

# **Fate of nitrogen during oxic submarine groundwater discharge into Stony Brook Harbor, Long Island, NY**

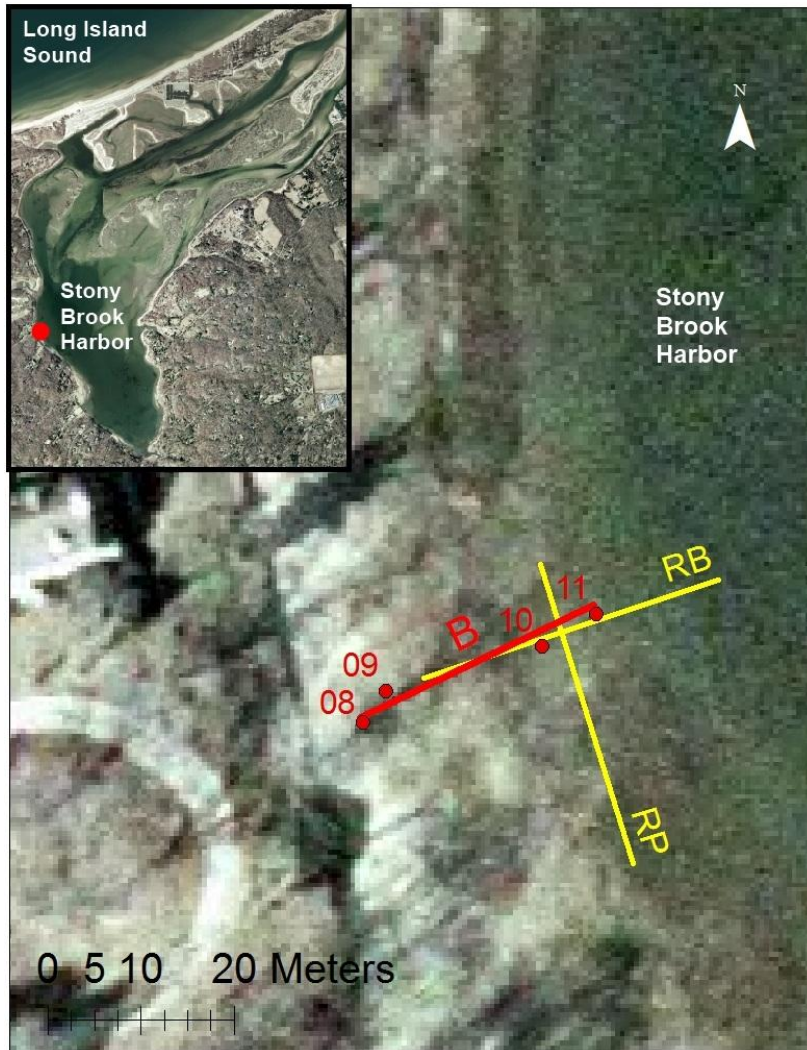
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## **Introduction**

Submarine groundwater discharge (SGD) nutrient fluxes from un-sewered suburban landscapes pose a significant eutrophication risk to coastal waters. In unconsolidated coastal aquifers, nutrients recharged to groundwater undergo diffuse discharge to the coastline during SGD. Defining pathways of nutrient attenuation is required for land management professionals to take effective nutrient remediation action. During diffuse SGD, geochemical transformations in at the freshwater-saltwater boundary, known as the subterranean estuary (STE), can dramatically reduce nutrient loads over short (less than 50m) spatial scales (Kroeger and Charette, 2008). Nitrogen loading calculations for Long Island Sound assume conservative transport of nitrogen during submarine groundwater discharge through the subterranean estuary (Team et al., 2007). In this study, electrical conductivity surveys, piezometer porewater sampling and ultrasonic seepage meter measurements were used to investigate nitrogen attenuation in a subterranean estuary in Stony Brook Harbor, an embayment with a direct connection to Long Island Sound.

Stony Brook Harbor is located on the north shore of Long Island and is connected to Long Island Sound via a narrow, northeastern inlet adjacent to the mouth of West Meadow Creek, see figure 1 (inset). Shoreline sediments are highly permeable glacial deposits comprised of medium to fine grain sand locally inter-bedded with clay deposits. Influent submarine groundwater originates upland in the Upper Glacial Aquifer where it receives nutrient inputs from septic tank/cesspool systems and lawn fertilizer leachate (Munster, 2008).



