

# NITROGEN LOSS IN A BARRIER ISLAND SHALLOW AQUIFER SYSTEM

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**Introduction:** Sediment cation exchange and groundwater denitrification are important attenuation process with great impact on downstream nitrogen loads. Many studies of nitrogen loss focus on losses within riparian and hyporheic systems with an eye on determining nitrogen transport to surface bodies. Loads to these transitions zones are often dependent on nitrogen dynamics in groundwater. In suburban and some rural areas groundwater is contaminated primarily by on site wastewater systems (OWS) comprised of septic tanks and an effluent distribution system, either cesspools or leach fields, depending on local regulations and hydrology.

On site wastewater systems (OWS) consist of two treatment steps. First wastewater is treated in a septic tank to eliminate solids and allow for microbial breakdown of some organic material. Then wastewater is discharged to an effluent distribution system. The effluent distribution system disperses the wastewater into the soil where nitrogen can undergo nitrification, denitrification, ammonification, ammonia volatilization or soil sorption depending on ambient redox conditions. The volume of soil area in contact with discharging wastewater varies depending on sediment permeability and vadose zone thickness, i.e distance to the water table. Within the vadose zone sediment cation exchange plays an important role in soil sorption removal of nitrogen from infiltrating wastewater. Vadose zone thickness also affects the transport of dissolved organic carbon (DOC) and dissolved oxygen to groundwater (SPITERI et al., 2008).

Coastal bodies are vulnerable to nutrient loading via submarine groundwater discharge (SGD) which contributes to eutrophication. SGD is increasingly recognized as an important source of nitrogen to shallow bays and estuaries (CRUSIUS et al., 2005; KROEGER et al., 2006). Great South Bay is a shallow bay typical of those found along the U.S east coast. Great South Bay is bound by Long Island, NY to the north and by Fire Island, NY to the south. Fire Island is a sparsely populated barrier island with a shallow freshwater lens contained in the Upper Glacial aquifer. Communities and recreation areas on Fire Island use on site wastewater systems which discharge through a thin vadose zone into the shallow groundwater lens. This groundwater is found to discharge into Great South Bay by submarine groundwater discharge, in some areas freshwater in sediments is found as far as 30 meters off shore (Bratton et al., in press).

The specific goals of this investigation were to: 1) Determine if sediment cation exchange can account for nitrogen loss in the thin vadose zone at Watch Hill, 2) Determine if groundwater denitrification can account for observed low groundwater nitrate concentrations at Watch Hill, and 3) determine the primary nitrogen species exported to Great South Bay via submarine groundwater discharge.

Site Description: Samples were taken from Fire Island National Seashore at Watch Hill. The U.S. Geological Survey emplaced monitoring wells along a north-south transect through Watch Hill park. Geologic framework consists of south sloping Paleozoic crystalline bedrock overlain by a complex system of Cretaceous aged marine and deltaic sediments that are hydrologically isolated from Pleistocene shallow system sediments by the Gardiners clay. The Gardiners clay is topped by Late Pleistocene outwash unit. The upper unit of Late Pleistocene outwash consists of fine to coarse sand mixed with gravel and streaks of silt and clay. Wells S125380, S125381, S125382, S1253990 have depths that reach the upper outwash and S1253990 penetrates it's full thickness (SCHUBERT, 2010). Holocene deposits overlie the Late Pleistocene outwash deposits on Fire Island and are separated into four units of estuarine mud, seagrass beds, peat deposits, barrier island and shelf sands.

Rising sea level paired with landward migration of the barrier island created a sequence of fine to coarse grained sediments interbedded with estuarine mud, sea grass beds and peat. Peat deposits are found beneath barrier island sands in drillers logs for four of the five wells sampled in this study. Deposits consist of black peat with some medium to fine sand (SCHUBERT, 2010). Barrier Island and shelf sands are found overlying buried peat deposits.

Fresh groundwater exists as a lens bounded below by saline water, to the north by brackish water in Great South Bay and to the south by the Atlantic Ocean. The groundwater divide is controlled by water table overheight which skews the divide slightly towards the Atlantic Ocean (south) side of Fire Island. Infiltrating groundwater flows north to Great South Bay or south to the Atlantic Ocean. All samples in this study were taken from the north of the water table divide.

