

Figure 2. Relationships between benthic algal biomass, incident light to the marsh surface, and aboveground plant biomass.

The benthic algal biomass is distributed very patchily throughout each site. As a result, even though six core samples were taken on each sampling day, more samples might be needed to truly estimate the actual biomass of each quadrat. The tremendous variability—not only within each area but also within each quadrat—confounds the algal chlorophyll measurements.

It is possible that significant algal growth occurred, but the algae were grazed heavily and thus did not show an actual increase in biomass. It is also possible that our removal of aboveground plant biomass resulted in desiccation of the marsh surface. Desiccation could limit algal growth directly and by preventing the remineralization of nutrients necessary for future algal growth.

Regrowth of marsh plants in the hayed site occurred particularly rapidly (to more than 70% of the biomass of an *S. patens* reference) over the 30 days of the experiment. Thus any stimulation of

algal growth by increased light due to haying is likely to be short term.

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Literature Cited

1. Greenbaum, A., and A. Giblin. 2000. *Biol. Bull.* **199**: 225–226.
2. Estrada, M., I. Valiela, and J. M. Teal. 1974. *J. Exp. Mar. Biol. Ecol.* **14**: 47–56.
3. Lorenzen, C. J. 1967. *Limnol. Oceanogr.* **12**: 343–346.

Reference: *Biol. Bull.* **201**: 288–290. (October 2001)

Dissolved Nitrogen Dynamics in Groundwater Under a Coastal Massachusetts Forest

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Land uses, such as agriculture and residential development, have greatly influenced the amount of nitrogen (N) transported from coastal watersheds to receiving estuaries. This is a concern to ecologists and management groups in coastal regions such as Cape Cod, Martha's Vineyard, and Nantucket, where precipitation percolates rapidly through sandy glacial sediments in the vadose zone (unsaturated layer between the soil and aquifer), causing rapid vertical transport of N to the aquifer (saturated layer) and horizontal movement of N to coastal waters (1, 2). In many forested watersheds, ammonium (NH_4^+) and nitrate (NO_3^-) are transported to receiving estuaries in low amounts relative to dissolved organic N (DON), which includes organic acids and other compounds (3, 4). However, in human-altered systems, high amounts of inorganic N, particularly in the form of NO_3^- , are often transported to aquatic systems, elevating primary production (5). To make management

decisions for coastal areas with high anthropogenic N inputs, it is important to study systems in which human influences are minimal so that background N transformations can be identified.

Our goal in this study was to quantify N concentrations and to identify N transformations in groundwater moving along a known flow path in a forested system with a known land-use history, minimal septic inputs, and no overland flow. We measured the relative concentrations of dissolved N species (NH_4^+ , NO_3^- , and DON) in throughfall, soil solution in the vadose (unsaturated) zone, and groundwater from an oak forest on Job's Neck peninsula in Edgartown, Massachusetts. We also measured N concentrations at the seepage face of the Edgartown Great Pond estuary which lies roughly 500–1000 m downgradient in the groundwater flowpath from the forest.

We collected throughfall, and water from the vadose zone, aquifer, and seepage face from June 2000 to August 2001 and analyzed samples for NH_4^+ , NO_3^- , and DON concentrations. We used spatially extensive sampling to capture fine-scale differences

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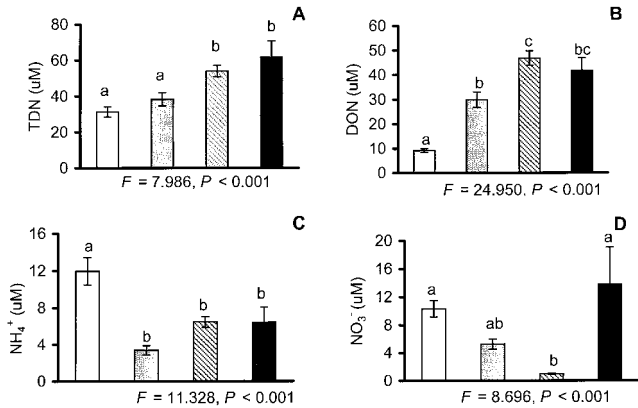


