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Hydrologic controls on nutrient cycling in an unconfined coastal aquifer

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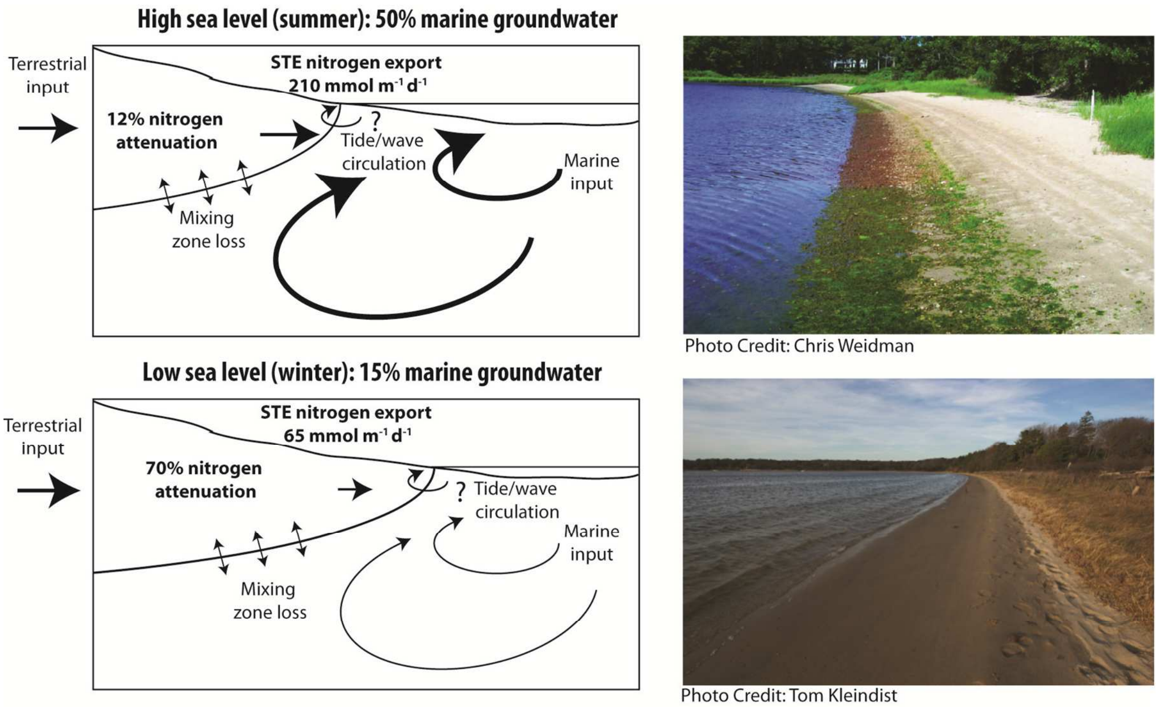
Graphical Abstract:



Abstract Groundwater is an important pathway for terrestrially-derived nutrients to enter the coastal ocean. In coastal aquifers, groundwater transits the subterranean estuary, a region of sharp gradients in redox conditions and the availability of reactants. In one such system (Waquoit Bay, MA, USA), we observed more than a doubling of the groundwater associated nitrogen flux to surface water during the summer compared to winter due primarily to a reduction in nitrogen attenuation within the subterranean estuary. Additionally, marine groundwater intrusion increased during the summer, contributing recycled nutrients from the coastal ocean to the subterranean estuary and back into the bay with return flow. We posit that the longer residence times within the subterranean estuary during the winter, which result from reduced marine intrusion, allow oxygen depletion of the groundwater, creating a favorable environment for important nutrient transformations such as nitrification, denitrification and anammox. The timing of nutrient delivery to the coastal ocean has important implications for coastal marine ecology including the potential development of harmful algal blooms.

