Differential Transport of Sewage-Derived Nitrogen and Phosphorus through a Coastal Watershed

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■ Changes of land use in coastal watersheds to residential development with on-site sewage disposal represent a potential change in both the quantity and quality of nutrient inputs to coastal marine systems. Measurements of dissolved N and phosphate P in septic system effluent indicated initial concentrations 100–1000-fold greater than receiving coastal waters, with inorganic N/P ratios (17/1) similar to phytoplankton growth requirements. Transformations of organic and inorganic N and retention of inorganic P occurred in the initial meters of groundwater transport with substantial (≈70%) nitrification of effluent ammonium to nitrate and retention of phosphate by the soil (≈60%). The degree of initial transformation and retention was directly related to unsaturated infiltration distance and is consistent with the requirements of these processes for oxidizing conditions. At greater distances (10–100 m), over 99% of the total dissolved N occurred as nitrate, phosphate concentrations were reduced to background levels, and groundwater N/P ratios exceeded 2500/1. The greater the importance of high-N, low-P groundwater inputs to the nutrient balance of a coastal water body, the greater the potential for shifts in the nutrient which limits primary production.

Introduction

Each year in the United States, approximately 3.8 billion cubic meters of sewage effluent is discharged to the subsurface by on-site septic systems (*1*); an increasing fraction of this total is discharged to coastal watersheds (*2*). Septic effluent contains a variety of microbial, inorganic, and organic constituents (*3–5*) and is highly enriched in nitrogen and phosphorus compared to most groundwaters and surface waters. Dissolved N and P concentrations in domestic effluent are on the order of 3000 and 400 μM, respectively (*4, 6*), which are 100–1000-fold higher than concentrations in typical receiving water bodies.

The fate of this anthropogenic contribution is of both ecological and management importance, because of the key role played by N and P in structuring aquatic ecosystems. Field studies have shown that primary production in freshwater ecosystems is generally P-limited (*7–9*). Coastal marine systems, by contrast, are more often N-limited (*10, 11*), while estuaries show great variation in nutrient limitation (*12*). One factor controlling the process of nutrient enrichment or eutrophication in these ecosystems is the rate at which "new" N or P is added from terrestrial sources.

In lakes, embayments, and estuaries where terrestrial nutrient inputs derive mainly from streamflow and point discharges, N and P transport is frequently modified by plant uptake and generally well-studied (*12–14*). In permeable, groundwater-dominated watersheds, where nutrients are injected to the subsurface by sewage disposal or other activities, the total mass flux and subsurface behavior of N and P are poorly understood and appear to be controlled by bacterial and chemical interactions (*15–17*). While simple loading models are available for estimation of nutrient inputs to such watersheds (*18*), assumptions regarding subsurface behavior are usually necessary in order to quantify watershed nutrient outputs.

In the present study, we followed the transport of effluent-derived, plant-available inorganic N and P through the freshwater portion of a Massachusetts coastal watershed. Our goal was to determine both the overall nutrient retention and the change in the ratio of N to P during groundwater transport, since both factors are central to understanding the potential impact of this nutrient source on coastal waters. It should be noted that all studies of septic system impact must address a difficult problem of scale. Most previous workers have concentrated either on the microscale and mapped individual septic system plumes in detail (*19, 20*) or on the regional scale and examined the relationship between residential land use and groundwater quality across entire basins (*21–25*). To evaluate thoroughly the fate of on-site sewage inputs in this study area, it was necessary to use a combination of both approaches, since our purpose was both to characterize the source and to quantify the overall extent of N and P transport through the watershed.

Study Area

The Indian Heights subbasin is located adjacent to Buttermilk Bay, at the northern tip of Buzzards Bay in southeast Massachusetts (Figure 1). The regional geology is dominated by medium-to-coarse sands, which were deposited in a 200-km^2 outwash plain during the retreat of

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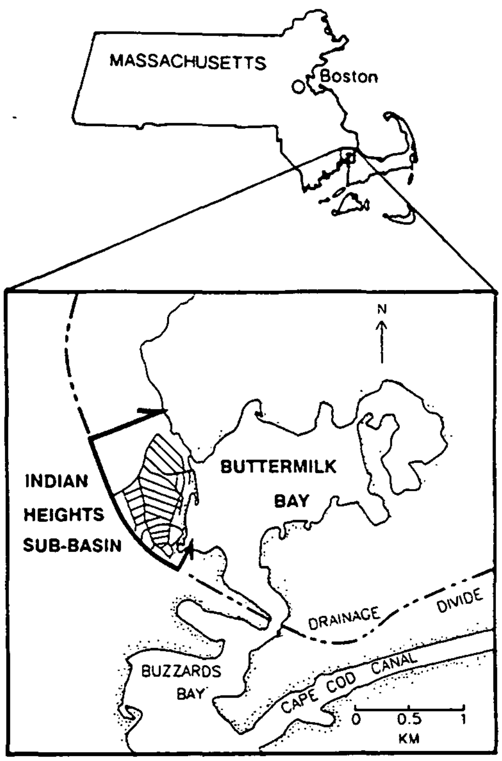

Figure 1. Location of Buttermilk Bay and the Indian Heights subbasin.

the Buzzards Bay and Cape Cod Bay lobes of the Laurentide ice sheet (*26*). Derived from the granitic bedrock of the Cape Cod region, the sands are 90% orthoclase, plagioclase, and quartz, with minor amounts of ferromagnesian minerals and metal oxides, and very little clay [generally <0.1% (*27*)]. The aquifer underlying these deposits (the Plymouth–Carver aquifer) is one of the largest in southern New England, with a specific yield of ~0.25, a saturated thickness of ~30 m, and a mean storage of 1.5×10^9 m^3 (*28*). In the Indian Heights subbasin, the horizontal hydraulic conductivity is approximately 0.025–0.045 cm s^{-1} (*29*). The subbasin is recharged by the infiltration of precipitation and septic effluent at a total rate of ~60 cm $year^{-1}$ (*29*). A large part of its shoreline is underlain by a fringing salt marsh, which has been artificially filled with sand and gravel (Figure 2).

Like many coastal watersheds in southern New England, the subbasin is densely populated with a mixed, year-round/summer population of 1237 persons occupying 524 houses distributed over 53 ha. The subbasin was selected for study because (1) the area is served by a public water supply and individual septic systems, (2) neither the population nor the housing density has changed significantly in the past 10 years, and (3) the upgradient portion of the subbasin (extending to a groundwater divide) is overlain by an undeveloped area of pine/oak forest (Figure 2). These features allow accurate estimation of total effluent discharge, assumption of steady-state conditions, and measurement of local background nutrient concentrations.

