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## Nitrogen Flux and Speciation Through the Subterranean Estuary of Waquoit Bay, Massachusetts

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Fresh groundwater discharge is an important vehicle for nitrogen transport to coastal waters (1). In near-shore aquifers, mixing of fresh groundwater with saline pore waters produces groundwater of intermediate salinity that fluxes to sea as submarine groundwater discharge (2). Discharge of this mixed water, known as a subterranean estuary (3), may affect the rate of delivery of nitrogen to the water column. In this study we estimated the flux of dissolved inorganic nitrogen ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) to the head of Waquoit Bay through both the fresh and intermediate-salinity portions of the near-shore aquifer and investigated the behavior of N during transport through the subterranean estuary.

To quantify nitrogen concentrations in the aquifer, we collected groundwater samples from four locations on the shore of Waquoit Bay along a 12-m transect that was perpendicular to shore and extended 6 m above and below the mean tide line on the beach. At each location we collected groundwater samples at depth intervals of 0.15 to 0.6 m to a depth of 7 to 8.5 m below the land surface. Samples were collected using an AMS Retract-a-Tip piezometer with a peristaltic pump and filtered through an in-line 0.45- $\mu\text{m}$  polyethersulphone filter. About 20 groundwater samples from each profile were obtained and stored frozen until analysis. Salinity was measured by salinometer (4); pH, temperature, dissolved oxygen, and redox potential were measured on-site with a YSI 600 multiprobe. Samples were analyzed colorimetrically for dissolved ammonium and nitrate concentration with a QuickChem FIA+ Lachat nutrient auto-analyzer (Zellweger Analytics, QuickChem 8000 Series) within 3 weeks of collection.

In each profile, salinity (Fig. 1A) increased with depth beneath an area of fresh groundwater. This follows the Ghyben-Hertzberg model of high-density seawater intrusion beneath the lower density fresh groundwater (5). Nitrate was the most abundant DIN species present in the relatively oxidizing fresh groundwater (Fig. 1B). This N traveled as a plume and apparently discharged to the bay within the intertidal zone. DIN was present almost exclusively as ammonium in the reducing intermediate-salinity portion of the aquifer (Fig. 1C). Low concentrations were found near the salt-fresh groundwater interface and approached a uniform concentration with depth. These results are consistent with collections from across the head of the bay (Kroeger and Charette, unpubl.).

Low concentrations of  $\text{NH}_4^+$  in Waquoit Bay surface water and in fresh groundwater (Fig. 1D) suggested that ammonium is transported into the subterranean estuary by advection through marine sediments where organic N is mineralized. Our data show that ammonium moved conservatively through the intermediate-salinity zone (Fig. 1D). High concentrations of  $\text{NH}_4^+$  in saline groundwater may be explained by cation exchange and ion pairing, but

considering the linear relationship with salinity, such activity is negligible. This conservative transport suggests that the  $\text{NH}_4^+$  must travel with intermediate-salinity groundwater discharging to sea.

Absence of  $\text{NO}_3^-$  within the subterranean estuary, low concentrations in bay surface water, and high concentrations in fresh groundwater (Fig. 1E) suggest loss of  $\text{NO}_3^-$  by denitrification within the reducing conditions of the saline groundwater. However, it may be that much of the fresh groundwater containing high  $\text{NO}_3^-$  discharges without mixing with the subterranean estuary. Assessing the amount of  $\text{NO}_3^-$  that is mixing with the saline groundwater is difficult since nitrate tends to travel as a plume and concentration in the freshwater endmember is not clear.

