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Multiple Approaches to Tracing Nitrogen Loss in the West Falmouth Wastewater Plume

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Wastewater transported through groundwater to receiving estuaries is a major contributor of nitrogen (N) in densely settled watersheds, and contributes to coastal eutrophication (1–3). Although nitrate removal by microbial denitrification, adsorption, and uptake by plants is well documented, little is known about the nitrogen loss in the vadose zone and aquifer (1, 4).

This project focused on the fate of nitrogen leaving the Falmouth Wastewater Treatment Plant (FWTP) in Falmouth, Massachusetts. The plant lies on the Snug Harbor sub-watershed of West Falmouth Harbor (WFH), and the wastewater it discharges percolates through 25–30 m of vadose zone before meeting the aquifer and traveling in groundwater to WFH (3). This site provides a good model for a study of N loss due to the well-documented history of wastewater discharge and previous research involving N loading and removal.

The two principal objectives of this study were (1) to assess the efficiency of N removal as wastewater travels from FWTP to WFH, and (2) to determine where N loss is occurring. To satisfy our first objective, we quantified N loss using two independent methods: a mass balance calculation, and a conservative tracer technique. We then compared these results to a previous study conducted in 1999 (3). The site of N removal was examined using the same conservative tracer technique applied to samples within the path of the plume in the aquifer. We further investigated whether denitrification was the primary mechanism responsible for N loss in the aquifer by using dissolved N_2 and Ar gas analysis (5). With the development of the membrane inlet mass spectrometer, it has recently become possible to measure dissolved N_2/Ar ratios with sufficient precision and accuracy to estimate denitrification (6).

We measured dissolved inorganic nitrogen (DIN; nitrate + ammonium), and boron (B) in wastewater effluent at FWTP and in monitoring wells located within and outside of the treatment plant. Boron, a component of laundry detergent, can be used as a conservative tracer for wastewater (7). We also sampled groundwater about to enter WFH within the boundaries of the Snug Harbor watershed. Samples were taken from 0.5 to 1.5 m below the sediment surface, using well-points. These shoreline samples were analyzed for DIN, B, and dissolved N_2 and Ar gas concentrations. Samples with elevated salinity, indicating seawater intrusion, were rejected. Nitrate, ammonium, and B concentrations were measured using standard colorimetric techniques.

We compiled discharge data for the FWTP from its establishment in 1987 to the present, and observed that loading increased during the first 7 years of operation (Fig. 1A). Based upon an estimated 10-year groundwater travel time from the center of the plant to WFH (3), we used the 1993 discharge value of 13,177 kg N/y to compare with the loading now reaching the harbor. To