Methods

Near-Field Effluent and Groundwater Sampling. Effluent and groundwater samples were obtained monthly from four septic system sites chosen to encompass the range of system designs (both cesspool and tank/leaching field combinations), ages (10–75 years), pumpout fre-

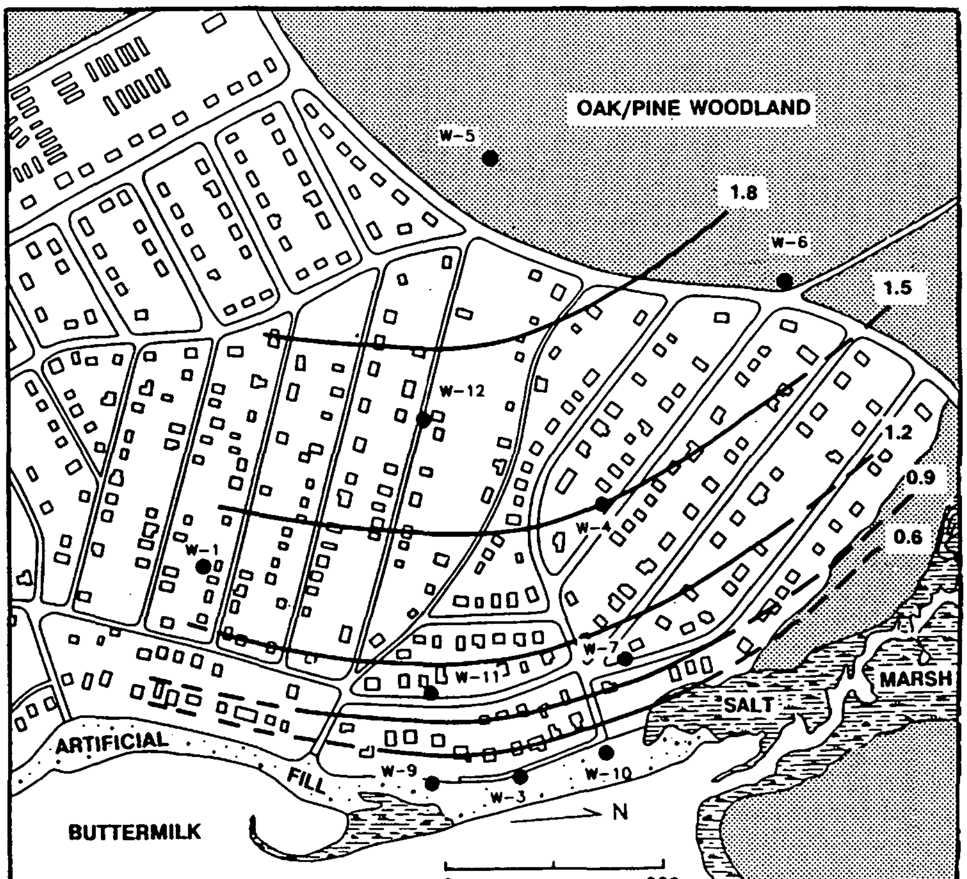

Figure 2. Indian Heights land use/land cover, observation well network, and mean water table elevations during the November 1986–January 1988 period. Elevations in meters above mean sea level; contour interval 0.3 m.

quencies (0.5–2 times per year), depths to groundwater (1–4 m), and loading rates (20–190 L m^{-2} day^{-1} or 2–19 cm day^{-1}) typical of the Massachusetts coastal margin, and specifically in Indian Heights. All four systems serve year-round households and are underlain by medium-to-coarse sand (D_{50} = 0.30–0.80 mm).

The plume of contaminated groundwater from each system was first mapped in cross section, 1-m downgradient of the cesspool or leaching field edge, with a portable well point sampler and a calibrated, temperature-compensated specific conductance meter (YSI Instruments, Yellow Springs, OH). After the position of the plume core was determined, a steel monitoring well (1.6-cm o.d., 0.95-cm i.d.) with a 300-μm slotted screen was installed in the core, just below the water table.

Effluent and groundwater samples were collected monthly at each of the four systems from December 1987 to June 1988. Samples were collected through 0.64-cm polyethylene sampling tubes (installed permanently in each monitoring well and septic tank), with a gauged, hand-operated vacuum pump. The sample trap was located in line before the pump. Before sample collection, the water level in each well was measured by first raising the sampling tube above the air–water interface and then lowering it (while evacuating the tube) until the vacuum gauge indicated contact with the interface. The position of the premarked tube was then recorded relative to a land surface datum. Groundwater samples were collected after three bore volumes were purged from each monitoring well. All samples were filtered (0.45-μm Millipore), and transported to the laboratory in HCl-washed, polyethylene bottles at 4 °C. Specific conductance was determined in the field on a second set of samples. Phosphate analyses (*30*) and ammonium analyses by the phenol–nitroprusside technique (*31*) were performed immediately upon return to the laboratory. Samples were then frozen for subsequent analysis of nitrate + nitrite by cadmium reduction (*32*) using a Lachat (r) autoanalyzer. Total dissolved N (TDN) was also determined in one set of filtered effluent and near-field groundwater samples with the autoanalyzer, following persulfate digestion (*33*).

In order to obtain a "snapshot" of nutrient distribution at the microscale, a portable well point sampler was used to collect samples from a 3.75-m-wide transverse cross section, located 5 m downgradient of septic system 1, and extending 1.25 m below the water table. A grid of 16 sampling points was spaced 0.5 m apart in the vertical direction (except for the top two levels, which were 0.25 m apart) and 1.25 m apart horizontally. Four additional points were sampled at depth in the central portion of the cross section, between 1.25 and 3.25 m below the water table. Nutrient and conductance data from each sampling level were used to obtain transversely integrated, vertical profiles of ammonium, nitrate, phosphate, and specific conductance.

