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Evolution of a Ground-Water Sewage Plume After Removal of the 60-Year-Long Source, Cape Cod, Massachusetts: Inorganic Nitrogen Species

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ABSTRACT

High concentrations of nitrate and ammonium in ground water are often associated with sewage disposal practices. However, little is known about the combined effect of physical and biological processes upon the long-term fate of inorganic nitrogen in ground water, particularly after the source of contamination has been removed. Discharge of treated sewage onto surface infiltration beds at the Massachusetts Military Reservation on Cape Cod for 60 years created a ground-water contaminant plume more than 3 miles long. This plume is characterized by a suboxic to anoxic, ammonium-containing core surrounded by an oxic to suboxic, nitrate-containing outer zone. Historically, the sewage effluent contained varying amounts of nitrate and ammonium (200-2000 micromolar (μM)), oxygen (about 350 μM), and dissolved organic carbon (about 1000 μM). The geochemical evolution of the up-gradient portion of the plume has been extensively monitored for 2 years following the cessation of disposal in December 1995. Although nitrate concentrations in the core of the plume increased initially after cessation, nitrate levels have gradually decreased in and below the core of the plume. Nitrate concentrations have remained elevated (about 1 millimolar (mM)) near the water table, however, well after non-reactive solutes were flushed from this zone. Ammonium concentrations initially increased after cessation, then gradually decreased to low levels. These observations indicate that, while the effluent was being discharged, nitrification of ammonium to nitrate was occurring in the aquifer under the infiltration beds and was fueled by the oxygen in the treated sewage. Following the shutoff, nitrification stopped because oxygen was no longer being introduced with the treated sewage, and oxygen consumption up-gradient of the ammonium zone prevented oxygen in uncontaminated water from reaching the ammonium zone. Thus, ammonium moved down-gradient away from the disposal area, even though ammonium transport was slowed by cation exchange.

INTRODUCTION

A major source of ground-water contamination in the United States is sewage disposal, with several million septic systems currently in operation. Sewage contamination is typically associated with high concentrations of nitrate, ammonium, and organic carbon. Although several studies have examined sewage-related ground-water contaminant plumes, little is known about the recovery of an aquifer once the contaminant source has been removed.

The composition of a contaminant plume is the result of the complex interaction between physical, biological, and hydrological processes. Often, large reservoirs of sorbed or insoluble phases associated with the aquifer solids may serve key contributory roles to this interaction. The latter is the case for organic carbon and ammonium in sewage-related plumes. Important questions, then, are: (1) how will the contamination associated with the solids continue to affect aquifer restoration after the contaminant source is removed and, (2) what will the short-term and long-term production, consumption, and migration patterns for nitrate, ammonium, and organic carbon be in such a system?

In 1995, the disposal of treated sewage at a site on Cape Cod, Massachusetts, was stopped after 60 years of continuous discharge. The major processes that are known to be affecting nitrogen species in the aquifer, either directly or indirectly, are shown in table 1. Ground-water chemistry at this site was monitored before and after cessation in considerable detail, both spatially and temporally, to follow the natural restoration of the contaminated aquifer. Particular emphasis was placed on each of these processes to determine their combined effect upon the post-cessation evolution of the contaminant plume.

Table 1. Major processes affecting nitrogen species at Cape Cod study site.

Process	Reactants	Products
Aerobic heterotrophic respiration	O_2 + organic C	CO_2
Nitrification	$NH_4^+ + O_2$	NO_3^-
Denitrification	NO_3^- + organic-C	$N_2 + CO_2$
Ammonium cation exchange	NH_4^+ + solids	retarded transport

STUDY SITE

The study site is an unconfined sand and gravel aquifer located on Cape Cod, Massachusetts (fig. 1) that has been contaminated by the disposal of treated wastewater for 60 years. The sewage was discharged onto infiltration sand beds and percolated down to the water table. The practice produced a contaminant plume that is currently greater than 3 miles long and consists of a suboxic to anoxic ammonium-containing core, surrounded by an oxic to suboxic, nitrate-containing outer zone. In December 1995 the sewage discharge to the sand beds was stopped. A long-term study was initiated by the U.S. Geological Survey to follow the dissipation of the up-gradient portion of the contaminant plume near the disposal site and to examine key processes affecting the evolution of that portion of the plume. Methods for sample collection, preservation, and analyses are detailed in Savoie and LeBlanc (1998). Wells used to construct a transect aligned with the direction of ground-water flow are shown in figure 1.