Figure 1. Mean concentrations of TDN, DON, NH_4^+ , and NO_3^- in water inputs to and outputs from the forest. □ = Throughfall, ▨ = Vadose zone, ▩ = Aquifer, ■ = Seepage face. Means represent the average concentrations of samples taken from June 2000–August 2001. Only samples for which all three N analyses were completed are included. Throughfall $N = 72$, Vadose zone $N = 79$, Aquifer $N = 138$, Seepage face $N = 62$. Bars are ± 1 SE and letters above bars indicate significant difference to the $P < 0.001$ level.

in vegetation and topography: 60 throughfall collection units and 50 zero-tension lysimeters installed at 40-cm depth in a stratified random pattern throughout the forest, 40 iron piezometers installed to the water table along the groundwater flow paths, and 34 points for shallow groundwater discharge sampling at the seepage face of Edgartown Great Pond. All water samples were filtered with ashed (2 h at 550 °C) Whatman GF/F filters and frozen in 60-ml polyethylene bottles until analyzed colorimetrically for NH_4^+ , NO_3^- , and TDN concentrations (TDN was analyzed by persulfate digestion). DON concentrations were calculated by subtracting $\text{NH}_4^+ + \text{NO}_3^-$ from TDN concentrations of each sample. We used a one-way analysis of variance and a Tukey’s post-hoc test to determine statistical differences between means (at 0.05 level of significance). All statistical analyses were performed using SYSTAT (SPSS Inc., 1997, Version 7.0).

TDN increased significantly ($P < 0.001$) from $31.44 \pm 2.71 \mu\text{M}$ in throughfall to $54.08 \pm 3.21 \mu\text{M}$ in the aquifer (Fig. 1A). DON was the principal component of dissolved N in the vadose zone, aquifer, and at the seepage face (Table 1). These data are consistent with other studies that show dominance of DON in soil solution and groundwater of forested watersheds (3, 4). DON increased significantly ($P < 0.001$) from $9.15 \pm 0.76 \mu\text{M}$ in throughfall inputs to $46.63 \pm 2.96 \mu\text{M}$ in the aquifer (Fig. 1B). Most DON consists of organic acids and other compounds that originate in the upper layers of the forest floor and move to groundwater during periods of heavy precipitation (4, 6). There was no significant difference between DON concentrations in the aquifer and at the seepage face, suggesting that further removal or accumulation of DON may not occur as groundwater moves horizontally to receiving waters.

NH_4^+ decreased significantly ($P < 0.001$) from $11.97 \pm 1.48 \mu\text{M}$ in throughfall to $3.38 \pm 0.50 \mu\text{M}$ in the vadose zone (Fig. 1C). This suggests that plants or microbes in the rooting zone immobilized NH_4^+ . NH_4^+ concentrations were higher in the aquifer and

the seepage face compared with the vadose zone, but these differences were not significant and suggest that little additional NH_4^+ uptake occurs below the 40-cm depth at which the vadose zone samples were collected. NH_4^+ composed about 12% of TDN in the aquifer, indicating some export of NH_4^+ -N could occur as groundwater moves to the seepage face (Table 1). NH_4^+ movement from the vadose zone to the aquifer is consistent with data from other coastal systems with sandy soils on Cape Cod and may be caused by low soil pH and low soil cation exchange capacity (2). These characteristics may cause NH_4^+ to be more mobile in forests with very coarse-textured soils compared with other upland forests on finer-textured soils (7, 8).