Figure 1 shows the study site monitoring wells and leach field. Monitoring wells were sampled 4 times from 2008-2010. Leach field soil samples were taken in August and October of 2010.



**Figure 1 Watch Hill National Seashore field area. Five monitoring wells were sampled in this study. Leach field area is outlined to show proximity to monitoring wells.**

**Methods:** Sediment samples were collected adjacent to leach field pipe discharge holes at three depths; 10cm, 30cm and 60cm. Sediment samples were analyzed for exchangeable ammonium ( $\text{NH}_4^+$ ) using KCl method. Ammonium analysis was done by phenol hypochlorite method, modified for plate reader. Finally, the septic tank was sampled to get an estimate of nitrogen inputs to the system.

A Grundfos submersible pump was used to collect groundwater samples. Three well volumes were evacuated prior to collection of all samples. Dissolved gas samples for MIMS analysis were collected in Labco Exetainer® vials with gas impermeable screw cap, dimensions of 101x15.5mm, 12ml volume. Nitrogen and argon gas concentrations were analyzed using a membrane inlet mass spectrometer (MIMS) at the USGS Woods Hole facility.  $\text{N}_2$  and Ar concentrations were determined from mass spectrometer intensities at masses 28 and 40, respectively. Analytical precision for MIMS analysis was taken as the standard deviation for eight replicate injections of a standard at 10°C, 0 ppt salinity. A comparison of these injections with theoretical concentrations give percent error for  $\text{N}_2$  of +/- 0.4% and percent error for  $\text{N}_2/\text{Ar}$  of +/- 0.1%. Standard deviation for  $\text{N}_2/\text{Ar}$  is 0.025. Standard deviation for  $\text{N}_2$  is 1.77  $\mu\text{M}/\text{l}$ , or 0.05 ppm  $\text{N-NO}_3^-$ .

Groundwater dissolved organic carbon samples were filtered through Whatman 0.45 micron flow-through filters and stored in acid washed combusted vials. DOC analysis was done using a Shimadzu TOC-5000. The overall precision for a group of samples is +/- 5% of the reported value. Raw results are given as mg L<sup>-1</sup> carbon.

Groundwater samples for nitrate and ammonium analysis were collected in acid rinsed vials and frozen within 6 hours of collection. Nitrate analysis was done by vanadium chloride method (Miranda et al., 2001) modified for plate reader. Ammonium analysis was done by phenol hypochlorite method (Solorzano, 1969) modified for plate reader.

Results and Discussion: We investigated two methods of nitrogen loss in the Watch Hill system; sediment cation exchange and groundwater denitrification. We also consider dissimilatory nitrate reduction to ammonium as a nitrogen transformation that preserves nitrogen in the system. We used a cation exchange model to compare our field determined concentrations with predicted concentrations. Our model also allowed us to determine the transit time between leach field discharge and monitoring well.

The cation exchange capacity (CEC) is the capacity of specific sediment for cation exchange between the particle and solution. The total amount of charged sites on soil particle surface is given in milliequivalents per 100 grams (meq/100g). The CEC of particular sediment is fixed while the proportion of cations on the sediment reflects the cation signature of fluid(s) it's interacted with. The single element distribution coefficient describes the ratio of the concentration of exchangeable cation on the solid to the concentration in solution at equilibrium, as in equation 1.

$$K_d = \frac{C_s}{C_L} \quad \text{Equation 1}$$

Where C<sub>s</sub> is the concentration of cation absorbed on the sediment (meq/100g) and C<sub>L</sub> is the concentration of cation in the effluent (meq/100g).

Septic tank concentrations of ammonium ranged from 203-251 mg/l N-NH<sub>4</sub>. These numbers represent the range of nitrogen inputs to the system. Concentrations of soil exchangeable ammonium did not vary significantly with distance from leach field pipe. Table 1 presents the range of data for each depth. An anomalously high value at the 60cm depth was likely due to the inclusion of peat in one sample at that level.