Table 2. Composition of sewage effluent in February 1995 [μS/cm, microsiemens per centimeter at 25 degrees Celsius; μM, micromolar].

Specific Conductance	516 μS/cm
Oxygen	>300 μM
Dissolved Organic Carbon	1300 μM
Chloride	1500 μM
Nitrate	1500 μM
Ammonium	180 μM
Organic nitrogen	140 μM
Nitrite	1.5 μM

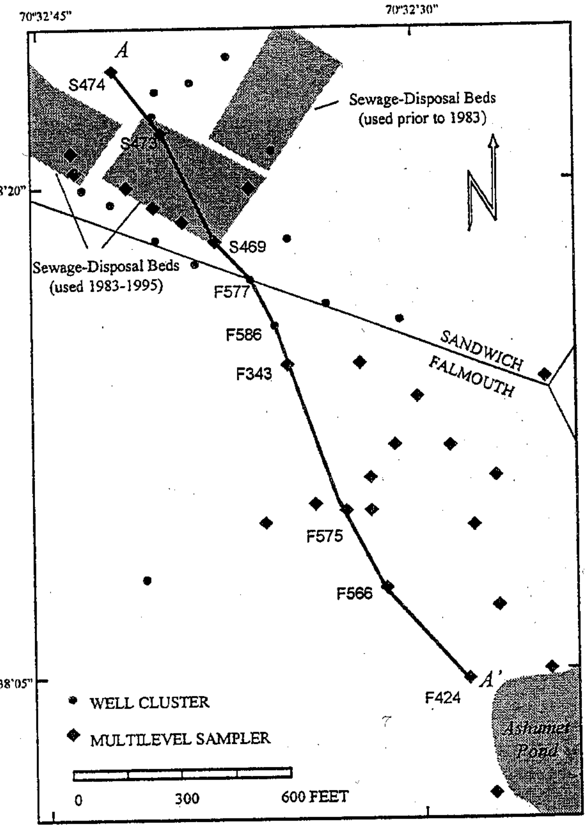

Figure 1. Ground-water study site on Cape Cod, Massachusetts, showing location of wells sampled for this study. The line depicts the longitudinal transect shown in Figures 3 and 5.

OBSERVATIONS OF GROUND-WATER QUALITY

The sewage effluent entering the aquifer prior to shutoff was well oxygenated, being in near-equilibrium with the atmosphere, and it contained dissolved nitrogen, primarily as nitrate but also as ammonium and organic nitrogen (table 2). At the time of shutoff, ground water under the infiltration beds was characterized by vertical gradients of dissolved solutes, such as oxygen, nitrate, and ammonium. The oxygen gradient at

