

# Long-Term Natural Attenuation of Carbon and Nitrogen within a Groundwater Plume after Removal of the Treated Wastewater Source

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Disposal of treated wastewater for more than 60 years onto infiltration beds on Cape Cod, Massachusetts produced a groundwater contaminant plume greater than 6 km long in a surficial sand and gravel aquifer. In December 1995 the wastewater disposal ceased. A long-term, continuous study was conducted to characterize the post-cessation attenuation of the plume from the source to 0.6 km downgradient. Concentrations and total pools of mobile constituents, such as boron and nitrate, steadily decreased within 1–4 years along the transect. Dissolved organic carbon loads also decreased, but to a lesser extent, particularly downgradient of the infiltration beds. After 4 years, concentrations and pools of carbon and nitrogen in groundwater were relatively constant with time and distance, but substantially elevated above background. The contaminant plume core remained anoxic for the entire 10-year study period; temporal patterns of integrated oxygen deficit decreased slowly at all sites. In 2004, substantial amounts of total dissolved carbon (7 mol C m<sup>-2</sup>) and fixed (dissolved plus sorbed) inorganic nitrogen (0.5 mol N m<sup>-2</sup>) were still present in a 28-m vertical interval at the disposal site. Sorbed constituents have contributed substantially to the dissolved carbon and nitrogen pools and are responsible for the long-term persistence of the contaminant plume. Natural aquifer restoration at the discharge location will take at least several decades, even though groundwater flow rates and the potential for contaminant flushing are relatively high.

## Introduction

Natural attenuation is an approach for groundwater remediation that has been a focus of interest and controversy (1). It has been increasingly used over the last 10–15 years as a

cost-effective means to deal with many types of subsurface contaminants, including hydrocarbons from oil and fuel spills, chlorinated solvents and metals from industrial practices, leachates from wastewater disposal facilities and landfills, radionuclides from weapons production, and explosives from military operations (1–5). The ability of an aquifer to self-remediate depends on many factors, including the type and amount of contamination and the biological, chemical, and physical processes that affect the speciation, transport, and fate of the contaminants. The importance of each process at a specific site depends on the chemical composition of the groundwater, redox conditions within the aquifer, and hydrogeological characteristics of the aquifer (1, 6).

Contaminant monitoring is vital for characterizing the effectiveness of natural attenuation. In practice, regulatory requirements usually limit the focus of natural attenuation studies to a rather specific set of toxic contaminants, to those situations in which contaminant levels are exceedingly high, or to a demonstration that contaminant migration has not extended beyond some delineated location downgradient. As a result, there is little information regarding the long-term bulk recovery of an entire groundwater contaminant plume following the removal of the contamination source. The sequence and timing of such a recovery are largely subjects for speculation.

Wastewater disposal practices have resulted in large numbers of groundwater contaminant plumes throughout the United States and are an issue of global concern. These include large-volume surface disposals from wastewater treatment plants and small-volume septic systems from individual households and businesses. These plumes typically contain relatively high levels of carbon, nitrogen, and phosphorus, as well as other soluble and sorbed constituents (7–10). Conventional secondary treatment reduces the total amount of organic carbon entering an aquifer relative to septic treatment. However, elevated levels of dissolved organic carbon (DOC) are still seen at many disposal sites and the presence of volatile organic compounds often poses a serious contamination problem (11–12). Behavior of organic contaminants in groundwater varies greatly with respect to degradation and transport, depending on the nature of the compound. Conventional secondary treatment has a minimal effect on total inorganic nitrogen loads entering groundwater, with nitrate more likely to predominate due to nitrification during the treatment process (13). Processes that can affect nitrogen speciation during transport in an aquifer include ammonium sorption/desorption, assimilation, mineralization of organic nitrogen, nitrification, and denitrification. Many of these processes are coupled with or interact with carbon-cycling processes.

The unconfined sand and gravel aquifer that underlies most of Cape Cod, Massachusetts is used as a sole-source water supply (14). In many Cape Cod locations, wastewater disposal practices have resulted in groundwater contaminant plumes that affect water quality and the suitability for human consumption (8, 10). In 1995, the source of a large plume of treated wastewater from the Massachusetts Military Reservation (MMR), was removed after more than 60 years of disposal onto rapid infiltration beds. Processes that control the fate and transport of carbon and nitrogen within the MMR wastewater plume have been well-documented (8, 11, 15–18). The purpose of this study was to determine the long-term evolution and dissipation of carbon, nitrogen, and general aquifer geochemistry after the contaminant source had been removed. A 10-year record of the integrated effects

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of key processes (hydrological, biological, and chemical) within the contaminated aquifer system provides a basis for defining the general time frame for natural attenuation of wastewater-contaminated aquifers, the sequence of events involved during recovery, and the overall perspective for complete aquifer recovery.

