated zone has become more reducing.

pH, Trace Metals, and Phosphorus

Hess and others (1996) predicted that sorbed trace metals would be mobilized following cessation of sewage disposal as low-pH uncontaminated ground water from upgradient areas entered the sewage-contaminated zone and organic matter was degraded. Although pH values have fluctuated slightly (fig. 4F), large decreases in pH have not been observed (fig. 7). The pH values at the downgradient edge of the disposal beds (fig. 4F) were greater than 5.7 throughout the sewage-contaminated zone, most likely because anaerobic biodegradation reactions consume hydrogen ions and, therefore, counteract the acidity of the inflowing ground water and the additional acidity generated by aerobic biodegradation occurring in the oxygen-consumption zone (Kent and Maeder, 1999).

The concentrations of trace metals, such as zinc (fig. 4G) and copper, have changed little since disposal ended because the pH has not changed (Kent and Maeder, 1999). The fluctuations of zinc concentrations at individual sampling depths were caused by small fluctuations in pH because zinc sorption is strongly dependent on pH (Kent and others, 1999). Small decreases in copper concentrations observed from November 1995 to May 1997 probably were caused by desorption of weakly sorbing copper complexes as the sewage-contaminated zone was initially flushed by uncontaminated ground water from upgradient areas (Kent and Maeder, 1999).

Concentrations of phosphorus beneath the disposal beds were elevated, but decreased with depth prior to cessation (fig. 4H). Phosphorus sorbs strongly to the sediments, and a large

