

Contrasting Nitrogen Biogeochemistry and Fluxes to Coastal Waters from a Temperate and Subtropical Coastal Aquifer

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Eutrophication of coastal waters due to non-point-source land-derived nitrogen (N) loads is a world-wide phenomenon and perhaps one of the greatest agents of coastal ecological change. Within the U.S., a majority of estuaries has recently been determined to be moderately to severely impaired by eutrophication associated with increasing nutrient loads (Bricker et al. 1999).

In coastal watersheds with soils of high hydraulic conductivity and permeable coastal sediments, groundwater is a major route of transport of freshwater and its solutes from land to sea. Freshwater flowing down gradient from aquifers may either discharge from a seepage face near the intertidal zone or flow directly into the sea as submarine groundwater discharge (SGD). The hydraulic gradient that drives freshwater toward the sea also drives saltwater back to sea, creating a saltwater circulation cell. In addition, entrainment of saline pore water occurs prior to discharge, producing a gradient in groundwater salinity from land to sea, referred to as a subterranean estuary (Moore 1999). Hence, SGD often consists of a substantial amount of recirculating seawater, and that mixing of fresh and saline groundwaters in the context of coastal sediments may alter the chemical composition of the discharging fluid. Depending on the biogeochemical setting, removal of fixed N due to N₂ gas-producing processes in the nearshore aquifer and subterranean estuary may significantly attenuate land-derived N loads. On the other hand, processes such as ion exchange and tidal pumping in the subterranean estuary may substantially accelerate the transport of both land-derived and sediment re-mineralized N to estuarine water columns.

We are contrasting nitrogen transport and biogeochemistry in nearshore portions of coastal aquifers in west-central Florida and on Cape Cod, Massachusetts. The N biogeochemical investigations are being carried out in concert with radiochemical and isotopic-tracer approaches, seepage-meter studies, and streaming-resistivity surveys to identify locations and sources of SGD and to quantify fluxes to receiving estuaries. Examination of N biogeochemistry has included measurements of concentrations, natural-abundance stable isotopic ratios, N₂ and argon gas concentrations, and preliminary experiments employing a modification of the isotope pairing technique.

Results to date suggest that conditions in the Florida surficial aquifer are generally much more reducing than in the Cape Cod aquifer, so that both fresh and saline groundwater are devoid of nitrate and high in ammonium and dissolved organic nitrogen (DON). There has been very little prior study of the surficial aquifer discharging to Tampa Bay, yet our early results suggest that it may be a substantial source for loading of reduced N species (ammonium and DON) to Tampa Bay. In contrast, fresh groundwater in the Cape Cod aquifer contains high nitrate concentrations in many locations. Advection associated with SGD entrains saline, reducing, ammonium-rich pore waters, and creates a salinity gradient within discharging water. Dilution and removal of mineralization products occurs to > 6 m below sediment surface. A plot of ammonium vs. salinity in brackish to saline groundwater is approximately linear, suggesting that ammo-

nium may transport conservatively (without transformation) during mixing of water masses. Advection introduces dissolved oxygen and nitrate into the saline pore waters, yet nitrate is largely absent in brackish to saline pore waters. Where nitrate and ammonium do co-occur, concentration and natural-abundance stable-isotope data consistently suggest substantial loss of both species through a fractionating process. Examination of N_2 -gas concentrations suggest that excess N_2 is present both at the low-salinity portion of the subterranean estuary and in saline groundwater near the sediment/water interface. Preliminary experiments employing a modification of the isotope-pairing technique support the hypothesis that fixed N loss occurs with mixing of nitrate and ammonium-bearing waters, and that denitrification may co-occur with an anammox-type process. In-situ energetics calculations suggest anammox is, indeed, favored over nitrification in zones of N loss.

Our results, therefore, suggest that N is actively cycled in nearshore portions of coastal aquifers, and that mixing of fresh and saline groundwater prior to discharge may result in transport to the water column of mineralization products from estuarine sediments. In addition, in some locations, land-derived N loads to estuaries may be modified by fixed N loss.

References

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