Watershed Groundwater Sampling. Groundwater samples and water table elevations were also obtained from a network of 10 observation wells installed throughout the subbasin (Figure 2). The observation wells (5.1-cm-i.d. PVC) were set with their 3.3-m screens straddling the mean water table position. A flow net was then constructed from mean water level data, and three "stream tubes" (*34*), each consisting of a longitudinal aquifer slice bounded by a pair of flow lines orthogonal to the mean water table contours, were defined (Figure 3). Two to three multilevel samplers, with an average of 18 ports each, were then installed near the mouth of each stream tube (Figure 3). The multilevel samplers were constructed of 3.8 cm i.d. PVC casing; each

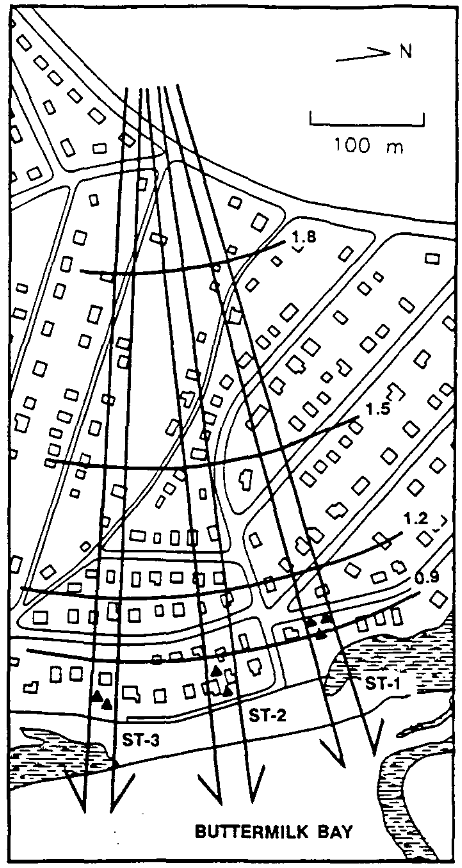

Figure 3. Stream tubes 1–3: (▲) multilevel sampler.

port was screened with nylon mesh and fitted with 0.6-cm polyethylene tubing (*35*). Vertical spacing between sampler ports ranged from 25 to 100 cm, depending on preliminary measurements of the nutrient concentration gradient at each site.

Groundwater elevations were measured biweekly throughout the subbasin from November 1986 to July 1988. The observation wells were purged with a PVC bailer (three bore volumes) and samples were collected for nutrient analysis in January 1988 and June 1988. Multilevel samples (100 mL) were drawn with a peristaltic pump after three bore volumes were purged from each sampling tube. Three sampling rounds were conducted at each stream tube between June 1988 and July 1989, with one additional round at stream tube 1. Specific conductance measurements and sample filtration, storage, and nutrient analyses were performed as described above for the near-field samples.

Nutrient Attenuation and Transport. The fractions of N and P input transported to the downgradient edge of the watershed were estimated with a steady-state approach commonly used in both groundwater and estuarine mixing studies (*36, 37*). The watershed transport fraction (TF) for each nutrient was determined from the change in the (background-corrected) ratio of nutrient concentration to specific conductance between the effluent and downgradient groundwater sample sets. While the mean and variance of TF cannot be directly measured at the subregional scale, they can be estimated from the mean and variance of the respective ratios X and Y, which are obtained from field data as follows. TF = X/Y, where

$$X = \frac{C_{\text{gw-}i} - C_{\text{b}}}{\text{SC}_{\text{gw-}i} - \text{SC}_{\text{b}}} \qquad Y = \frac{C_{\text{eff-}j} - C_{\text{b}}}{\text{SC}_{\text{eff-}j} - \text{SC}_{\text{b}}} \tag{1}$$

and where $C_{\text{gw-}i}$ and $\text{SC}_{\text{gw-}i}$ are the nutrient concentration

Table I. Effluent and Near-Field Nutrient Concentrations, Sites 1–4 (Mean ± SEM)

constituent[a]	effluent	near-field groundwater[b]	% change[c]
NH_4^+, μM	2634 ± 307	488 ± 95	−70
NO_2^- + NO_3^-, μM	9.8 ± 4.2	1292 ± 250	+21600
DIN, μM	2641 ± 306	1780 ± 313	0
DON, μM	499 ± 86	468 ± 378[d]	0
TDN, μM	3140 ± 364	1980 ± 465[d]	0
PO_4^{3-}, μM	165 ± 13	43 ± 9.6	−57
DIN/P (median)	17	69	+406
spec conduct., μS/cm	511 ± 43	312 ± 31	0

[a] See text for abbreviations. [b] Collected monthly, 1 m downgradient of four septic systems, 12/87–6/88. [c] Corrected for dilution (eq 1). [d] Site 4 only (1 m downgradient); groundwater DON was below detection at all other sites.

and specific conductance of the ith groundwater sample, C_b and SC_b are the background nutrient concentration and conductance, and $C_{eff\text{-}j}$ and $SC_{eff\text{-}j}$ are the nutrient concentration and conductance of the jth effluent sample.

As has been noted (*36*), this approach assumes that (a) specific conductance is a conservative property in both effluent and groundwater and (b) septic effluent is the only significant, nonbackground nutrient and conductance source. Both of these assumptions are consistent with field conditions in the Indian Heights subbasin. Assumption a is supported because dissolved inorganic nitrogen (DIN) and phosphate comprise only ~10% of the total ionic species in septic effluent, and specific conductance is largely imparted to effluent by species such as Na^+ and Cl^-, which are relatively nonreactive in sand and gravel aquifers (*4*, *6*). To the extent that conductance is semiconservative during transport (*38*), this approach will tend to overestimate actual nutrient transport. Assumption b is supported by the high septic system density (10 systems ha^{-1}), the chemically resistant character of the sandy aquifer matrix (largely quartz and feldspar), and the relatively minor input of lawn fertilizer and road salt to the watershed (*29*). In addition, most of the street runoff from the watershed is conveyed directly to Buttermilk Bay through a storm sewer system (*39*) and is therefore not available to recharge the aquifer. To the extent that assumption b is violated, nutrient concentrations and conductance will be less well correlated and the standard error of the transport estimates will increase.

Results and Discussion

Effluent and Near-Field Nutrient Concentrations. As expected, the effluent samples contained high concentrations of dissolved inorganic nitrogen (DIN = NO_3^- + NO_2^- + NH_4^+) and orthophosphate (mean ± SEM of 2641 ± 306 μmol L^{-1} (μM) and 165 ± 13.2 μM, respectively; Table I). Near-field groundwater samples, collected 1 m downgradient of each septic system, had DIN and phosphate concentrations of 1780 ± 313 μM and 43 ± 9.6 μM, respectively. After correcting for dilution effects (eq 1), overall DIN losses during near-field transport were found to be insignificant ($p > 0.10$), while the PO_4 loss was approximately 60%. Near-field phosphate losses caused a sharp increase in the median molar ratio of DIN to P, from 17 in the effluent to 69 in the near-field groundwater. Near-field DIN/P ratios were found to vary exponentially with mean infiltration distance (the distance between the base of the septic absorption system and the water table; Figure 4).

Significant changes also occurred in the relative proportions of dissolved N species during early transport.