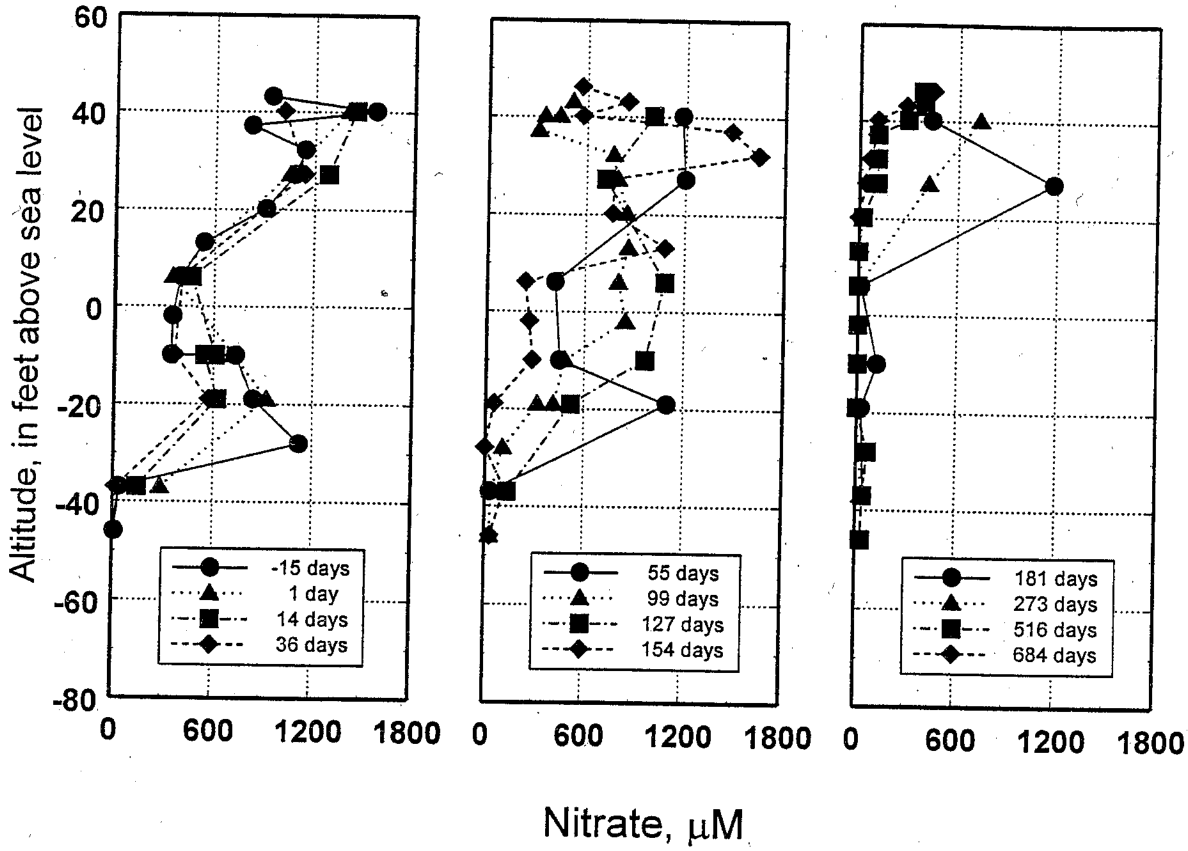

Figure 2. Depth profiles of ground-water nitrate concentrations at well site S469 relative to the date of sewage disposal cessation (December 13, 1995).

the top of the plume was approximately 10 feet thick; concentrations varied from air equilibrium (about 350 µM) at the water table to suboxic levels (less than 100 µM; data not shown) in the plume. After cessation, this gradient became narrower with time, and a second oxygen gradient, from suboxic levels in the core of the plume to oxic levels below the core, developed at the bottom of the plume (LeBlanc and others, 1999).

There was a pre-shutoff bimodal distribution of nitrate with depth under the infiltration beds. The lowest nitrate concentrations occurred in the center of the plume, with higher concentrations above and below (fig. 2). After shutoff, nitrate concentrations under the infiltration beds initially increased in the center of the plume before gradually decreasing from the bottom upward. After 273 days, nitrate concentrations exceeded 200 µM only in the shallowest samples. Along the longitudinal transect shortly after shutoff, nitrate was present at most depths throughout the contaminant plume (fig. 3), except in a zone in the center of the plume (at approximately sea level). During steady state loading prior to cessation, this zone of low nitrate concentration increased in size with downgradient transport as a result of denitrification (Smith and others, 1991, 1996). In June 1997, more than 500 days after shutoff, nitrate concentrations within 700 ft down-gradient of the infiltration beds had significantly decreased below an altitude of 30 feet, but had increased in the shallow horizons (fig. 3).

At shutoff, ammonium was present only in the center of the contaminant plume (fig. 4), even though it was present in the sewage effluent (table 2). However, ammonium concentrations increased with distance down-gradient to at least 500 feet from the beds (fig. 5). Ammonium concentrations under the infiltration beds after shutoff increased to high values at some depths (for example, 20-foot altitude), before subsequently decreasing. At greater depths, ammonium concentrations varied, but remained below 200 µM. The longitudinal transect shows that ammonium concentrations generally decreased within 700 feet of the infiltration beds by 500 days after shutoff (fig. 5).