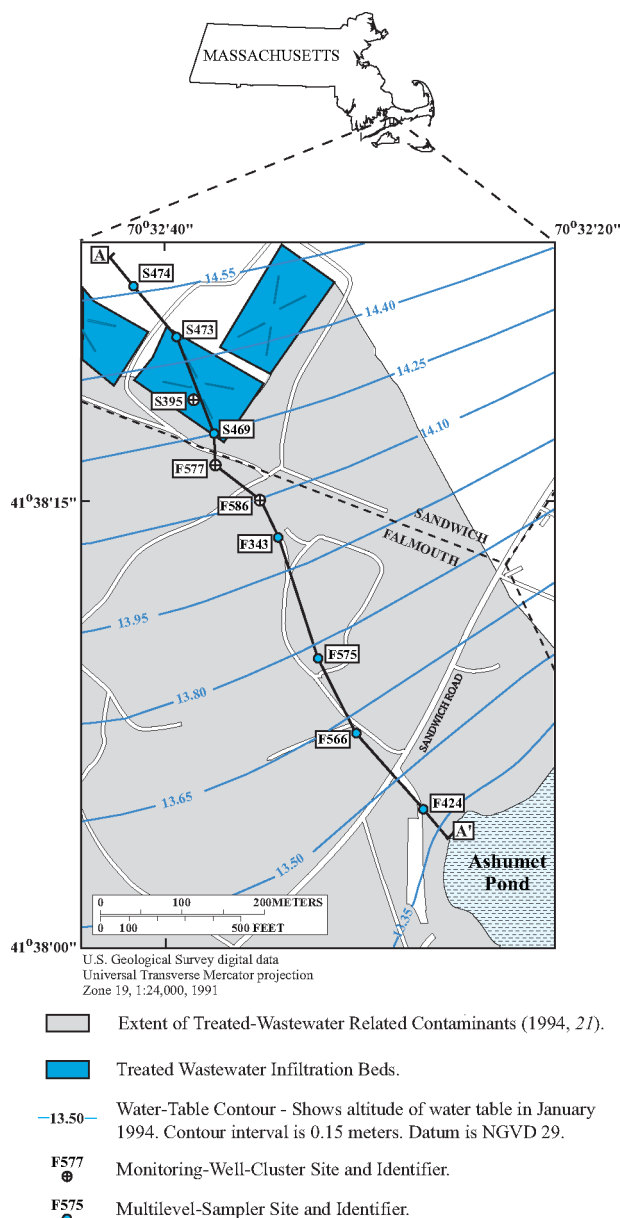
## Experimental Section

**Study Site.** The study site is an unconfined, noncalcareous, sand and gravel aquifer located on Cape Cod, Massachusetts. Pristine groundwater at this site is oxic ( $>300 \mu\text{M O}_2$ ), contains low concentrations of total dissolved solids, total nitrogen, nitrate ( $<30 \mu\text{M N}$ ), ammonium ( $<0.7 \mu\text{M N}$ ), total organic carbon ( $<20 \mu\text{M C}$ ), boron ( $<1 \mu\text{M}$ ), and chloride ( $<250 \mu\text{M}$ ) (8, 15). However, a portion of the aquifer has been affected by more than 60 years of secondarily treated wastewater disposal onto rapid infiltration sand beds. The water table is located  $\sim 6.5$  m below the surface of the infiltration beds, and the long-term disposal resulted in a groundwater contaminant plume that is more than 6 km long, 30 m thick, and 1000 m wide. The plume is typically characterized by vertical gradients of dissolved constituents (19), despite the relatively homogeneous nature of the aquifer (20), and consists of a suboxic to anoxic ammonium-containing core, surrounded by an oxic to suboxic nitrate-containing outer zone (8, 16, 19, 21). Extensive studies of the contaminant plume, including reactive and nonreactive tracer tests, have provided detailed information about the transport and fate of contaminants throughout the aquifer (11, 15, 16, 19, 22–24).

Wastewater effluents typically contain natural and synthetic organic compounds with chemical properties ranging from highly polar surfactant metabolites to hydrophobic alkanes and steroids (11, 25, 26). Human-derived biogenic compounds, surfactants, and volatile chlorinated hydrocarbons comprise much of the organic carbon component of the Cape Cod wastewater plume (11, 22). Sorption of organic matter to the Cape Cod aquifer sediments is complex and involves coulombic and hydrophobic interactions (27). Although the sediments are mostly quartz and feldspar, the mineralogical and sorption characteristics are variable (28). Natural and contaminant humic substances sorb to the metal oxyhydroxide grain coatings and accessory mineral substrates, and provide a partition media for hydrophobic organic contaminants. The combined electrostatic and hydrophobic interactions influence the transport of linear alkylbenzene-sulfonate, which has both an anionic and a hydrophobic moiety (29, 30). The sediment organic carbon content of the aquifer material varies from 0.001 to 1% (27) as a function of particle size, mineralogy, and location, and provides a significant pool of DOC upon desorption.

In this study, a 0.8-km transect (A–A', Figure 1) was intensively sampled for more than 8 years after shutdown of the disposal site in December 1995 to follow the dissipation of the contaminant plume originating below the infiltration beds. The travel time from site S469, located at the south end of the southern-most infiltration bed, to site F424 at the distal end of the A–A' transect is about 3 years. The transect generally follows the direction of groundwater flow and is composed of two well clusters (5.1-cm diameter with 0.6-m long screens) and seven 15-port multilevel samplers (MLS) as described in ref 21. This paper details the effect of the source cessation on dissolved and sorbed carbon and nitrogen in the aquifer. Other aspects of the effects of source cessation on the contaminant plume, including phosphorus and metal loads, and detailed changes in hydrology are presented elsewhere (see ref 15 for a current list).

**Methods.** Groundwater samples were collected from each well using a submersible pump and from each MLS port using a peristaltic pump. Field parameters were measured



**FIGURE 1.** Groundwater study site, Massachusetts Military Reservation, Cape Cod, Massachusetts, showing locations of wells and multilevel samplers sampled for this study along transect A–A'. Well S395 was used for water level monitoring.

on-site: dissolved oxygen (DO) was measured colorimetrically and by probe (24); specific conductance, pH, and temperature were measured with specific probes; and alkalinity was determined by titration in the field (21). Water samples for nitrate, nitrite, ammonium, chloride, boron, DOC, and DIC determinations were filtered with 0.45- $\mu\text{m}$  Millex filters, then preserved as described in ref 21. Nitrate, nitrite, ammonium, and chloride were analyzed using a flow-injection autoanalyzer and ion chromatography. Boron was analyzed using inductively coupled plasma atomic emission spectroscopy. DIC was converted to carbon dioxide by acidification and DOC was converted by heated persulfate oxidation; concentrations were determined with infrared or conductivity detection. In some cases DIC was calculated from alkalinity and pH data. See the Supporting Information for a table listing instrument and analytical methods used by sample date, and for DIC methodology comparison. Field and standard reference samples were run routinely for quality control and quality assurance purposes.

**TABLE 1. Composition of Treated Wastewater Disposed onto Rapid Infiltration Beds at the Massachusetts Military Reservation**

constituent	concentration <sup>a</sup> ( $\mu\text{M}$ )		estimated total load <sup>b</sup> metric tons
	mean	range	
oxygen	>300	NA <sup>c</sup>	NA
dissolved organic carbon	1105	533–1583	600
dissolved inorganic carbon	550	NA	300
nitrate - N	869	259–1568	550
nitrite - N	21	1–36	10
ammonium - N	329	51–800	210
organic N	243	143–400	155
boron	41	29–52	20
chloride	1095	931–1523	1760
specific conductance <sup>d</sup>	407	343–516	NA

<sup>a</sup> Samples collected from 1974–1995 (8, 19, 21, 32, 35). <sup>b</sup> Calculated for 1936–1995 using estimated effluent volumes (31). <sup>c</sup> NA = not available. <sup>d</sup> Units for specific conductance are  $\mu\text{S cm}^{-1}$ .