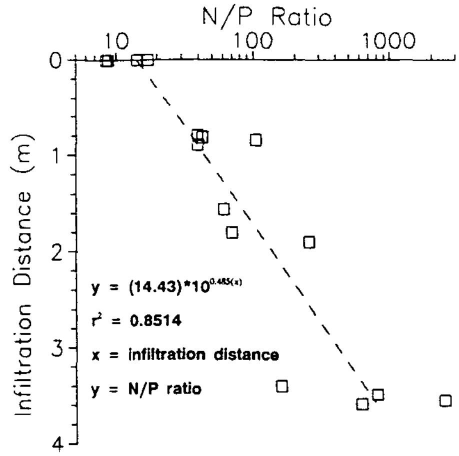

Figure 4. Near-field groundwater DIN/P ratio versus infiltration distance at the time of sampling, sites 1–4. Infiltration distance is the distance from base of leaching field or cesspool to the water table. Data from four dates, December 1987–June 1988.

While over 99% of the effluent DIN was ammonium, only 27% of the near-field groundwater DIN remained in this form, presumably due to the rapid conversion of NH_4^+ to NO_3^- by nitrifying bacteria. As with phosphate removal, the extent of nitrification was related to mean infiltration distance; nitrate fractions of DIN in near-field groundwater ranged from a low of 38% (site 4, with zero infiltration distance) to a high of 99% (site 2, with 3.5-m infiltration distance). Dissolved organic N (DON, obtained by difference from TDN and DIN data) averaged 499 ± 86 μM in the effluent samples (mean ± SEM) and comprised 16% of the TDN in the effluent (Table I). As with phosphate removal and nitrification, the degree of DON removal and/or mineralization during early transport was strongly related to infiltration distance. DON was below detection in 60% of the near-field groundwater samples and was only detected at site 4, where the mean concentration was 468 ± 378 μM and the infiltration distance was zero.

The increased phosphate removal, nitrification, and DON mineralization associated with increased infiltration distance suggests that these processes either require, or are strongly enhanced by, oxidizing conditions and/or free molecular oxygen. In the sandy soils of this study area, the likelihood of finding these conditions beneath an operating septic system is controlled, at least in part, by infiltration distance.

Vertical profiles obtained 5 m downgradient of septic system 1 confirmed the pattern of nutrient behavior described above. Specific conductance and nitrate concentration were well correlated over the upper four sampling levels ($n = 16$; $r^2 = 0.88$; Figure 5A,B), with both conductance and nitrate profiles showing peak values at the water table. [The conductance peak at the 2.35-m depth is due to a tongue of saline groundwater from Buttermilk Bay; mean high water is 9 m downgradient of the cross section and the conductance observed (14 800 μS cm^{-1}) is >10 times higher than the measured effluent conductance and about half the conductance of seawater.] Peak ammonium and phosphate concentrations, by contrast, were found not at the water table, but ~35 cm below it (Figure 5C,D). The depressed ammonium and phosphate concentrations at the water table are probably not due to dilution with natural recharge, since the nitrate and conductance profiles are not similarly affected. Rather, ammonium transformation and phosphate removal appear to be enhanced by redox conditions at the water table, which are likely to be oxidizing relative to the plume core. The conductance, nitrate, and ammonium profiles decline

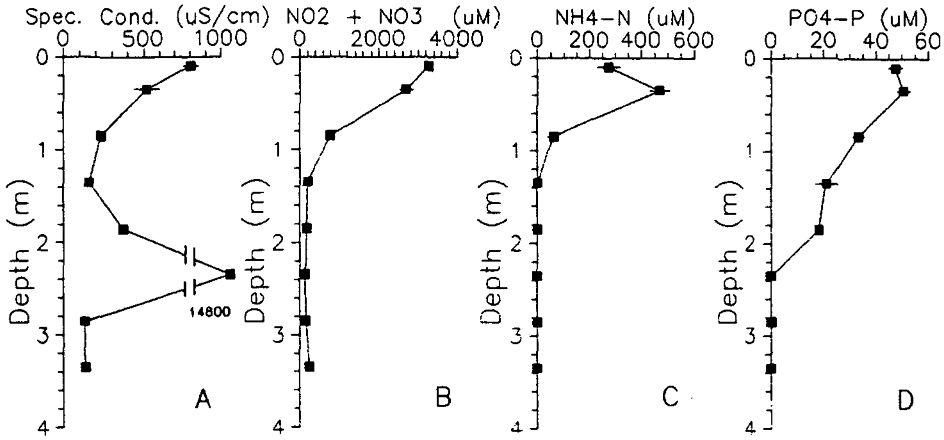

Figure 5. Near-field groundwater profiles, 5 m downgradient, site 1, September 1988. Mean at each depth, averaged across four sampling points in transverse cross section: (A) specific conductance, (B) nitrate + nitrite, (C) ammonium, (D) phosphate. Error bars = SEM.

Table II. Watershed Nutrient Concentrations and Specific Conductance (Mean ± SEM)

well or sampler	spec conduct., μS/cm	NH_4^+ μM	NO_2^- + NO_3^- μM	DIN, μM	PO_4^{3-}, μM
		Upgradient Wells[a]			
W-5	40	0.7	1.6	2.3	0.5
W-6	34	0.7	0.8	1.5	0.3
		Midgradient Wells[a]			
W-1	270	<0.1	917	917	0.3
W-4	188	0.4	1060	1061	0.3
W-11	104	1.5	89	91	0.5
W-12	114	0.4	186	186	0.2
		Downgradient Samplers[b]			
ST-1	123 ± 7	0.5 ± 0.07	422 ± 36	423 ± 36	0.6 ± 0.2
ST-2	198 ± 12	1.9 ± 0.7	431 ± 44	433 ± 44	1.6 ± 0.6
ST-3	133 ± 4	0.36 ± 0.03	318 ± 28	318 ± 28	0.06 ± 0.01

[a] Upgradient and midgradient NO_3^- samples collected on 1/21/88; upgradient and midgradient SC, NH_4^+, and PO_4^{3-} samples collected on 1/21/88 and 6/9/88; means are stated. [b] Mean ± SEM of samples from stream tube mouths, 1988/1989.

sharply below 35-cm depth, while above-background phosphate concentrations persist somewhat deeper (Figure 5D), probably due to redox controls, which will be discussed further below.

Watershed Nutrient Concentrations. Specific conductance, DIN, and phosphate levels in upgradient groundwater beneath the forested portion of the watershed were quite low (37 μS/cm, 1.9 μM, and 0.4 μM, respectively; Table II), reflecting regional background levels (*18*, *24*). It is important to note that upgradient DIN concentrations were only 20% of the concentration in local precipitation, which averages 20 μM (*18*). Net uptake by the pine/oak forest and denitrification during infiltration through the soil zone probably account for this removal.