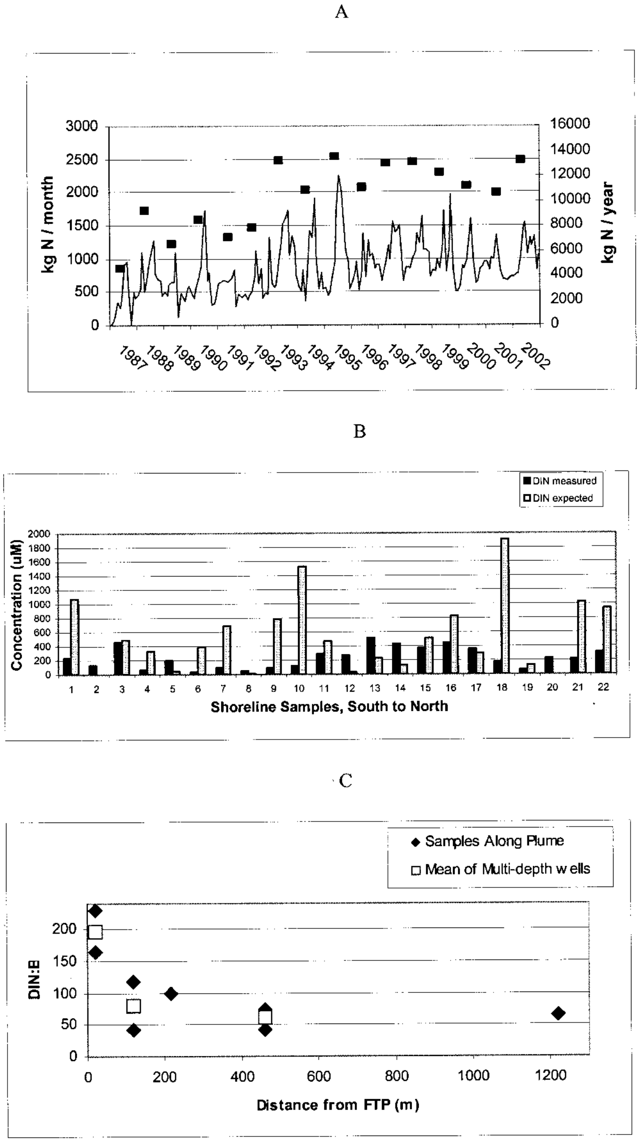

Figure 1. *Loading data from the Falmouth Wastewater Treatment Plant (FWTP), and data from the wells and shoreline well points down gradient of the plant. (A) Monthly (line) and annual (filled squares) discharge (DIN concentration in effluent * flow), in kg N, from FWTP, 1987–2002. (B) Comparison of measured DIN to expected DIN at each shore well-point based on dilution correction estimated from the DIN/B ratio. (C) DIN/B ratios from the effluent in the last holding pond from FWTP, from monitoring wells located 100 to 460 m down gradient, and from average of shoreline samples. Squares represent the average value for replicate samples of the effluent in the last holding pond and multi-depth wells.*

calculate the DIN entering WFH, we used the average DIN concentration of shoreline groundwater, 208.5 μM ($n = 28$, se = 27.8), multiplied by a literature value for the groundwater flux ($1737 * 10^3 m^3/y$) (3). Thus, 5070 kg/y of DIN is currently discharging from the Snug Harbor sub-watershed. To isolate DIN originating at FWTP, we subtracted 554 kg of DIN reaching the shore derived from fertilizer, atmospheric deposition, and septic wastewater (3). Thus, we calculate that 66% of the DIN discharged from the FWTP in 1993 was lost en route to the harbor.

The conservative tracer method produced similar results. Changes in the DIN/B were used to calculate N loss based on the following formulas:

$$\text{DIN expected (at each wellpoint)} = (\text{DIN effluent} * \text{B measured})/\text{B effluent}$$

$$\%\text{DIN loss} = (1 - (\text{Average (DIN measured)}/\text{Average (DIN expected)})) * 100$$

Expected and measured concentrations refer to shoreline samples (Fig. 1B), and DIN and B effluent concentrations (2017 μM and 13.3 μM respectively) were measured from the last holding pond at FWTP. This method estimates that 56% of DIN is lost. The method corrects for dilution, but it does not account for N input from fertilizers or atmospheric deposition and thus may slightly underestimate DIN loss.

Using the DIN shoreline load measured in 1999 (3) compared with 1989 effluent data, we calculated an 81% DIN loss. The lower percent removal that we found in 2003, in addition to the two-fold increase in DIN concentration in shoreline samples over 4 years (109 μM in 1999, 208 μM in 2003), suggests that the efficiency of N removal may be declining over time. Alternatively, we may have underestimated groundwater travel time, thus underestimating losses (Fig. 1A).

To ascertain where the loss occurred, we used DIN/B ratios from the monitoring wells in the wastewater plume (Fig. 1C). The DIN/B data show that about 60% of the DIN is lost between the point of effluent discharge and the first monitoring well. Thereafter, DIN/B ratios decrease little with distance traveled in groundwater, suggesting that the primary loss due to denitrification and retention occurs either in the vadose zone, at the interface of the aquifer and vadose zone, or during the initial 100 m of travel in the aquifer.

A second approach to examining the loss of DIN within the aquifer was to use N_2/Ar ratios to calculate the excess N_2 gas present in the shoreline samples. The Ar content of the water was used to calculate the temperature of the water entering the aquifer. We assumed that when the water entered the aquifer, both gases were in atmospheric equilibrium at that temperature. The amount by which the N_2 measured in the water exceeded the amount expected with atmospheric equilibration was used to estimate denitrification within the aquifer. Values of excess N_2 along the shore averaged 46.8 μM N ($n = 18$, se = 3.9), indicating that only 8% of the DIN in the effluent leaving the FWTP was denitrified within the aquifer. Because high rates of denitrification within the aquifer should have been detected as N_2, we believe that denitrification is not a major process in the initial 100 m of the aquifer. However, we cannot ignore the interface, where N_2 gas can escape, as a possible site of N removal.

These results, coupled with the DIN/B data from within the plume, suggest that denitrification within this aquifer is small and most of the removal may occur in the vadose zone, as has been reported previously (1). This is consistent with the idea that dissolved organic carbon, a component of the denitrification process, is largely consumed in vadose zones thicker than 5 m, therefore allowing for little denitrification activity in the aquifer (8).

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