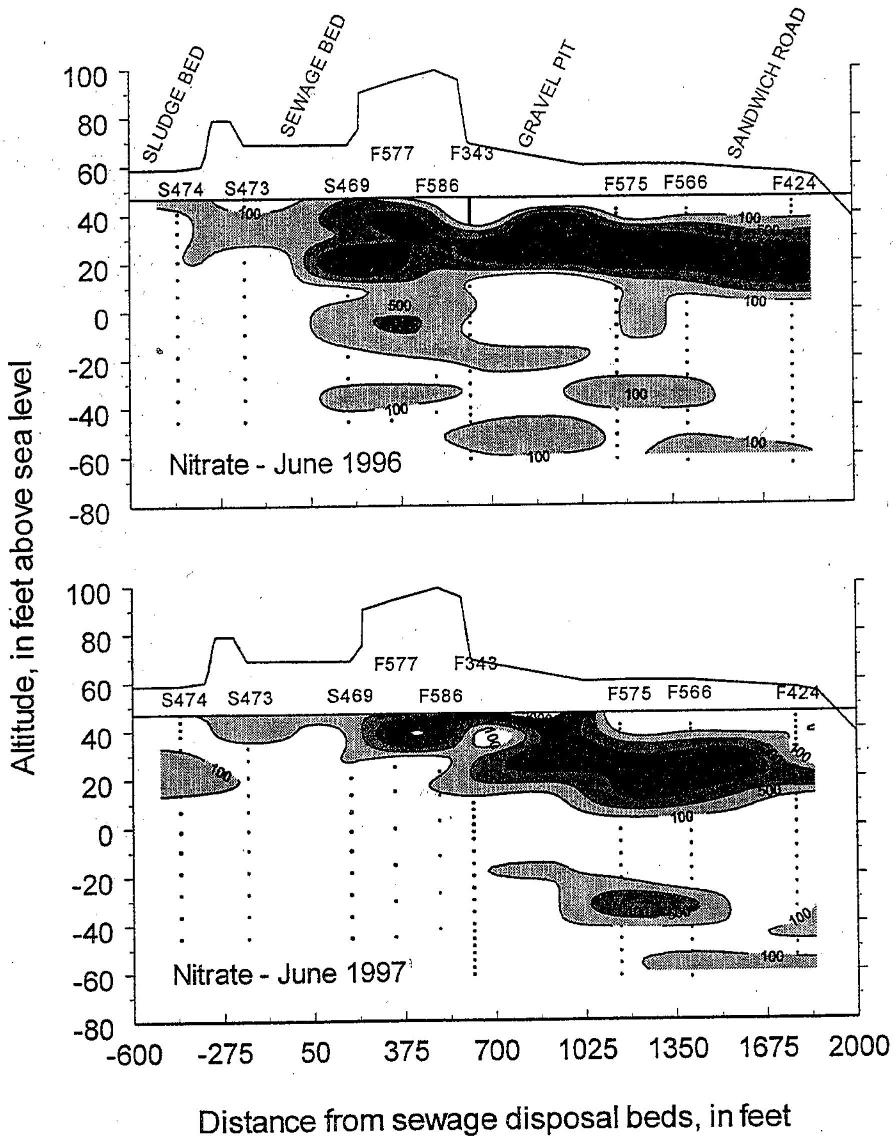

Figure 3. Longitudinal vertical section showing nitrate concentrations (µM) in ground water in June 1996 and June 1997.

PROCESSES AFFECTING INORGANIC NITROGEN SPECIES

Prior to shutoff, nitrate entered the aquifer with the sewage effluent and increased in concentration as a result of nitrification in the aerobic zone. Nitrate and any ammonium that were not oxidized were transported down-gradient, but at different rates, because ammonium transport was slowed by sorption due to cation exchange (Ceazan and others, 1989). The total ammonium pool in the contaminant plume was actually larger than indicated from ground-water concentrations alone because of the sorption. Prior to shutoff, the largest ammonium reservoir was deep below the water table. When oxygen became depleted along the flowpath, denitrification began to consume the large nitrate pool. This pool was cumulatively diminished in the core of the contaminant plume by denitrification during transport away from the beds. Ammonium persisted in this same zone because nitrification was limited by oxygen availability.