In contrast, the mean DIN concentration of the "midgradient" samples, collected from the developed portion of the subbasin, was 564 ± 215 μM (Table II), or ~300 times the measured background DIN concentration. The large spatial variation between wells (10-fold range in concentration) is consistent with the multipoint character of the main nitrogen source (over 500 individual septic systems), the discrete structure of septic system plumes near the water table [Figure 5 (*21*)], and the low transverse-horizontal dispersivity typical of glaciofluvial aquifers (*40*, *41*). Nitrate comprised 99.4% of the total DIN, indicating nearly complete nitrification, and/or sorption of effluent ammonium by the aquifer (*17*) during transport to these wells. Phosphate concentrations, by contrast, were at background levels (mean ± SEM of 0.33 ± 0.06 μM), indicating nearly complete phosphate retention during transport.

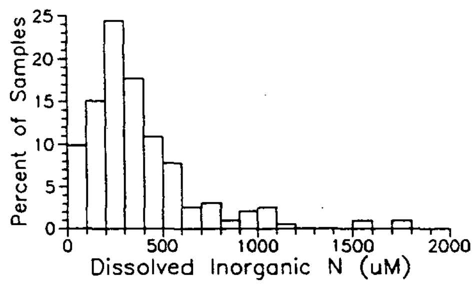

Figure 6. Frequency distribution of DIN concentration, nonbackground (>4 μM) downgradient samples, stream tubes 1–3 (n = 190).

DIN concentrations in the downgradient multilevel samplers (Figure 3, Table II) ranged from background levels (1–4 μM) to 1720 μM and exceeded background in 83% of the samples (n = 230). All background samples from the multilevel samplers were obtained at depths greater than 3.5 m below water table and represent uncontaminated recharge which entered the aquifer from the forested area upgradient of the development. The frequency distribution of nonbackground DIN is slightly skewed, with 11% of the samples above 600 μM (Figure 6). The median DIN concentration of the nonbackground, downgradient groundwater was 313 μM. As with the midgradient samples, virtually all (>99%) of the downgradient DIN occurred as nitrate; ammonium was at background levels (<0.7 μM) in 70% of the downgradient samples, and DON was below detection in the downgradient samples. These findings are consistent with the near-field results and confirm the nearly complete nitri-

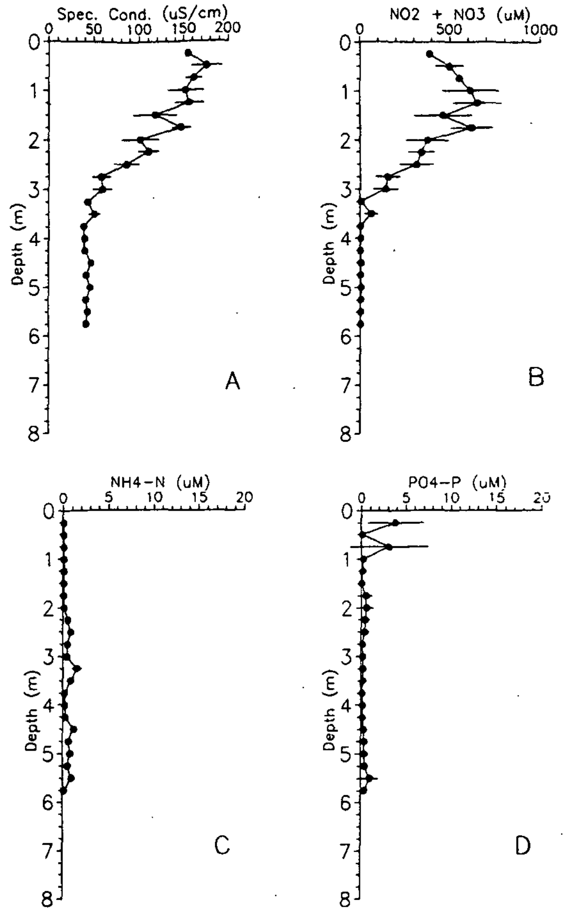

Figure 7. Groundwater specific conductance and nutrient profiles at mouth of stream tube 1; mean of three samplers over four dates (±SEM at each depth), June 1988–July 1989: (A) specific conductance, (B) nitrate + nitrite, (C) ammonium, (D) phosphate.

fication of effluent ammonium and/or ammonium sorption by the aquifer during longer term transport. In contrast to nitrate, phosphate was reduced to background levels (<0.75 μM) in virtually all (>90%) of the downgradient samples; the median concentration was 0.12 μM.

The downgradient profiles at the mouth of stream tube 1 (Figures 3 and 7) depict, in effect, the composite plume contributed by anthropogenic sources located between the multilevel samplers and the upgradient forest. At depths greater than 1 m below the water table, a strong correlation was observed between nitrate and specific conductance (r^2 = 0.99; Figure 7A,B), though the mean values of both parameters were lower than those observed in the near-field plume (Figure 5A,B) due to longitudinal dispersion during transport. The top meter of the saturated zone, by contrast, showed a poor correlation between conductance and nitrate (r^2 = 0.02; Figure 7A,B).

One explanation for the poor correlation is bacterial denitrification near the water table; however, this process requires moderately reducing conditions (*15, 16*) and is therefore unlikely in the well-oxidized shallow groundwater of the study area. The observed pattern is more likely due to the accretion of relatively high conductance/low nitrate recharge from noneffluent sources located between the samplers and the nearest upgradient N source. Unlike the near-field sampling cross section, which was located only 5 m downgradient of an effluent source and could be expected to receive minimal noneffluent recharge over the intervening distance, the stream tube 1 samplers were installed 30 m from the nearest effluent source (Figure 3) and could be expected to show the effects of noneffluent recharge, including recharge from high-conductance/low-nitrate street runoff not captured by the storm drain system. The impact of this conductance source on the accuracy of nutrient transport estimates derived from eq 1 will be considered in the next section.

Elevated phosphate levels were occasionally observed just below the water table at stream tube 1 (Figure 7D), but the concentrations were low relative to the near-field profile (Figure 5D) and the source is unclear. The downgradient ammonium concentrations observed at depth (Figure 7C) are consistent with up- and midgradient observation well concentrations (Table II). The absence of even trace levels of ammonium near the water table may be due to more efficient nitrification and/or sorption in this zone, which is likely to be highly oxidizing. The results from this stream tube were supported by specific conductance and nutrient profiles from stream tubes 2 and 3 (profiles not shown).