NO_3^- decreased significantly ($P < 0.001$) from $10.33 \pm 1.16 \mu\text{M}$ in throughfall to $0.99 \pm 0.08 \mu\text{M}$ in the aquifer (Fig. 1D). NO_3^- was about 2% of TDN in the aquifer (Table 1), indicating that very little NO_3^- moves from the plant-rooting zone to the aquifer. In the aquifer, concentration of NO_3^- was also lower than NH_4^+ , which suggests low rates of nitrification along the flowpath from soil solution to the aquifer. This pattern is consistent with NH_4^+ and NO_3^- concentrations measured in soil solution and groundwater in Cape Cod coastal forests (2, 6).

NO_3^- increased significantly ($P < 0.001$) from $0.99 \pm 0.08 \mu\text{M}$ in the aquifer to $13.79 \pm 5.26 \mu\text{M}$ at the seepage face (Fig. 1D). NO_3^- concentrations were highly variable but this overall pattern suggested that NO_3^- from additional sources was detected at some locations along the Edgartown Great Pond shoreline. There are several possible explanations for this result. Long-distance transport of NO_3^- from septic discharges farther inland are possible but, we feel, unlikely, given the relative hydrological isolation of Job’s Neck, the west-to-east groundwater movement under the forest, and our measurements of higher NO_3^- concentrations at the southern (coastal) end of the pond shoreline. It is also possible that increases in NO_3^- result from zones of oxidation of NH_4^+ or DON to NO_3^- within the seepage face, or from inputs of fixed N derived from the N-fixing shrub *Myrica pensylvanica*, which is present at many places along the pond shoreline.

From these findings, we conclude that: (1) relatively low NH_4^+ and NO_3^- and high DON are transported from the forest to the coastal pond, (2) incomplete retention of NH_4^+ above the aquifer and comparatively low NO_3^- concentrations in the aquifer suggest that nitrification rates are low in forest soils and in the aquifer, and (3) there is the possibility that in some places the seepage face may contribute a small amount of NO_3^- to discharging groundwater rather than remove it, because of NH_4^+ or DON oxidation or N inputs derived from N-fixing species. These findings can serve as a baseline for understanding how N transformations change with increasing human development and a shift toward a greater proportion of NO_3^- reaching the seepage face from the coastal aquifer.

Table 1

Percentage of TDN for each N species measured

	NH_4^+	NO_3^-	DON
Throughfall	38.1	32.8	29.1
Vadose zone	8.8	13.7	77.6
Aquifer	12.0	1.8	86.2
Seepage face	10.4	22.3	67.3

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Literature Cited

1. Valiela, I., M. Geist, J. McClelland, and G. Tomasky. 2000. *Biogeochemistry* 49: 277–293.
2. Lajtha, K., B. Seely, and I. Valiela. 1995. *Biogeochemistry* 28: 33–54.
3. Hedin, L., J. Armesto, and A. Johnson. 1995. *Ecology* 76: 493–509.
4. Qualls, R., B. Haines, and W. Swank. 1991. *Ecology* 72: 254–266.
5. Valiela, I., G. Collins, J. Kremer, K. Lajtha, M. Geist, B. Seely, J. Brawley, and C. Sham. 1997. *Ecol. Appl.* 7: 358–380.
6. Seely, B., K. Lajtha, and G. Salvucci. 1998. *Biogeochemistry* 42: 326–343.
7. Vitousek, P., and W. Reiners. 1979. *Science* 204: 469–474.
8. Gorham, E., P. Vitousek, and W. Reiners. 1979. *Annu. Rev. Ecol. and Syst.* 10: 53–84.

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Small-Scale Heterogeneity of Nitrogen Concentrations in Groundwater at the Seepage Face of Edgartown Great Pond

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Groundwater transports nitrogen to receiving estuaries (1, 2), but the details of nitrogen exchange, transformations, and losses are insufficiently known (3). We examined small-scale heterogeneity of salinity, ammonium (NH₄), nitrate (NO₃), dissolved organic nitrogen (DON), and boron in both vertical and horizontal profiles near the sandy seepage face of Edgartown Great Pond (Martha's Vineyard, Massachusetts). The water level of this pond is managed by dredging an outlet to release accumulated groundwater; from April to June 2001 the pond was open to the sea. Sampling for this study was done in June 2001. We focused on nitrogen because of its role in limiting estuarine production (4), and on boron because it can be used as a tracer of both wastewater (5) and seawater (6). Relationships among these solutes allow inquiry as to sources of the materials and identity of some major processes (5).