**Figure 1** Stony Brook Harbor, NY. Field location is shown in red on inset map. Conductivity transects RB and RP are marked in yellow. Piezometer well point locations 08-11 are shown in red, with a cross section line 'B' for reference. Cross section profiles given in figure 3 are generated from porewater sample data taken from these 4 wells along transect B.

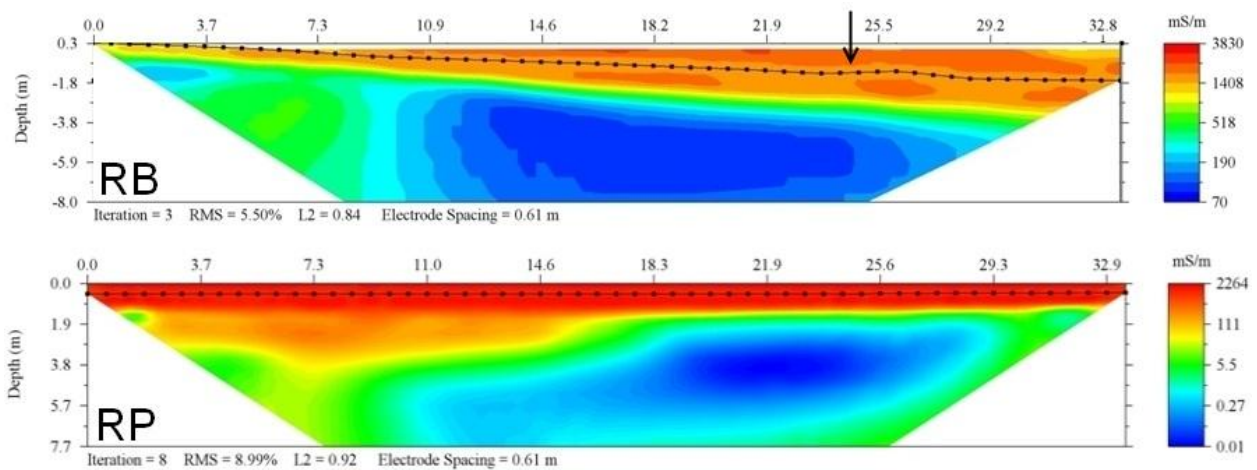
## Methods

Electrical conductivity surveys, piezometer porewater sampling and ultrasonic seepage meter measurements were combined to assess nitrogen transformations in a subterranean estuary in Stony Brook Harbor. Coupled land-sea electrical conductivity surveys were performed to determine the saltwater-freshwater structure of the STE. A combination of shore parallel and shore perpendicular transects provides information about the depth of tidal recirculation, position of lower salinity zone and along shore extent of freshwater discharge. This is important as SGD is a heterogeneous process with widely varying discharge rates over tens of meters along shore.

Piezometer well locations (figure 1) were selected based on STE structure information gained from conductivity surveys. The piezometer transect consisted of 4 piezometer wells with sample depth intervals ranging from 50-100cm to a maximum sampling depth of 8-10m. Porewater samples were analyzed for dissolved oxygen, reactive silica,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^- + \text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{2-}$ , DOC, dissolved  $\text{N}_2\text{O}$  and  $\text{N}_2/\text{Ar}$  to assess major nitrogen transformation processes. During piezometer sampling, an Ultrasonic Seepage meter was deployed to measure the SGD rate (Paulsen et al., 2001). Porewater sampling took place over the course of 7 days during falling to low tide.