Estimates of Watershed Nutrient Transport. Application of eq 1 to the available effluent and groundwater data indicates that 74 ± 10% of the effluent DIN, 61 ± 9% of the effluent TDN, and 0.3 ± 0.2% of the effluent phosphate P discharged to the subsurface reaches the bay margin (mean ± SEM). These results are expressed graphically in Figure 8A–C, which plots the conductance and nutrient concentration of each downgradient sample, together with the conservative mixing line which connects the background groundwater and mean effluent compositions. (In each case, the line is actually an envelope due to variance in effluent composition.) Most of the DIN and TDN samples fall just below their respective mixing envelopes, indicating moderately conservative transport, while none of the phosphate P samples even approach the mixing envelope, indicating nearly complete retention by the subsurface. It should be noted that noneffluent sources with relatively high conductance and low nitrate concentrations (such as street runoff) have probably contributed to sample conductance in some cases (for example, the uppermost samples from stream tube 1). For this reason, the mean nutrient transport fractions obtained with eq 1 should be considered underestimates. However, because both the N and P transport fractions are affected similarly by this error, the strong contrast in N and P transport behavior predicted by eq 1 remains valid.

The contrast described above is also consistent with the findings of a parallel study of nutrient loading in the watershed (*29*), in which a variety of field measurements and loading models were used to quantify nutrient mass flux to the Buttermilk Bay margin from all sources. Average fluxes per unit aquifer width observed for DIN, TDN, and phosphate P in the course of the loading study were 129 ± 15, 132 ± 15, and 0.036 ± 0.032 mol m^{-1} aquifer width $year^{-1}$, respectively (mean ± SEM). In the case of the nitrogen species, the observed flux represents a 200-fold increase over predevelopment, background conditions, while the postdevelopment increase in phosphate P flux was found to be insignificant ($p < 0.05$). The causative factors and ecological implications of this large divergence in subsurface behavior will be discussed further below.

Biogeochemical Controls on Subsurface N and P Transport. The moderately conservative subsurface behavior of effluent DIN and TDN may be attributed to several biogeochemical factors. First, effluent ammonium undergoes rapid nitrification because the aquifers of the region are replenished with well-oxygenated recharge at a high rate [45–60 cm $year^{-1}$ (*28, 42*)]. Second, the end product of this process (nitrate) is highly soluble and not easily sorbed to aquifer materials (*43*). Third, the bacterial reduction of nitrate to $N_{2(g)}$ or $N_2O_{(g)}$ (denitrification) re-

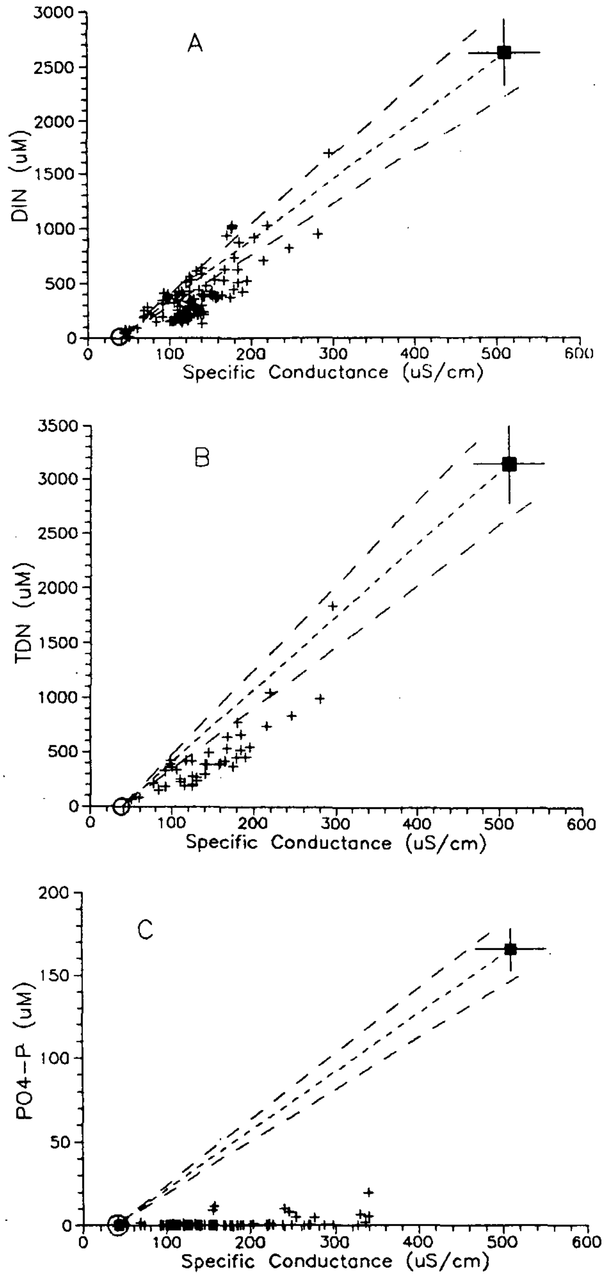

Figure 8. Nutrient concentration versus specific conductance of effluent and downgradient groundwater samples: (A) DIN, (B) TDN, (C) phosphate; (■) mean septic effluent (±SEM; n = 24); (O) mean background groundwater (n = 4); (+) nonbackground, downgradient groundwater samples (n = 125 for DIN; n = 42 for TDN; n = 157 for phosphate); (---) dilution line between mean effluent and background end members; (– –) dilution envelope defined by 95% confidence interval around slope of dilution line. (DIN and TDN samples from stream tube 2 were excluded due to high degree of scatter.)

quires moderately reducing conditions and is therefore minimal in the well-oxygenated, upper portion of the saturated zone (*15*), where most septic effluent transport takes place in this study area.

To the extent that nitrogen removal occurs in this "oxic" sedimentary environment (*44*), it is probably confined to distinct microenvironments where the above conditions do not prevail. For example, denitrification may be important beneath some septic system sites (*36, 45*), and during the final stage of groundwater transport through or beneath fringing salt marshes, freshwater wetlands, and lacustrine or subtidal sediments (*46*). Likewise, ammonium sorption is quantitatively significant at high-volume effluent discharge sites where redox conditions inhibit the rapid nitrification observed in the present study (*17*).