## Results and Discussion

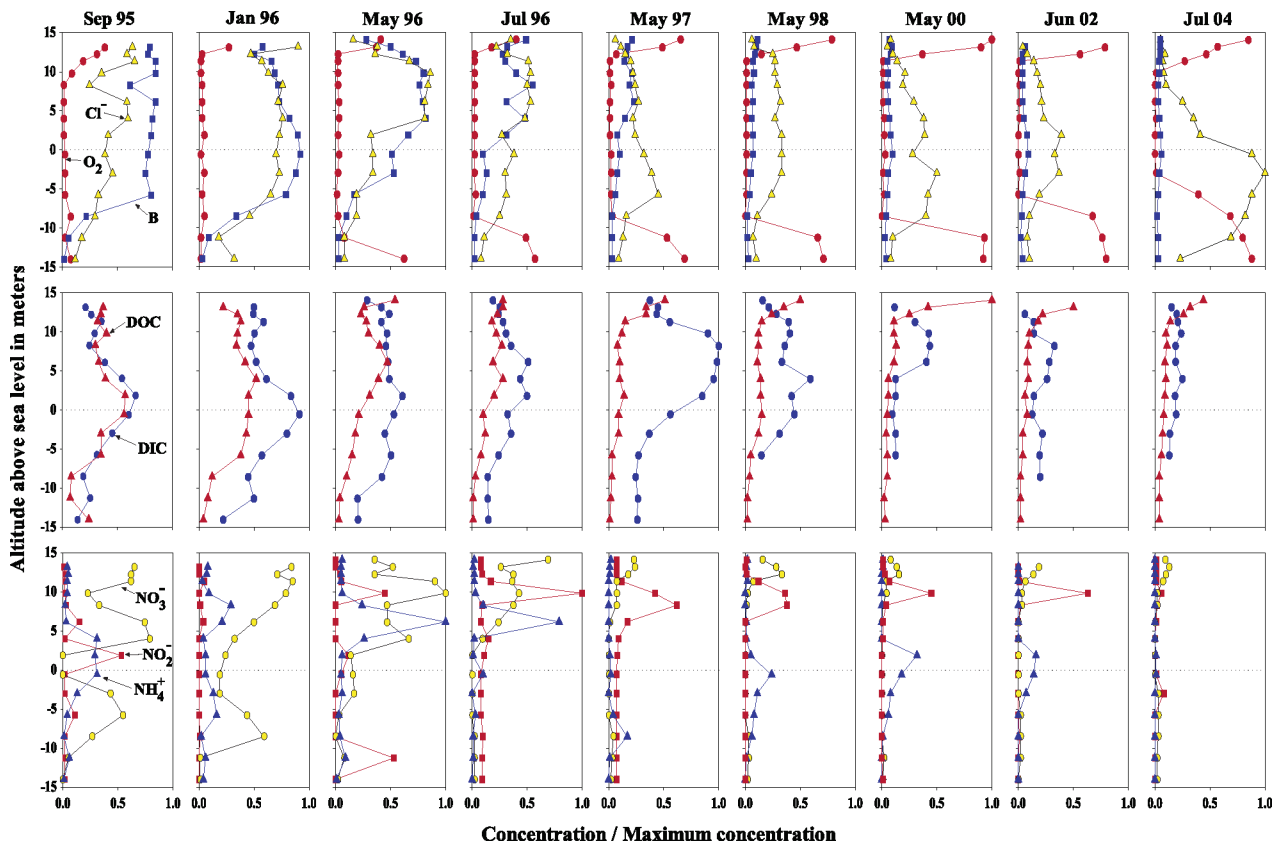
**Wastewater Effluent.** Treated wastewater effluent was discharged onto rapid-infiltration beds at the MMR for six decades. It was estimated that 45 billion L of wastewater were treated and disposed at the MMR facility between 1936 and 1995 (31). Periodic sampling of the effluent from 1974 to 1995 (Table 1) revealed high, but variable, concentrations of dissolved nitrogen (primarily as nitrate and ammonium), dissolved organic and inorganic carbon, and chloride, and lesser concentrations of boron, organic nitrogen, and nitrite. Assuming that the average concentrations in Table 1

represent the entire 60-year disposal period, the estimated total loads were 925, 900, 20, and 1760 metric tons for total dissolved nitrogen, total dissolved carbon, boron, and chloride, respectively.

### Groundwater Chemistry Under the Infiltration Beds.

Detailed vertical profiles of groundwater chemistry were collected below the infiltration beds at site S469 prior to the cessation of wastewater disposal (September 1995) and compared to more than 8 years of post-cessation sampling (January 1996 to July 2004, Figure 2). Prior to the cessation of disposal, evidence of wastewater intrusion into groundwater was present over the entire 28-m vertical interval sampled below the water table. Water-table mounding occurred below the beds (2), forcing the contaminants deep into the aquifer due to downward water flow. Groundwater specific conductance at S469 prior to cessation was  $>100 \mu\text{S cm}^{-1}$ , while typical uncontaminated groundwater in the aquifer has a specific conductance of  $<100 \mu\text{S cm}^{-1}$  (2). Following cessation of wastewater disposal, uncontaminated groundwater from upgradient began flowing through the aquifer underlying the infiltration beds in a more horizontal flow path typical of regional groundwater flow (2). This resulted in displacement of the discharged wastewater and a noticeable decrease in specific conductance, particularly in the deeper portions of the vertical profile (data not shown). After cessation, the vertical section of the aquifer affected by natural recharge through the infiltration beds was considerably smaller and shallow relative to the situation during wastewater discharge, as described elsewhere for decommissioned septic systems (see 33).

Boron is a common component of detergents and its presence at elevated concentrations in groundwater on Cape



**FIGURE 2.** Vertical profiles below the wastewater infiltration beds at S469 from September 1995 to July 2004. The wastewater source was removed in December 1995. Concentrations were normalized to highest value for each species within the dataset ( $C/C_{\text{max}}$ ). ( $C_{\text{max}}$  values:  $371 \mu\text{M O}_2$ , May 2000;  $2023 \mu\text{M Cl}^-$ , July 2004;  $41 \mu\text{M B}$ , November 1995;  $0.85 \text{ mM dissolved organic carbon (DOC)}$ , May 2000;  $4.14 \text{ mM dissolved inorganic carbon (DIC)}$ , May 1997;  $1643 \mu\text{M NO}_3^-$ , May 1996;  $8.7 \mu\text{M NO}_2^-$ , July 1996;  $540 \mu\text{M NH}_4^+$ , May 1996). The water table elevation at well S395 (Figure 1) ranged from 13.91 to 15.63 m (mean 14.67,  $n = 26$ ) from January 1996 to July 2002.