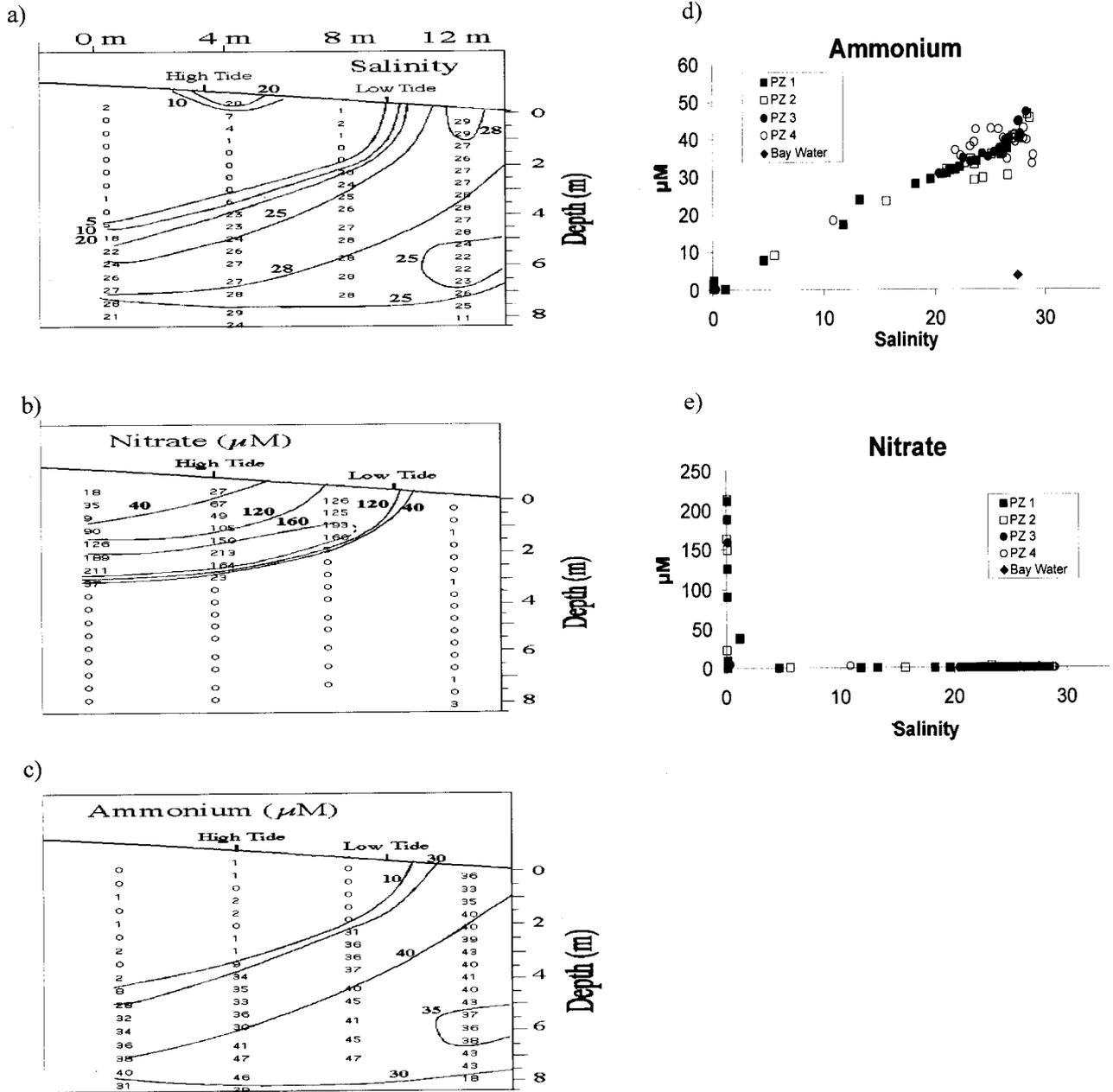
To estimate relative groundwater flux of N to estuarine surface waters, we multiplied the average DIN concentration in each portion of the aquifer by estimated rates of groundwater advection through each zone. We calculated average DIN concentrations using our collections plus previously collected samples from an along-shore transect across the head of the bay (Kroeger and Charette, unpubl.). Freshwater flux of N was calculated using a freshwater discharge rate of 6500  $\text{m}^3/\text{day}$ , determined from hydrological measurements of head gradient and hydraulic conductivity at our sampling sites (Mulligan and Hutchinson, unpubl.). A rate of intermediate-salinity groundwater discharge of 3400  $\text{m}^3/\text{day}$  was calculated as the difference between an estimated total (fresh + saline) groundwater discharge rate of 9900  $\text{m}^3/\text{day}$  and the fresh groundwater discharge rate. Total groundwater discharge to the head of the bay was based on mass-balance-derived estimates of submarine groundwater discharge using measurements of radon activity in groundwater and bay surface waters (6). Total DIN flux to the bay was calculated as the sum of the DIN flux through each portion of the aquifer.

On the basis of these calculations, the freshwater portion of the aquifer discharged 6.2 kg N/day to the head of the bay. DIN flux through the intermediate-salinity zone was 1.5 kg N/day, which accounts for 20% of the total DIN flux to the head of the bay of 7.7 kg N/day.

These results suggest that DIN flux through the subterranean estuary of Waquoit Bay may be significant relative to DIN flux due to freshwater discharge. The DIN transported is composed entirely of regenerated ammonium, as opposed to the terrestrially derived (7) nitrate transported by fresh groundwater. Despite mixing of fresh and saline groundwater masses (Fig. 1A), the subterranean estuary is not a site of net biogeochemical transformations of ammonium.

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**Figure 1.** Behavior of nitrate and ammonium in near-shore aquifer. Cross-sectional contour plots based on depth profiles collected in a transect beginning 6 m above mean tide line for (A) salinity, (B)  $\text{NO}_3^-$  concentration, and (C)  $\text{NH}_4^+$  concentration. Concentrations of (D) ammonium and (E) nitrate versus salinity for each profile. Different symbols indicate samples collected at piezometer locations 1, 2, 3, and 4 from 0–12 m, depicted in panels A, B, and C of this figure. Filled diamond symbols indicate average ammonium ( $3.3 \mu\text{M}$ ) and nitrate ( $1.2 \mu\text{M}$ ) concentrations in Waquoit Bay surface water.

**Literature Cited**

1. Valiela, I., K. Foreman, M. LaMontagne, D. Hersh, J. Costa, C. D'Avanzo, M. Babione, P. Peckol, B. DeMeo-Andreson, C. Sham et al. 1992. *Estuaries* 15: 443–457.
2. Li, L., D. A. Barry, F. Stagnitti, and J.-Y. Parlange. 1999. *Water Resour. Res.* 35: 3253–3259.
3. Moore, W. S. 1999. *Mar. Chem.* 65: 111–125.
4. Knapp, G. P., M. C. Stalcup, and R. J. Stanley. 1990. *Technical Report WHOI-90-35*, Woods Hole Oceanographic Institution, Woods Hole, MA. 25 pp.
5. Freeze, R. A., and J. A. Cherry. 1979. *Groundwater*. Prentice Hall, Edgewood Cliffs, NJ. Pp. 375–378.
6. Abraham, D. M., M. A. Charette, M. C. Allen, A. Rago, and K. D. Kroeger. 2003. Radiochemical estimates of submarine groundwater discharge to Waquoit Bay, Massachusetts. *Biol. Bull.* 205: 246–247.
7. Valiela, I., G. Collins, J. Kremer, K. Lajtha, J. Geist, B. Seely, J. Brawley, and C. H. Sham. 1997. *Ecol. Appl.* 7: 358–380.