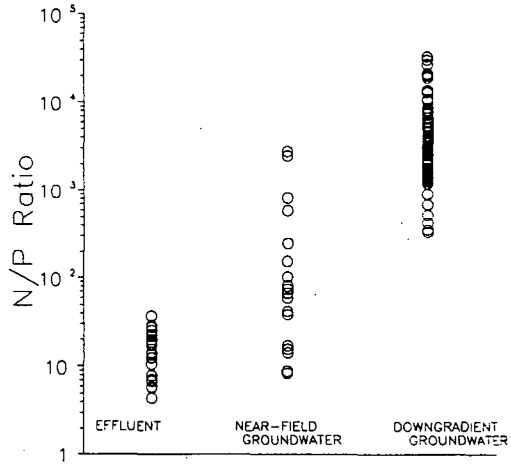

Figure 9. Molar ratio of DIN to phosphate in septic effluent (n = 24), near-field groundwater 1 m downgradient of four septic systems (n = 18) and downgradient samples where DIN is above background and phosphate is above the detection limit (n = 91).

The high degree of observed phosphate removal can be attributed to inorganic adsorption and precipitation reactions. The stable phosphate forms [$H_2PO_4^-$ and HPO_4^{2-} at pH 4–10 (*47*)] have a strong affinity for oxides of Fe, Al, and Ca (*48*). Because the granite-derived sand and gravel materials composing the aquifers of the Cape Cod region are relatively rich in iron and aluminum oxides (*27*), they probably play a role in phosphate removal. In addition, ferric oxides occur as secondary coatings on other sediment grains, where their sorption effectiveness is enhanced. Precipitation reactions also remove phosphate; under oxidizing conditions, phosphate will combine with extremely low concentrations of Al^{3+}, Ca^{2+}, and Fe^{3+} to form the minerals varisite, hydroxyapatite, and strengite, respectively (*4*). Conversely, reducing conditions promote phosphate transport by dissolving the metal oxides (particularly ferric oxides), which would otherwise bind the phosphate (*47*). The limited phosphate transport observed in this study is probably enhanced in the near-field (Figure 5D) by locally reducing conditions often associated with minimal infiltration distances and high effluent loading rates (*6*).

Ecological Implications. Septic systems are clearly a major potential source of N and P to coastal waters. Both nutrients are highly concentrated in septic effluent, in a molar proportion (Figure 9) close to the "Redfield ratio" typical of marine phytoplankton [16/1 (*49*)]. Upon discharge to a well-oxygenated aquifer, however, oxidation of effluent N to nitrate by nitrifying bacteria is both rapid and nearly quantitative, and nitrate transport with flowing groundwater is nearly conservative. Phosphate, by contrast, is strongly retained by the aquifer materials during transport. As a result, groundwater at the downgradient edge of the Indian Heights subbasin has a median DIN/P ratio more than 2 orders of magnitude higher than the effluent source (Figure 9).

The results are consistent with those of other studies in similar environments (*20, 36, 50, 51*) and bear directly on current efforts to understand the nutrient dynamics and eutrophication of coastal ecosystems. Along permeable segments of the coastal margin, where groundwater discharge forms a significant portion of a bay or estuarine water budget, the groundwater pathway is a potentially major source of "new" nitrogen (*46, 52, 53*). In large, N-limited bays (*10*), influx of high N/P groundwater may increase primary production but do little to change the character of nutrient limitation (that is, such systems will remain N-limited). In smaller coastal systems, where flux of high N/P groundwater may greatly exceed surface runoff and precipitation as a source of new nitrogen, effluent discharge to the watershed could conceivably shift the system to P limitation. To the extent that a bay or estuary is permanently or seasonally P-limited (*12*), flux of high N/P groundwater, like that observed in the present study, will probably do little to promote eutrophication.

Conclusions

In summary, N and P inputs from widely dispersed, on-site sewage disposal are transported through groundwater-dominated, well-oxygenated watersheds in a highly differential fashion. Subsurface conditions in such watersheds promote rapid DON mineralization and ammonium transformation upon effluent release and inhibit denitrification losses during subsequent transport of nitrate. Net transport of both DIN and TDN through the watershed was found to be moderately conservative ($74 \pm 10\%$ and $61 \pm 9\%$, respectively). Effluent phosphate, by contrast, was strongly retained by the aquifer ($0.3 \pm 0.2\%$ net transport). As a result, the molar ratio of DIN to phosphate P in the effluent samples (17/1) increased to 40/1 during the first meter of transport and generally exceeded 1000/1 at the downgradient edge of the watershed.

Though a minor source of phosphate to the receiving waters of this study area, septic effluent is a potentially major source of dissolved nitrogen to coastal waters. To the extent that marine or estuarine ecosystems in the region are P-limited, septic systems appear to contribute little to eutrophication. To the extent that they are N-limited, septic systems may contribute substantially to eutrophication. Attempts to model nonpoint nutrient loadings to coastal waters should consider not only the respective loads entering the watershed, but the relative importance of surface versus subsurface transport pathways. Further research is also needed to assess the effect of reducing microenvironments on subsurface nutrient transport through otherwise well-oxygenated, permeable watersheds. If the nutrient dynamics of coastal ecosystems are to be understood adequately, they must be viewed in their full hydrologic and biogeochemical context.

Acknowledgments

We thank N. Millham, D. Schlezinger, S. Garabedian, and C. Quadri for field assistance and D. Goehringer, R. Van Etten, and A. Arenovski for laboratory analyses. J. Teal provided useful comments on the manuscript.

Registry No. NH_4, 14798-03-9; N_2, 7727-37-9.