Cod can be traced to contamination from wastewater disposal (8, 11). Because boron has a specific anthropogenic source and likely interacts minimally with sediments under the chemical conditions of the groundwater plume, it provides a qualitative representation of the plume development and movement (11). Prior to cessation, boron concentrations at S469 were  $>30 \mu\text{M}$  at most depths (Figure 2), similar to the wastewater effluent concentration (Table 1). Boron concentrations decreased steadily after cessation of wastewater discharge, reaching near background levels ( $<4 \mu\text{M}$ ) by May 1998. Chloride behaves similarly to boron in that it is transported conservatively in groundwater, but concentrations over time can be more variable due to contributions from other contaminant sources, such as road salt. At S469, chloride reached a concentration of  $2010 \mu\text{M}$  in November 1995 (data not shown), then generally decreased with time after cessation of wastewater disposal. However, as with specific conductance, chloride concentrations in deeper ports at S469 and at upgradient sites were still elevated (up to  $2023 \mu\text{M}$ ) above background in July 2004, indicating inputs of chloride from sources other than the wastewater infiltration beds.

DO concentrations at S469 in September 1995 ranged from  $70$  to  $150 \mu\text{M}$  in the top 5 m below the water table and were near  $0 \mu\text{M}$  throughout the rest of the monitored interval (Figure 2). Because the wastewater recharging the aquifer was oxygenated, the upper portion of the pre-cessation profile at S469 contained some DO. Immediately after cessation, the DO concentrations at the shallow depths decreased due to oxygen-consuming processes and/or transport. As oxygen demand decreased with time, the top portion of the profile once again became oxic from precipitation recharge and flushing by uncontaminated groundwater. Beginning in May 1996, DO concentrations in the bottom part of the profile increased. By July 2004, the top 3–4 m and the bottom 6 m of the S469 profile had DO concentrations typical of recharge water ( $\sim 330 \mu\text{M O}_2$  at  $12.5^\circ\text{C}$ ). At a comparable depth interval upgradient from S469, DO concentrations were  $>185 \mu\text{M O}_2$  throughout the profile both pre- and post-cessation, indicating transport of DO to the downgradient sites within the plume. However, a large portion of the plume core at S469 (10 to  $-3$  m altitude) remained anoxic after more than 8 years, suggesting that microbial processes and oxidation of reduced constituents, such as ammonium, were consuming oxygen entering the core of the plume underlying the infiltration beds.

DOC concentrations in groundwater prior to cessation ranged from  $<0.06 \text{ mM C}$  in the deepest part of the S469 vertical profile to nearly  $0.5 \text{ mM C}$  in the core of the plume (Figure 2). Typical uncontaminated groundwater DOC concentrations near this site were  $<0.02 \text{ mM}$  (21). Following cessation, DOC concentrations decreased at most ports of the depth profile. The exception was the uppermost ports where DOC concentrations were  $>0.3 \text{ mM C}$  for the entire post-cessation period. As was the case for oxygen, DOC concentrations recovered first in the lower MLS ports. Presumably this decrease was due to lesser amounts of sorbed carbon at the lower ports within the profile. Post-cessation groundwater DOC just below the infiltration beds was probably derived from desorption of sediment organic carbon as well as bacterial biomass associated with the aquifer sediment. The sustained elevated DOC concentrations help to explain the low DO concentrations more than 8 years after cessation; DO transported into the site was consumed during biodegradation of organic compounds.

DIC concentrations showed a pattern similar to DOC prior to cessation (Figure 2), ranging from  $<0.8 \text{ mM C}$  at the deepest ports to almost  $3.0 \text{ mM C}$  in the middle of the profile. Post-cessation, DIC concentrations at S469 were similar to pre-cessation concentrations during the first year but then

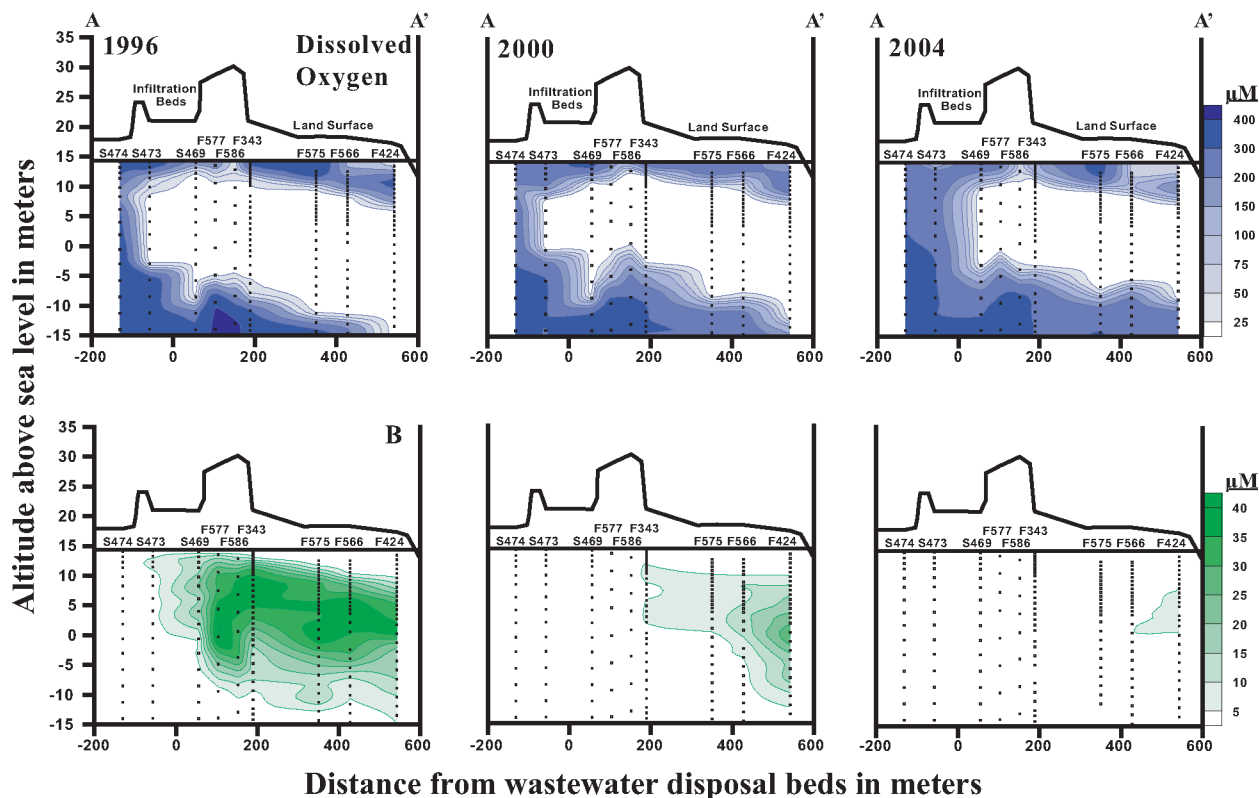
increased markedly in May 1997 to  $4.1 \text{ mM C}$ , presumably the result of oxidation of the sorbed and dissolved organic carbon to inorganic carbon, which contributed to the sustained suboxic to anoxic conditions below the beds.