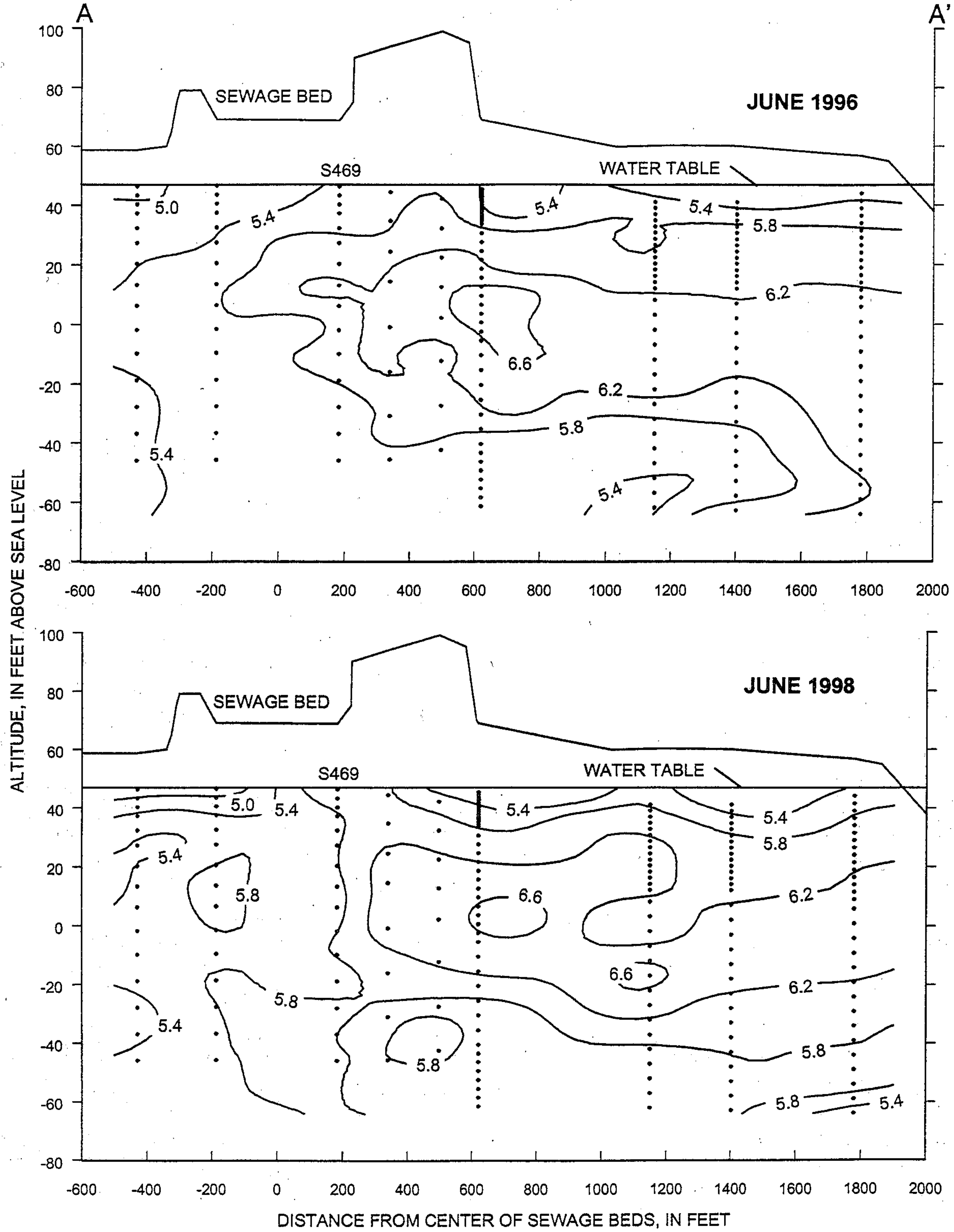

Figure 7. Longitudinal sections showing the distribution of pH between the sewage-disposal beds and Ashumet Pond, western Cape Cod, Massachusetts, June 1996 and June 1998. Lines of equal value in standard pH units.. Dots show positions of well screens and multilevel-sampler ports. Location of section line shown in figure 2.

reservoir of sorbed phosphorus was associated with the dissolved phosphorus (Walter and others, 1996). During the first 6 months after sewage disposal ended, phosphorus concentrations increased significantly in the lower part of the plume beneath the beds (fig. 4H). This increase was probably caused by desorption of phosphorus resulting from a transient increase in pH as uncontaminated ground water initially flushed through the sewage-contaminated zone (Walter and others, 1999; Kent and Maeder, 1999). The small but steady decreases in phosphorus concentrations since May 1996 (fig. 4H) indicate that phosphorus will slowly desorb and be transported away from the disposal beds.

Geochemical Modeling

Stollenwerk and Parkhurst (1999) used a one-dimensional reaction-transport model to simulate the development of the sewage plume during the 60 years of disposal and to predict the evolution of the plume after cessation of disposal. Simulation results showed that reducing conditions could persist near the disposal site for more than 60 years during natural restoration, although the prediction was sensitive to the estimated reactivity and amount of sorbed organic matter in the aquifer. Simulation results also showed that pH buffering by anaerobic biodegradation and sorption reactions on the sediments may retard the advance of the low-pH environment at the trailing edge of the sewage-contaminated zone. Therefore, pH could take decades to decrease to levels typical of uncontaminated ground water. Because ionic-strength, redox, and pH conditions change at different rates, changes in concentrations of individual contaminants affected by these parameters are likely to propagate away from the disposal site in correspondingly complex spatial and temporal patterns.

SUMMARY AND CONCLUSIONS

Natural restoration has received increased attention as an option for the cleanup of contaminated aquifers. This option relies on the natural physical, chemical, and biological processes to restore the quality of ground water to acceptable levels.

Sixty years of sewage disposal at the Massachusetts Military Reservation created a plume characterized by distinct geochemical zones and steep geochemical gradients. The cessation of sewage disposal at the site in December 1995 provided a unique opportunity to study the natural restoration processes in a sand and gravel aquifer.

Observations made by analyzing water samples collected from 116 wells and 43 multilevel samplers in the 30 months since cessation of sewage disposal show that the conservative, nonreactive contaminants, such as boron, are being flushed from beneath the disposal site. Organic matter continues to degrade slowly near the site, however. Biodegradation of organic matter consumes dissolved oxygen and nitrate and thus maintains suboxic to anoxic conditions and elevated pH in the sewage-contaminated zone. As a result, ammonium is being flushed from the sewage-contaminated zone rather than being oxidized to nitrate, and trace metals remain sorbed to the sediments rather than being desorbed as a result of pH changes. Results of geochemical modeling indicate that water quality will return to pre-contamination conditions slowly because of the persistent oxygen demand in the sewage-contaminated zone.

These observations indicate that natural restoration of plumes formed by disposal of organic-rich wastes involves many interacting physical, chemical, and biological processes. Uncontaminated ground water entering contaminated zones may be altered geochemically for many years after the source of contamination is removed because of the persistence of sorbed contaminants and slowly degrading organic matter. The successful reliance on natural restoration to remediate aquifers will depend on understanding how the complex geochemical environment that is characteristic of many plumes evolves with time and affects the fate of redox- and pH-sensitive contaminants.

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