Literature Cited

(1) *Septic Systems and Groundwater Protection: A Program Manager's Guide and Reference Book*; U.S. Environmental Protection Agency, Office of Groundwater Protection, U.S. Government Printing Office: Washington, DC, 1986.
(2) Lee, V.; Olsen, S. *Estuaries* **1985**, *8*, 191.
(3) Hagedorn, C. In *Groundwater Pollution Microbiology*; Bitton, G., Gerba, C. P., Eds.; Wiley and Sons: New York, 1984; pp 181–195.
(4) Canter, L. C.; Knox, R. W. *Septic Tank System Effects on Groundwater Quality*; Lewis Publishers: Chelsea, MI, 1985; pp 45–101.
(5) Viraraghavan, T.; Hashem, S. *Water, Air, Soil Pollut.* **1986**, *28*, 299.
(6) Cogger, C. G.; Hajjar, L. M.; Moe, C. L.; Sobsey, M. D. *J. Environ. Qual.* **1988**, *17*, 401.
(7) Hutchinson, G. E. *Am. Sci.* **1972**, *61*, 269.
(8) Schindler, D. W. *Science* **1974**, *184*, 897.
(9) Lee, G. F.; Rast, W.; Jones, R. A. *Environ. Sci. Technol.* **1978**, *12*, 900.
(10) Ryther, J. H.; Dunstan, W. M. *Science* **1971**, *171*, 1008.
(11) Goldman, J. C.; Tenore, K. R.; Stanley, H. I. *Science* **1973**, *180*, 955.
(12) D'Elia, C. F.; Sanders, J. G.; Boynton, W. R. *Can. J. Fish. Aquat. Sci.* **1986**, *43*, 397.
(13) Lewis, W. L.; Saunders, J. F.; Crampacker, D. W.; Brendecke, C. *Eutrophication and Land Use: Lake Dillon, Colorado*; Springer-Verlag: New York, 1984; pp 1–10.
(14) Malone, T. C.; Crocker, L. H.; Pike, S. E.; Wendler, B. W. *Mar. Ecol. Prog. Ser.* **1988**, *48*, 235.
(15) Smith, R. L.; Duff, J. H. *Appl. Environ. Microbiol.* **1988**, *54*, 1071.
(16) Smith, R. L.; Howes, B. L.; Duff, J. H. *Geochim. Cosmochim. Acta* **1991**, *55*, 1815.
(17) Ceazan, M. L.; Thurman, E. M.; Smith, R. L. *Environ. Sci. Technol.* **1989**, *23*, 1402.
(18) Frimpter, M. H.; Donohue, J. J.; IV; Rapacz, M. V. *Open-File Rep.—U.S. Geol. Surv.* **1990**, *No. 88–493.*
(19) Childs, K. E.; Upchurch, S. B.; Ellis, B. *Ground Water* **1974**, *12*, 369.
(20) Robertson, W. D.; Cherry, J. A.; Sudicky, E. A. *Ground Water* **1991**, *29*, 82.
(21) Morrill, G. B.; Toler, L. G. *J. Res. U.S. Geol. Surv.* **1973**, *1*, 117.
(22) Katz, B. G.; Lindner, J. B.; Ragone, S. E. *Ground Water* **1980**, *18*, 607.
(23) Thomson, J. S. M.; Foster, S. S. D. *J. Inst. Water Eng. Sci.* **1986**, *40*, 527.
(24) Persky, J. *Water Resour. Invest.* (*U.S. Geol. Surv.*) **1986**, *No. 86–4093.*
(25) Cain, D.; Helsel, D. R.; Ragone, S. E. *Ground Water* **1989**, *27*, 230.
(26) Larson, G. J., Stone, B. D., Eds. *Late Wisconsinan Glaciation of New England*; Kendall Hunt Publishing: Dubuque, IA, 1982; pp 101–114.
(27) Barber, L. B., II *Open-File Rep.—U.S. Geol. Surv.* **1987**, *No. 87–109*, B-47.
(28) Williams, J. R.; Tasker, G. D. *U.S. Geol. Survey Hydrol. Invest. Atlas* **1974**, *No. HA-507*, **1974**, 1.
(29) Weiskel, P. K.; Howes, B. L. *Water Resour. Res.* **1991**, *27*, 2929.
(30) *Methods for Chemical Analysis of Water and Wastes*; EPA-600/4-79-020; U.S. Environmental Protection Agency, U.S. Government Printing Office: Washington, DC, 1979.
(31) Scheiner, D. *Water Res.* **1976**, *10*, 31.
(32) Wood, E. D.; Armstrong, F. A. J.; Richards, F. A. *J. Mar. Biol. Assoc. U.K.* **1967**, *47*, 23.
(33) D'Elia, C. F.; Steudler, P. A.; Corwin, N. *Limnol. Oceanog.* **1977**, *22*, 760.
(34) Freeze, R. A.; Cherry, J. A. *Groundwater*; Prentice Hall: Englewood Cliffs, NJ, 1979; p 169.
(35) LeBlanc, D. R.; Garabedian, S. P.; Hess, K. M.; Gelhar, L. W.; Quadri, R. D.; Stollenwerk, K. J.; Wood, W. W. *Water Resour. Res.* **1991**, *27*, 895.
(36) Alhajjar, B. J.; Harkin, J. M.; Chesters, G. *Ground Water* **1989**, *27*, 209.
(37) Boyle, E. A.; Collier, R.; Dengler, A. T.; Edmond, J. M.; Ng, A. C.; Stallard, R. F. *Geochim. Cosmochim. Acta* **1977**, *38*, 1719.
(38) Alhajjar, B. J.; Chesters, G.; Harkin, J. M. *Ground Water* **1990**, *28*, 559.
(39) Heufelder, G. H. *Bacteriological Monitoring in Buttermilk Bay*; EPA-503/4-88-001; U.S. Environmental Protection Agency, Office of Marine and Estuarine Protection, U.S. Government Printing Office: Washington DC, 1988.
(40) Sudicky, E. A. *Water Resour. Res.* **1986**, *22*, 2069.
(41) Garabedian, S. P.; LeBlanc, D. R.; Gelhar, L. W.; Celia, M. A. *Water Resour. Res.* **1991**, *27*, 911.
(42) LeBlanc, D. R.; Guswa, J. H.; Frimpter, M. H.; Londquist, C. J. *U.S. Geol. Surv. Hydrol. Invest. Atlas* **1986**, *No. HA-692*, 1.
(43) Fetter, C. W. *Applied Hydrogeology*, 2nd ed.; Merrill Publishing: Columbus, OH, 1988; p 346.

(44) Berner, R. A. *J. Sediment. Petrol.* **1981**, *51*, 359.
(45) Cogger, C. G.; Carlile, B. L. *J. Environ. Qual.* **1984**, *13*, 137.
(46) Capone, D. G.; Bautista, M. F. *Nature* **1985**, *313*, 214.
(47) Hem, J. D. *U.S. Geol. Surv. Water-Supply Pap.* **1985**, *No. 2254*.
(48) Goldberg, S.; Sposito, G. *Soil Sci. Am. J.* **1984**, *48*, 772.
(49) Redfield, A. C.; Ketchum, B. H.; Richards, F. A. In *The Sea*; Hill, M. N., Ed.; Interscience: New York, 1963; Vol. 2, pp 26–77.
(50) Fetter, C. W. *Ground Water* **1977**, *15*, 365.
(51) Reneau, R. B.; Pettry, D. E. *J. Environ. Qual.* **1976**, *5*, 34.
(52) Johannes, R. E. *Mar. Ecol. Prog. Ser.* **1980**, *3*, 365.
(53) Valiela, I.; Costa, J.; Foreman, K.; Teal, J.; Howes, B.; Aubrey, D. *Biogeochemistry* **1990**, *10*, 177.

Received for review November 5, 1990. Revised manuscript received July 15, 1991. Accepted August 15, 1991. This work was supported by U.S. EPA Grant CX812886-01-3, Sea Grant NA 86-AA-D-SG090, and the Jessie B. Cox Charitable Trust. Contribution No. 7050 of the Woods Hole Oceanographic Institution.