Pre-cessation concentrations of nitrate, nitrite, and ammonium show an outer suboxic nitrate-containing zone and an inner anoxic ammonium-containing core (Figure 2). At S469, nitrate showed a slight concentration increase immediately after cessation followed by a gradual decrease with time. Denitrification is a primary mechanism for nitrate loss and nitrite production within the contaminant plume (18, 19, 24). After the oxygenated wastewater discharge was removed, nitrite increased in the region from 6 to 10 m above sea level. Nitrite concentrations subsequently decreased with time to very low levels at S469 ( $<1 \mu\text{M}$ ). Natural background concentrations of nitrate in recharging groundwater in the vicinity of the wastewater plume were  $<50 \mu\text{M}$ , so dilution likely contributed to the nitrate concentration decrease. However, there was still  $200 \mu\text{M}$  nitrate in the shallow groundwater (13-m altitude) as of July 2004. The elevated nitrate concentrations clearly indicate that processes related to past wastewater disposal provided a sustained source of nitrate. Nitrate probably originated from a combination of mineralization and oxidation of sorbed nitrogen and leaching from the unsaturated zone under the disposal beds.

Groundwater ammonium concentrations at S469 increased within a narrow band near sea level during the first six months after cessation. In May 1996 dissolved ammonium concentrations were  $>500 \mu\text{M}$  at an altitude of 6 m. Laboratory experiments with aquifer cores suggested that nitrification was important in converting sorbed ammonium to nitrate under the infiltration beds (17). However, with the removal of the oxygenated wastewater source, nitrification apparently ceased, allowing ammonium initially to increase in the core of the plume before decreasing to below pre-cessation levels. The spike in ammonium concentration immediately after cessation coincided with an increase in sodium and potassium and a decrease in calcium and magnesium at the same depth (data not shown). As the primary water source in this vicinity changed from wastewater to ammonium-free groundwater from upgradient, ammonium and potassium probably were released into the groundwater by cation exchange with a corresponding decrease in calcium and magnesium concentrations, as was observed in previous field experiments (16). By May 1997, relatively little dissolved ammonium remained at S469. However, in May 1998 ammonium concentrations began increasing within a 5-m interval around sea level and by May 2000 ammonium concentrations were  $\sim 170 \mu\text{M}$  within the core of the plume. This increase in ammonium was likely the result of mineralization of organic nitrogen from the sediments and, to a lesser extent, desorption of tightly bound inorganic nitrogen below the wastewater infiltration beds. Ammonium concentrations then decreased and by July 2004 were  $<7 \mu\text{M}$  at all depths. Typical uncontaminated groundwater concentrations of ammonium near this site were  $<1 \mu\text{M}$  (8).

#### Groundwater Chemistry Along The Plume Transect.

Vertical sections of the 0.8-km longitudinal transect (A–A', Figure 1) show the spatial distribution and down gradient movement of the contaminant plume constituents in the  $8^{1/2}$  years after cessation (Figures 3 and 4). Specific conductance (not shown), boron, DOC, nitrate, and ammonium concentrations all decreased with time along the transect, but were still elevated relative to the natural background in 2004. Groundwater boron concentrations decreased to the largest relative extent (Figure 3). In contrast, dissolved oxygen remained relatively unchanged (Figure 3) and the anoxic nitrate-free zone within the core of the plume persisted for the entire period of sample collection (Figure 4). The highest



**FIGURE 3.** Longitudinal vertical sections (A–A', Figure 1) showing dissolved oxygen and boron ( $\mu\text{M}$ ) in groundwater along the transect in 1996 (0.5 yrs), 2000 (4.5 yrs), and 2004 (8.5 yrs post-cessation). Dots show positions of well screens and multilevel-sampler ports. Sample collection for each transect generally required  $\sim 2$  months, starting in May (2000), June (1996), or July (2004). Contour plots were generated as described in the Supporting Information.