Depth (cm)	Minimum NH <sub>4</sub> <sup>+</sup> (meq/100g)	Maximum NH <sub>4</sub> <sup>+</sup> (meq/100g)
10	0	3.0x10 <sup>-3</sup>
30	3.5x10 <sup>-4</sup>	5.2x10 <sup>-3</sup>
60	1.2x10 <sup>-3</sup>	2.4x10 <sup>-2</sup>

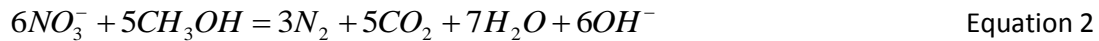
**Table 1 Exchangeable N-NH<sub>4</sub><sup>+</sup> from soil samples at different representative depths below leach field pipes.**

We compare the ammonium values obtained from soil samples with a calculated value obtained from our model. The model obtained value of 7.73x10<sup>-3</sup> is 2.14% higher than the average value for samples at

the same depth. This discrepancy could be due to partial nitrification of ammonium during transport through the unsaturated zone. Our model only accounts for sorption and does not include the effects of nitrification on total ammonium concentration in the residual sewage fluid.

To determine the amount of time it would take for sewage derived ammonium to reach monitoring wells at Watch Hill, we modeled transport in both sand and peat. Model parameters defined one pore volume as 25 meters, the distance from leach field edge to nearest monitoring well. We determined that the plume traverses one pore volume in 1.9 days traveling in sand and 91.5 days traveling in peat. While the CEC of peat (150-400meq/100g) is much higher than that of uncoated sand (0.33meq/100g) peat has a much lower bulk density and increased hydraulic conductivity, which partially offsets the increase in cation exchange sites when determining plume travel time. From our model it is clear that groundwater receives nitrogen from leach field discharge within one summer tourism season. Therefore leach field derived nitrogen is replenished each season by a new flux of OSW effluent. As cation exchange is not a primary mechanism for nitrogen loss in the system, we investigated the potential for denitrification as a nitrogen loss mechanism. We also determined the primary nitrogen forms dissolved in groundwater.

Microbial denitrification produces dissolved nitrogen ( $N_2$ ) concentrations above atmospheric equilibrium, as shown in equation 2.



We used dissolved  $N_2/Ar$  to determine concentrations of nitrate denitrified in monitoring well samples. Equation 3 was used to determine the excess nitrogen in the sample. Dissolved  $N_2O$  was measured to determine if partial denitrification could account for any nitrate loss.

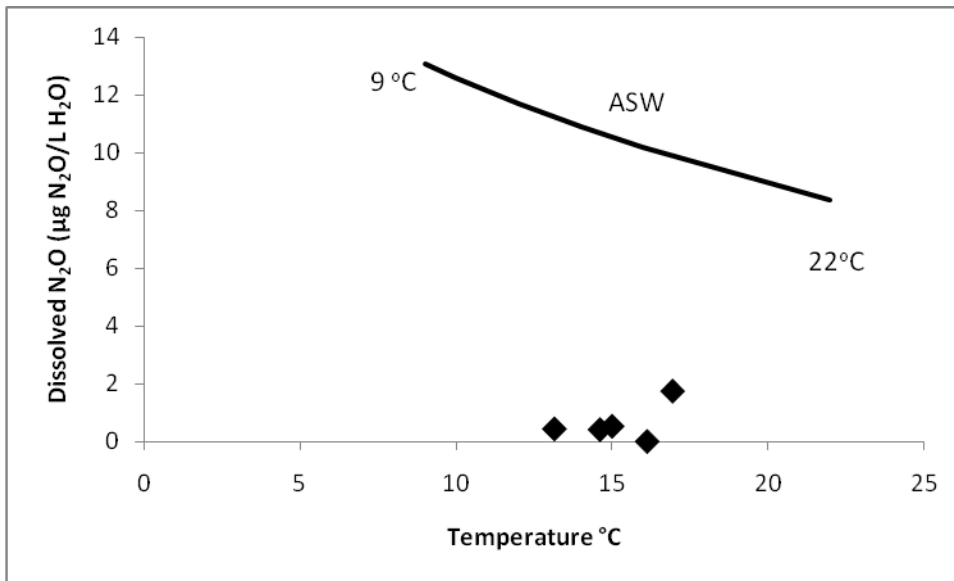
$$\frac{N_2}{Ar} = \frac{N_2 (atmosphere) + N_2 (denitrification)}{Ar (atmosphere)} \quad \text{Equation 3}$$

Nitrate denitrified ranged from 0.7-6.8 mg  $N-NO_3^- L^{-1}$  for groundwater during all sampling timeframes. Nitrate levels were below detection limits of 0.01mg/l in all groundwater samples. Ammonium represented the largest portion of nitrogen in the system. A summary of nitrogen speciation, along with dissolved oxygen and dissolved carbon concentrations from groundwater samples taken in October 2010 is given in Table 2.