After shutoff, nitrate was still being leached from the unsaturated zone by natural recharge, but at a much lower loading rate. The combination of lower oxygen-loading and lower nitrate-loading rates allowed denitrification and ground-water flushing to significantly decrease the nitrate pool below an altitude of 10 feet (fig. 3). The denitrification was likely fueled by sorbed organic carbon. On the other hand, the remaining ammonium in the plume was transported down-gradient (fig. 5). The ammonium-containing zone remained anoxic, so nitrification did not contribute to the observed decrease in ammonium concentration. It appears

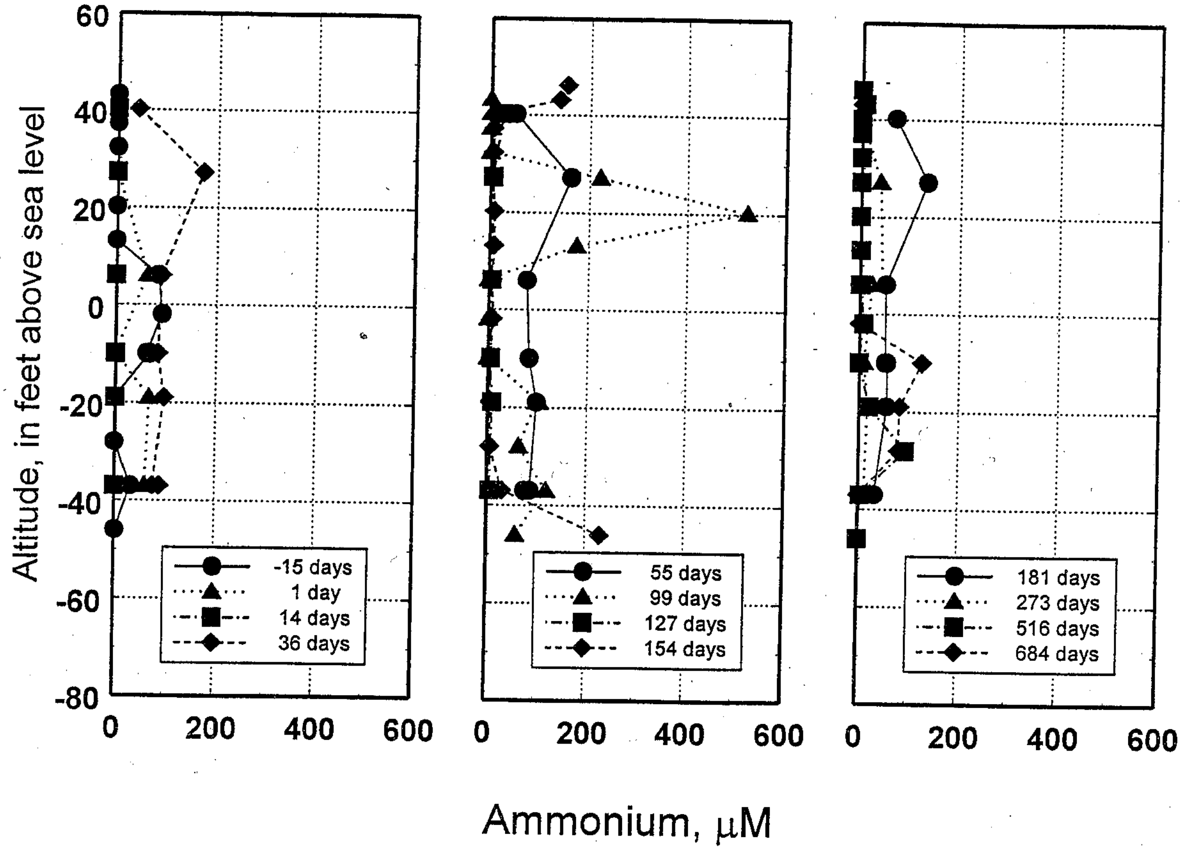

Figure 4. Depth profiles of ground-water ammonium concentrations at well site S469 relative to the date of sewage disposal cessation (December 13, 1995).

that oxygen demand at the up-gradient edge of the contaminated area was more than sufficient to remove oxygen from in-coming uncontaminated ground water, thus preserving the anoxic core. Later, as an iron reduction zone developed at well site S469 (Kent and others, 1999), ammonium was produced in the center of the plume by mineralization of organic nitrogen.