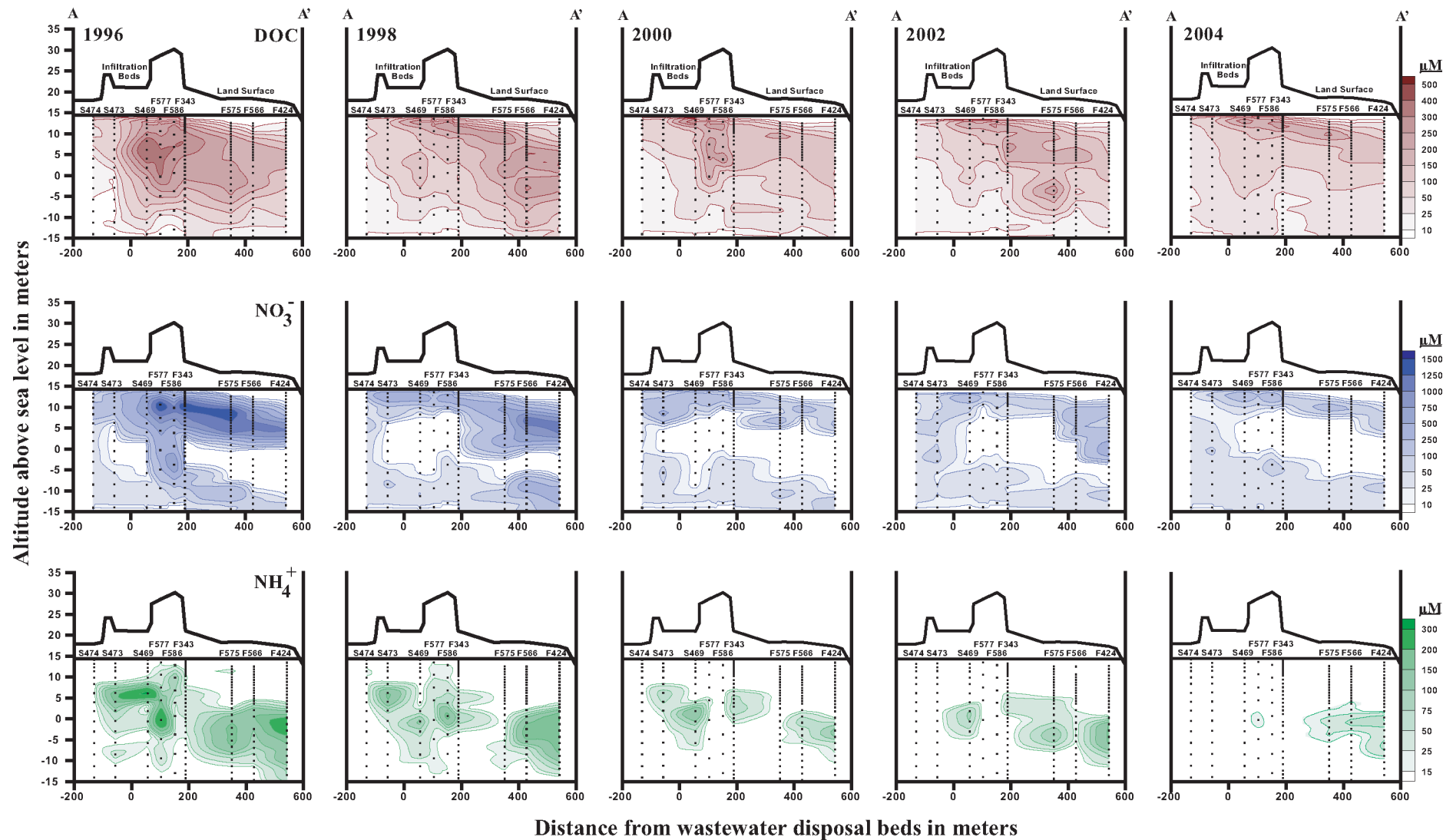
DOC concentrations were typically in the uppermost zone directly below the infiltration beds, although pulses of DOC between 200 and 300  $\mu\text{M}$  C traveled through the plume transect and were evident at other well sites (Figure 4). The highest groundwater DOC concentration (850  $\mu\text{M}$  C) was found at the top port (14 m altitude) of S469 4<sup>1</sup>/<sub>2</sub> years after cessation. In 2002 this port was dry due to a drop in the water table, but the next lower port had a DOC concentration of 426  $\mu\text{M}$  C, indicating that a pool of sediment organic carbon was gradually desorbing and contributing to groundwater DOC concentrations throughout the transect.

Groundwater nitrate concentrations decreased substantially in 8<sup>1</sup>/<sub>2</sub> years, from peak values of  $> 1000$   $\mu\text{M}$  throughout the oxic/suboxic zone during pre-cessation and early post-cessation, to  $\sim 230$   $\mu\text{M}$  in 2004. The anoxic, nitrate-free zone at the center of the plume increased in size after cessation as the oxygenated, nitrate-laden wastewater source was removed. In 2002 the nitrate-free zone started to decrease in size (Figure 4), especially at the most upgradient sites within the A–A' transect, as uncontaminated groundwater entered the plume area. However, as noted, there were still relatively high concentrations of nitrate (150–200  $\mu\text{M}$ ) in the shallow groundwater at S469 in 2004; mobilization processes beneath the beds appeared to be the predominant long-term source of nitrate along the A–A' transect. Ammonium concentrations in the groundwater also decreased throughout the plume transect after cessation, from peak concentrations in the anoxic zone in 1996 ranging from 100 to  $> 400$   $\mu\text{M}$  at most sites to  $< 90$   $\mu\text{M}$  at the distal end of the plume transect in 2004.

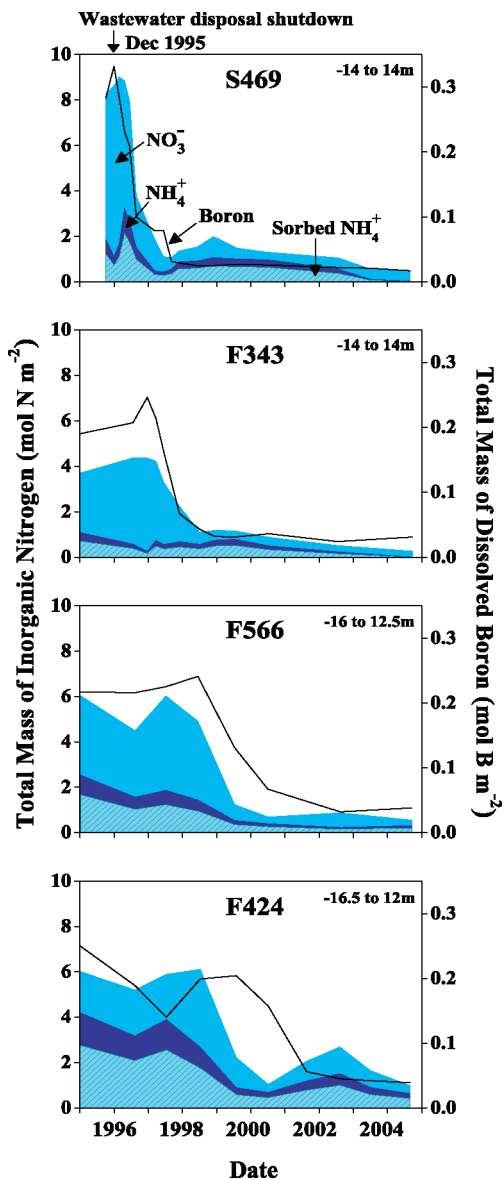
Relative proportions of dissolved inorganic nitrogen species changed with time along the A–A' transect. The concentration of each nitrogen species was integrated over a 28-m vertical interval at each of four sites along the A–A' transect, and multiplied by the sediment porosity (0.39) (23)

to give a total integrated mass in a vertical column of 1  $\text{m}^2$  in map view (Figure 5). The sorbed ammonium pool was calculated from measured dissolved ammonium concentrations using a distribution coefficient ( $K_d$ , ratio of sorbed to dissolved ammonium concentration) of 0.4  $\text{mL g}^{-1}$  dry weight sediment (34) and a conversion factor of 1867 g dry weight  $\text{L}^{-1}$  of aquifer. The change over time in the total dissolved nitrogen pool ( $\text{mol N m}^{-2}$ ) was compared to similar changes in the total dissolved boron pool. The mass of dissolved boron moved essentially unimpeded through the plume, affected only by variability in the source, travel time from the disposal beds, and dispersion. Based on a groundwater flow velocity of 0.42  $\text{m d}^{-1}$  (23), the travel time from S469 to F424 would be  $\sim 3.2$  years. The peak boron concentration at S469 near the time of disposal cessation (December 1995) reached F424 3–4 years later, and by 2001 boron concentrations were low throughout the transect (Figure 3).