Well #	NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	NH <sub>4</sub> (mg L <sup>-1</sup> )	Denitrified N-NO <sub>3</sub> (mg L <sup>-1</sup> )	Dissolved N <sub>2</sub> O µg N <sub>2</sub> O/ L H <sub>2</sub> O	DOC (mg L <sup>-1</sup> )	DO (mg L <sup>-1</sup> )
125380	<0.01	5.71	3.10	0.41	7.83	0
125381	<0.01	0.70	0.94	0.53	18.35	0.09
125383	<0.01	4.16	3.01	1.74	9.71	0.08
125384	<0.01	6.43	0.72	0.00	7.40	0.1
125990	<0.01	9.08	6.27	0.44	5.32	0.03

**Table 2 Summary of Nitrogen speciation, dissolved organic carbon (DOC) and dissolved oxygen concentrations for groundwater well samples taken in October 2010**

Dissolved nitrous oxide concentrations were analyzed for fall 2010 samples. Concentrations range from 0.00 to 1.74 µg N<sub>2</sub>O L H<sub>2</sub>O<sup>-1</sup>. This represents a depletion of dissolved nitrous oxide relative to atmospheric equilibration concentrations, as shown in Figure 2. These results indicate that nitrogen is being scavenged as an electron receptor due to low dissolved oxygen and an excess of dissolved organic carbon in groundwater.



**Figure 2 Depletion of dissolved nitrous oxide in groundwater samples. ASW is air saturated water line for relevant temperatures.**

Dissolved organic carbon concentrations range from 5.32 to 18.35 mg/l in groundwater samples. Without further work on isotopic signature of DOC it is impossible to accurately identify the source of high DOC concentrations. One possibility is from leach field effluent, but this is unlikely given the well aerated sediments which promote oxidation of DOC prior to groundwater recharge. Another possibility is leaching from extensive peat deposits found close to the water table at Watch Hill. Although peat is

typically thought to be a recalcitrant form of organic carbon, it cannot be ruled out as the source of elevated DOC concentrations at this site.

Conclusion and Future Work: Cation exchange modeling indicate short travel times in both sand and peat layers (9 days and 91 days respectively) of leach field sediments indicate all leach field nitrogen is cycled into the groundwater within one summer tourism season. Groundwater samples indicate denitrification is an important nitrogen cycling process at Watch Hill. Microbial denitrification and depleted  $\text{N}_2\text{O}$  concentrations are evidence that some ammonium from the leach field is nitrified during transport to the water table. Reducing conditions within the groundwater promote denitrification and likely dissimilatory nitrate reduction to ammonium (DNRA) as nitrogen cycling processes. High ammonium concentrations are the result of either direct contamination from leach field effluent or from DNRA. Further, depletion of  $\text{N}_2\text{O}$  indicates scavenging by microbes for available electron receptors in the system. We believe that nitrogen exports to coastal water via submarine groundwater discharge are primarily as ammonium for this site.

Future work is planned to investigate the isotopic signature of DOC at this site in order to determine the source of DOC in groundwater. This is crucial in understanding if peat layers, which are common in barrier island systems, contribute DOC to shallow groundwater systems driving the system anoxic and promoting denitrification. We will also investigate the natural abundance of  $^{15}\text{N-NH}_4^+$  at this site to determine if ammonium is transferred directly to groundwater via septic effluent or if it undergoes nitrification and then dissimilatory nitrate reduction to ammonium. A better understanding of these processes will provide us with insights on how barrier islands process inputs of nitrogen to shallow groundwater and expected impacts from future installation of on-site wastewater treatment systems.

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