CONCLUSIONS

1) Shutoff of the contaminant source decreased the amount of oxygen delivered to the contaminant zone. Thus, the plume geochemistry became more reduced, not more oxidized as might have been predicted.

2) Although the transport of ammonium was slowed by cation exchange, the desorption and transport rates were sufficient to flush the dissolved and sorbed ammonium down-gradient away from the beds after shutoff. Nitrification was a significant process under the loading beds prior to shutoff, but not after shutoff as the geochemical environment became more reducing.

3) The total nitrate loading was significantly decreased by shutoff. However, nitrate continues to leach from the unsaturated zone 2 years later.

4) The zone of denitrification under the loading beds diminished to a rather narrow vertical interval after shutoff due to the decrease in ground-water nitrate concentrations.

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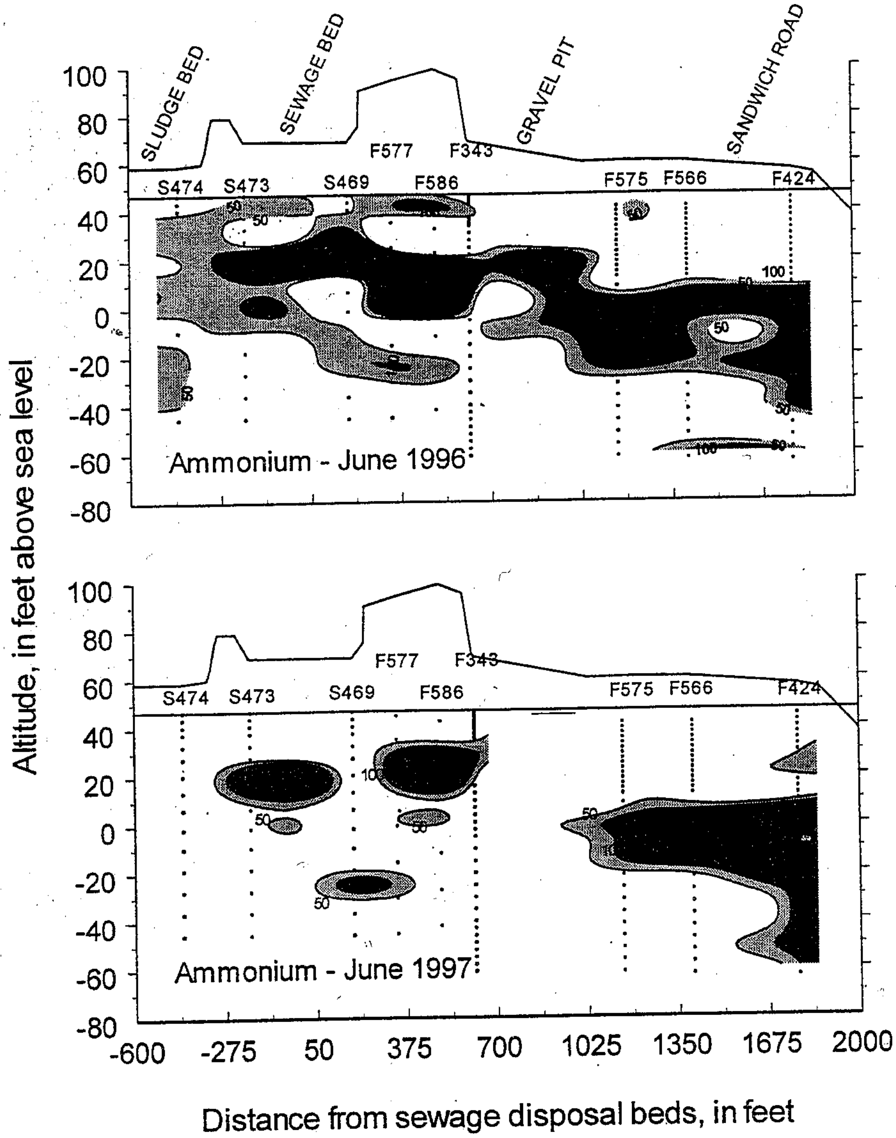

Figure 5. Longitudinal vertical section showing ammonium concentrations (µM) in ground water in June 1996 and June 1997.

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