Prior to cessation, the integrated pool of dissolved inorganic nitrogen species decreased from 7  $\text{mol N m}^{-2}$  (90.8%  $\text{NO}_3^-$ , 9.1%  $\text{NH}_4^+$ , 0.1%  $\text{NO}_2^-$ ) at S469 to 3.3  $\text{mol N m}^{-2}$  (55.5%  $\text{NO}_3^-$ , 44.0%  $\text{NH}_4^+$ , 0.5%  $\text{NO}_2^-$ ) at F424. The decrease resulted from loss of nitrate along the transect interval and occurred despite an increase in the ammonium pool with transport distance (compare F343 to F424 for January 1995; Figure 5). After disposal cessation the total dissolved nitrogen pool decreased with time at every location. The leading edge of the decrease could be followed downgradient along the transect (Figure 5), preceding the decrease in boron at F566 and F424. This decrease was primarily due to nitrate consumption by denitrification during transport along the A–A' transect (18, 19, 24) as confirmed by persistent elevated nitrite concentrations (up to 21  $\mu\text{M}$  in 2004) in some downgradient sites. Over time, the amount of nitrate relative to the total dissolved nitrogen pool at each site decreased while ammonium increased (Figure 5). During the 2000



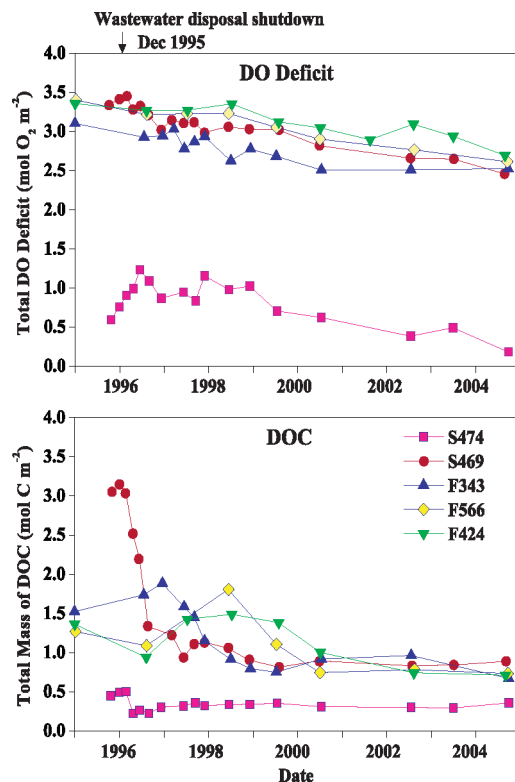
**FIGURE 4.** Longitudinal vertical sections (A–A', Figure 1) showing dissolved organic carbon (DOC), nitrate, and ammonium ( $\mu\text{M}$ ) in groundwater along the transect in 1996 (0.5 yrs), 1998 (2.5 yrs), 2000 (4.5 yrs), 2002 (6.5 yrs), and 2004 (8.5 yrs post-cessation). Dots show positions of well screens and multilevel-sampler ports. Sample collection for each transect generally required  $\sim 2$  months, starting in May (1998, 2000), June (1996, 2002), or July (2004). Contour plots were generated as described in the Supporting Information.



**FIGURE 5.** Temporal trends of total integrated mass of inorganic nitrogen species and boron within the core of the plume (vertical intervals listed in the upper right of each panel; calculations described in Supporting Information) at selected points along the A–A' transect. In all cases, the contribution of the total nitrite mass was less than the thickness of the boron line.

sampling, ammonium comprised >30% of the dissolved inorganic nitrogen pool at most sites compared to <10% pre-cessation. In addition to nitrate consumption, this change was also due to different rates of transport. Ammonium is transported with an average velocity of about 25% that of nitrate and water (34). Sorbed ammonium contributed substantially to the total pool of inorganic nitrogen. By 2004, <0.1 mol m<sup>-2</sup> sorbed NH<sub>4</sub><sup>+</sup> was present at S469 but >0.4 mol m<sup>-2</sup> sorbed NH<sub>4</sub><sup>+</sup> was present at F424.

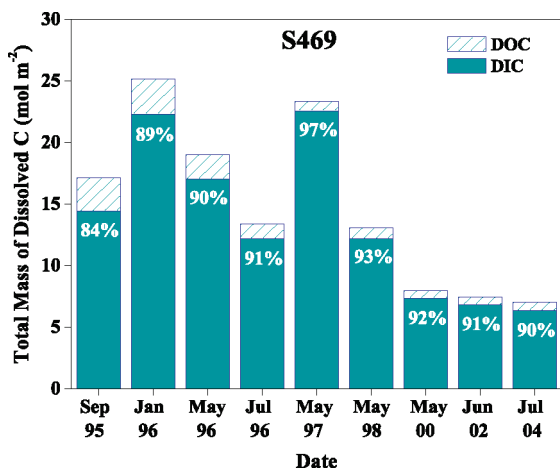
The presence of wastewater contaminants resulted in consumption of DO, causing a DO deficit relative to uncontaminated groundwater. The DO deficit was calculated by subtracting the measured DO concentration from an average DO concentration in uncontaminated groundwater of 331 μM, integrating the difference over a 28-m vertical interval and multiplying by the sediment porosity (Figure 6). The total, integrated DO deficit represents the amount of DO consumed (mol O<sub>2</sub> m<sup>-2</sup>) during transport to each respective sampling location. Over 8 years after cessation,



**FIGURE 6.** Temporal trends of integrated dissolved oxygen (DO) deficit (top) and total integrated mass of dissolved organic carbon (DOC) (bottom) within the core of the plume (vertical intervals listed in Figure 5; calculations described in Supporting Information) at selected points along the A–A' transect. DO deficit was calculated as the difference between measured DO concentration and an average DO concentration for uncontaminated groundwater of 331 μM.

the DO concentrations remained low within the core of the plume (Figure 3). The DO deficit decreased at a slow but consistent rate among the sites; the deficit decrease along the transect from S469 to F424 ranged from 1.0 to 0.7 mol O<sub>2</sub> m<sup>-2</sup> relative to pre-cessation levels. By comparison, the DO deficit at S474 (~200 m upgradient of the infiltration beds) fluctuated between 1.2 and 0.2 mol O<sub>2</sub> m<sup>-2</sup> pre- and post-cessation. Computed DO deficits for S474 may be the result of differences in recharge temperatures, DO consumption during recharge, and/or low-level sources of contamination. Extrapolation of the DO deficit recovery line for S469 ( $R^2 = 0.91$ ,  $n = 18$ ) predicts a return to the average value for S474 (0.8 mol O<sub>2</sub> consumed m<sup>-2</sup>) in 2021, more than 25 years after the wastewater disposal was stopped. A similar calculation for the post-1997 line for F424 ( $R^2 = 0.75$ ,  $n = 7$ ) predicts a recovery at that site in 2028. Long-term linearity of the recovery trend at these sites seems unlikely. So, while these extrapolations are useful for determining continued monitoring frequencies, we suspect that they represent overly optimistic recovery scenarios.