## Results

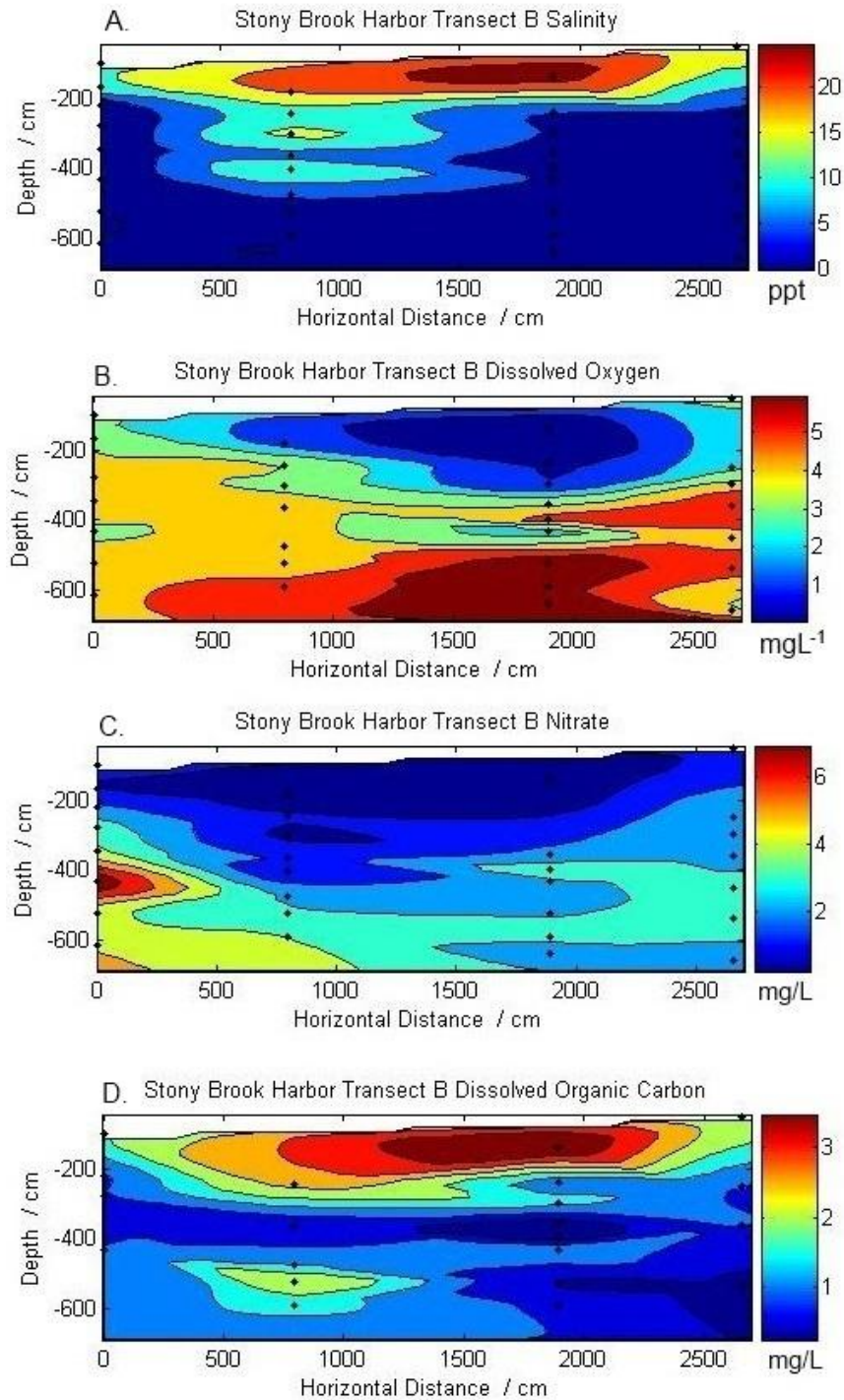
Coupled land-sea electrical conductivity surveys show a heterogeneous discharge zone with a distinct shallow saline recirculation cell overlying a 9m thick freshwater lens in the coastal aquifer (shown in figure 2). Electrical conductivity images taken shore perpendicular (2a) and shore parallel (2b) give a 3D view of the heterogeneity of the system. The clear freshwater body tapers southward, indicating significantly lower SGD rates exist less than 30m south of the porewater sampling transect.



**Figure 2** Conductivity profiles of Stony Brook Harbor Subterranean Estuary, locations RB and RP shown in figure 1. Shore normal profile (RB) spans the inter-tidal zone from high tide (top left) to just beyond the mean low tide line (top right). A distinct freshwater body, shown in blue, is present 0.8m below sediment surface. Overlying saline surface water is shown in red. A black arrow indicates cross point for shore parallel conductivity profile RP (bottom). RP shows the heterogeneity of the discharging water, where freshwater tapers in strength from north (right) to south (left).

Porewater in the upper saline transition zone is hypoxic to anoxic with dissolved oxygen concentrations below  $2.7\text{mgL}^{-1}$  in samples with salinity  $>21\text{ppt}$  (see figure 3). Nitrogen exists as nitrate in the saline recirculation cell, and no ammonium is present although  $\text{NH}_4^+$  is found in overlying surface water. Dissolved organic carbon is enriched in the upper saline zone, with concentrations ranging from  $1.1\text{-}3.8\text{mgL}^{-1}$ , likely due to remineralization of seawater carbon,

as shown in figure 3. The freshwater and lower saline transition zone are oxic with concentrations remaining between  $3.1\text{mgL}^{-1}$  and  $8.7\text{mgL}^{-1}$  and oxygen concentration increasing with increasing depth. In one transect  $\text{NO}_3^-$  concentrations decreased seaward  $5\text{mgL}^{-1}$  over a distance of 26 meters, see figure 3c. Freshwater dissolved organic carbon concentrations range from  $0-1.6\text{mgL}^{-1}$ , within the range of average groundwater DOC  $0.5\text{mgL}^{-1}$  (Leenher et al., 1974).