To describe in detail the pattern of distributions of the solutes, we collected groundwater samples along three parallel transects running perpendicular to shore from 4.5 m upland to 1.5 m beyond the shoreline of Edgartown Great Pond (Fig. 1A, B, C). Each transect consisted of seven points, each sampled at about 16 cm, 41 cm, 66 cm, 91 cm, and 116 cm below the ground surface. We collected 125 ml of water from each point using a well point piezometer and pressure pump. The samples were filtered through 47-mm glass fiber filters to remove particulates. We measured salinity using a refractometer and ammonium concentrations using the alkaline phenol method. Nitrate and TDN concentrations were measured on a Lachat autoanalyzer using the Quick Chem method, and DON was determined by subtracting NH₄ and NO₃ concentrations from TDN concentrations for each sample. Ward Laboratories (Kearney, NE) determined boron concentrations on a subset of the samples.

Salinity (Fig. 1A) and ammonium (Fig. 1B) concentrations in groundwater increased seaward. In contrast, NO₃ (Fig. 1C) concentrations decreased seaward. Vertical cross-sections of concentrations (Fig. 1D, E, F) along the top transect shown in Figure 1 (A, B, C) suggest how groundwater flow interacts with horizontal transportation to determine the small-scale patterns of concentra-

tion across the seepage face of this estuary (Fig. 1D, E, F). Salinity of groundwater was 0‰ and increased to 17‰–19‰ under the pond, about half the salinity of the pond (28‰) (Fig. 1D). The contours suggest that the fresh groundwater flows over the saltier water, and discharges in a seepage face a few meters wide. Ammonium concentrations were highest under the pond and at increasing depths, with one high value under land (Fig. 1E). NH₄ concentrations increase as salinities increase beyond 13‰ (Fig. 1G). This increase is not due to NH₄ imported from land to the pond, or from the pond (the pond has a concentration of only 2 μM NH₄). Nitrate concentrations were highest landward and decreased offshore, with a smaller peak seaward (Fig. 1F). DON did not change significantly through each transect (data not shown) and decreased only slightly with increasing depth.

One possible explanation for the high NH₄ associated with salty water may be that the pond bottom shares the vertical pattern of high NH₄ concentrations characteristic of anoxic coastal sediments, with upward diffusion of NH₄ regenerated within the sediments by decay of buried organic matter (7). This explanation seems implausible because 1) none of the water samples had a sulfide odor, hence were not anoxic, and 2) it is difficult to explain the peak in NO₃ concentrations if we simply had freshwater continually flowing toward the seepage face. Perhaps a more plausible idea is that during the open-to-the-sea stage of the year, seawater intrudes into the pore space in sediments at the seepage face, and the Na⁺ displaces NH₄ previously adsorbed to particles. Such a mechanism has been invoked in the displacement of radium from many shorelines (8). This mechanism also has the advantage that it will account for the NO₃ peak shoreward of the NH₄ peak: during the open-pond phase, saltwater may force its way landward, and nitrification could transform the exchanged NH₄ into NO₃ as the porewater moves landward. In most other such estuaries tidal forces may repeat the pattern that occurs once a year in Edgartown Great Pond and probably hide the local pattern of concentrations. This pond hence provides a slow-motion view of what probably occurs twice daily in tidal dominated estuaries.

The high NO₃ concentrations landward are likely to be associated with a wastewater source (Fig. 1H); the concentrations of NO₃ are too high to be atmospheric nitrogen passing through soil (W.

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