Integrated DOC pools were calculated over the 28-m vertical intervals at the same sampling sites (Figure 6). Prior to cessation, the DOC pool decreased along the A–A' transect from 3.1 mol C m<sup>-2</sup> at S469 to 1.4 mol C m<sup>-2</sup> at F424. This decrease likely represents degradation of organic carbon during transport within the aquifer. Although the amount of DOC at each site decreased with time, concentrations were still nearly 1 mol DOC m<sup>-2</sup> throughout most of the transect in 2004. Laboratory experiments with aquifer core material indicated a large pool of sorbed organic carbon remained on the sediments below the infiltration beds in 2002. Sediment obtained from S469 at an elevation of 13 m had ~4.9 μmol



**FIGURE 7.** Temporal trends of total integrated mass of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) within a 22-m vertical interval (13.2 to -8.5 m; calculations described in Supporting Information) under the infiltration beds at S469.

of water extractable C (g dry sediment)<sup>-1</sup>, which, if all dissolved at once, would result in a DOC concentration of ~23 mM. The extraction curves also suggested that additional carbon would have been removed with further extractions (R. L. Smith, unpublished data).

The integrated DIC pool was compared to the DOC pool within a 22-m vertical interval (13.2 to -8.5 m) at S469 over time (Figure 7). The 22-m interval was chosen to correspond to the available DIC data. In September 1995, DIC made up 84% of the total dissolved carbon pool under the infiltration beds. The DIC pool varied within the first 1½ years after cessation, peaking in May 1997 (23 mol C m<sup>-2</sup>, 97% of the total dissolved carbon pool) as the DOC pool declined. This may have resulted from changes in the degradability of the DOC pool. After May 1997, the pool of DIC declined steadily to ~6 mol C m<sup>-2</sup> by July 2004, and the ratio of DIC to DOC returned to near pre-cessation levels (90% DIC).

**Implications.** After more than 8 years of natural attenuation following the removal of the source of wastewater contamination, the prospect for a relatively rapid aquifer recovery at the MMR site depends on the context within which it is viewed. On one hand, the water discharged from the treatment process and the more mobile dissolved constituents (e.g. boron) have advected beyond 0.6 km downgradient. Likewise, concentrations and total pools of dissolved nitrogen, and to a lesser extent dissolved carbon, have diminished substantially under the infiltration beds to <6% and <40%, respectively, relative to pre-cessation values. Individually (as from a regulatory perspective for a single compound), these trends suggest that aquifer recovery is nearly complete in the vicinity of the disposal beds. On the other hand, other aspects of the contamination remain virtually unchanged and clearly contradict that conclusion. The contaminant plume size and shape (based on specific conductance > 100 μS cm<sup>-1</sup>) between pre- and post-cessation remained unchanged despite the relatively high potential for contaminant removal by flushing. Likewise, the DO profiles remained constant (except for the bottom few ports within the disposal bed), and the core zone of anoxia was virtually unchanged from 1994 to 2004, despite continued oxygen delivery to the plume vicinity by flow of upgradient uncontaminated groundwater. Finally, dissolved constituents (i.e. DOC, nitrate, and ammonium) that should have been transported beyond 0.6 km persisted.

These trends point to the continued long-term importance of sorbed constituents to the persistence of the contaminant plume and the ultimate overall return of the aquifer to pristine conditions. Indeed, after the initial concentration declines

that accompanied disposal cessation, concentrations and pools of many constituents have generally reached plateaus along the 0.6-km travel path from the source (Figures 5 and 6). In 2004, concentrations continued to decrease, but the rate of decrease was slow relative to the 10-year time frame. Anoxic conditions suggest that the sorbed constituents are primarily reduced, serving as a continual oxygen sink. Even more than 8 years after the source removal, the total biogeochemical oxygen demand apparently greatly exceeds the DO supply in replacement groundwater. As a consequence of the large oxygen demand, the migration of the DO front has been greatly retarded. DOC and DIC concentration trends suggest that the carbon that remains has become increasingly recalcitrant. Degradation and mineralization of organic contaminants by the resident microbial community continue, but carbon removal will take a long time given the limited oxygen supply. The relative distribution of nitrogen species has shifted, with total ammonium (dissolved plus sorbed) representing >50% of the inorganic nitrogen pool within the down gradient portion of the longitudinal transect. Nitrate was still present in groundwater immediately below the wastewater infiltration beds, although at much lower concentrations. The source of this nitrate was most likely oxidation of sorbed nitrogen at the disposal site, a source that will probably continue until DO concentrations return to pre-disposal values.

The MMR contaminant plume presented an opportunity to examine, in spatial and temporal detail, the net effect of natural in situ processes on the attenuation of wastewater contamination in groundwater prior to and following source removal. Prior to source cessation, sorption, dispersion, and denitrification were important processes affecting the fate and transport of contaminants, whereas post-cessation, desorption, mobilization, oxidation, and mineralization dominated. Clearly, desorption and mobilization of sorbed ammonium and carbon continued to contribute to the pool of nitrogen and carbon moving downgradient, even more than eight years after disposal ceased. Although the porous nature of the sand and gravel aquifer on Cape Cod allows groundwater to flow relatively quickly compared to other contaminated locations, it will take at least several decades before the carbon and nitrogen plumes are remediated and groundwater at the discharge location resembles its pre-disposal, aerobic condition.

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### Supporting Information Available

A table showing analytical techniques used by sample date, a comparison between different DIC methodologies, calculations for integrating total nitrogen and carbon pools and oxygen deficit, and a description of methods used to contour the data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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