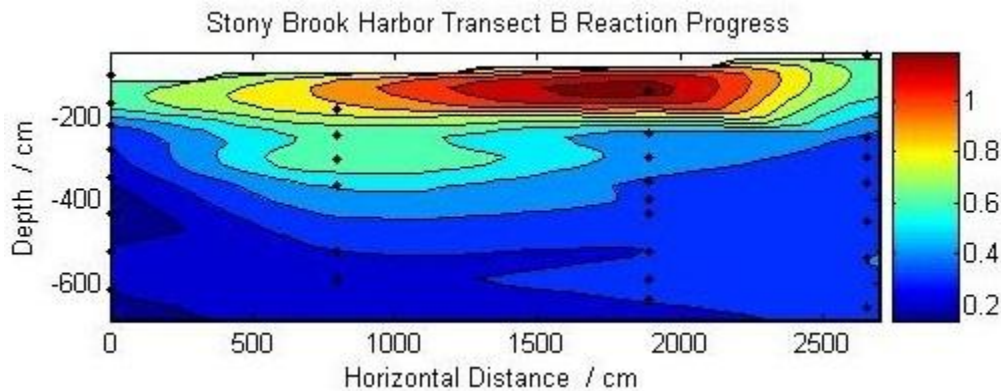
**Figure 3** Stony Brook Harbor transect B porewater profiles for salinity (A), dissolved oxygen (B), nitrate (C) and dissolved organic carbon (D). Individual sampling points are shown in black. Horizontal distance '0' corresponds to piezometer 08 and horizontal distance 2650 corresponds to piezometer 11, see figure 1 for locations. Porewater exhibits a shallow saline recirculation cell that is depleted in dissolved oxygen and enriched in dissolved organic carbon. Underlying freshwater is oxidic, and contains nitrate in excess of  $5\text{mgL}^{-1}$  in upland samples (3C).

Extent of denitrification was evaluated using a combination of total  $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$ , dissolved  $\text{N}_2\text{O}$  and dissolved excess  $\text{N}_2$  to assign a reaction progress value to each sample (Weymann et al., 2008), where 0 and 1 correspond to zero and complete denitrification, respectively. Reaction progress is calculated as the ratio of denitrification products over reactants:

$$RP = \frac{\text{Excess } N_2 + [N_2O]}{[NO_3^- - N_i]} \quad \text{eq.1}$$

Where excess  $\text{N}_2$  is calculated from dissolved  $\text{N}_2/\text{Ar}$ , as the excess  $\text{N}_2$  in the sample above atmospheric equilibration,  $\text{N}_2\text{O}$  is the dissolved nitrous oxide in the sample and  $\text{NO}_3^- - N_i = \sum [\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+ + \text{excess } \text{N}_2 + \text{N}_2\text{O}]$ .

Reaction progress in the freshwater portion of the STE is less than 0.2, indicating that denitrification is not a nitrogen attenuation pathway, see figure 3. Reaction progress in the upper saline recirculation cell ranges between 0.8-1, indicating complete denitrification of any nitrogen that enters this portion of the STE.



**Figure 4 Stony Brook Harbor transect B Reaction Progress.** Extent of denitrification is calculated using dissolved excess  $\text{N}_2$ ,  $\text{N}_2\text{O}$  and  $\text{NO}_3^-$ . Reaction progress is assigned to each sample where 0 is no denitrification and 1 is complete denitrification. Groundwater entering the system at depths greater than 4m does not denitrify, as evidenced by  $RP < 0.2$  in freshwater samples.

In STEs where groundwater is oxic, influent nitrate concentrations do not undergo microbial reduction but may be diluted during transport, as evidenced by silica and sulfate porewater distributions. Nitrogen attenuation occurs in the shallow saline transition zone, where saltwater derived dissolved organic carbon drives microbial reactions. Due to a combination low DOC and an oxic condition in fresh SGD, this system carries a diluted, not attenuated, nitrate load to receiving coastal waters.

## Acknowledgements

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