Introduction

Despite long-standing recognition of the deleterious impacts of anthropogenic nutrient enhancement on the coastal ocean, transport of nitrogen (N) and phosphorous (P) to the ocean is accelerating.[1] Nitrogen is considered the limiting nutrient in coastal marine systems, although excess phosphorous may also lead to adverse ecological impacts in estuaries.[2] In the coastal zone, approximately half of the reactive nitrogen loading comes from diffuse, non-point sources including atmospheric deposition, surface water run-off and groundwater discharge.[3] Coastal ocean nutrient loading associated with submarine groundwater discharge (SGD) has been implicated in eutrophication and the development of harmful algal blooms.[4-6]

The subterranean estuary (STE) is a region of the coastal aquifer where mixing between discharging terrestrial water and marine intrusion plays host to a range of biogeochemical processes that can modify the groundwater nutrient load.[7, 8] Temporal and spatial variability in STE nutrient cycling is likely due to differences in the oxygen and redox state of the STE, which in turn fluctuate due to differences in aquifer lithology, SGD rates and associated water residence times and whether the nutrient source is primarily terrestrial (new) or marine (recycled). In particular, groundwater residence time of the terrestrial and marine groundwater pools is likely to impact the cycling of reactants, including O_2, inorganic nitrogen (NO_3^-, NO_2^-, NH_4^+) and phosphorous (PO_4^{3-}), which in turn can modulate groundwater derived nutrient fluxes to the coastal ocean.

The ecosystem of Waquoit Bay, a coastal estuary on Cape Cod, MA, USA, has been negatively impacted by nutrient loading associated with SGD.[14, 15] For example, virtually all the eelgrass, and with it its ecosystem service to juvenile fish and shellfish, has disappeared from Waquoit Bay coincident with enhanced water column algal growth following increased nitrogen loading to the watershed.[6, 16] The prevalence of septic systems on Cape Cod has resulted in groundwater nitrogen loads that are elevated compared to aquifers in regions with centralized wastewater treatment.

In this study we evaluate groundwater nitrogen and phosphorous distributions and flow dynamics in an unconfined coastal aquifer to determine how seasonal variability in nutrient cycling within the STE influences nutrient fluxes to the coastal ocean. We evaluate both nutrient delivery and attenuation during transit across the STE. In this analysis, we evaluate the nutrient inventory change along the terrestrial groundwater flow path in different seasons. Nutrient transformations in the mixing zone are evaluated with a traditional estuarine mixing model since the complex circulation of marine groundwater results in numerous potential pathways with a wide range of residence times within the subterranean estuary.[17-19] Groundwater flow dynamics modeled with SEAWAT provide seasonal variability in terrestrial and marine groundwater mixing and discharge rates from the subterranean estuary.

Methods

Field Site. Waquoit Bay is a shallow estuary on the southern shore of Cape Cod, MA (Supplemental Figure 1). In this region, surface geology is dominated by sand and gravel glacial outwash plains formed during the last deglaciation ~14,000 years ago. The upper 10 m of the Cape Cod aquifer consists of fairly homogenous permeable sediments with a grain size of 450-650 microns; a fine sand and silt layer with a lower hydraulic conductivity sits below ~10 m. Within the upper layer, there is a well-defined subterranean estuary with a salinity transition zone that occurs over a narrow region (~1 m thick). This salinity interface moves on seasonal time scales, which results in migration of ion exchange (adsorption/desorption) and redox boundaries.[20, 21] For the purposes of this study, we define "terrestrial groundwater" as groundwater with a salinity less than 1, while the mixing zone encompasses salinity between 1 and "marine groundwater" which has the salinity of the overlying bay (25-28).

Sample Collection and Analysis. Groundwater samples were collected across transects consisting of 6-7 profiles to a depth of ~10 m in the Waquoit Bay subterranean estuary in March 2003 (as reported in Kroeger & Charette[11]), June 2004 and April and June 2005. The April 2005 transect was located 80 m west, in a region where hydraulic gradients are elevated compared to the site of the other transects and the time series well (transect B in Supplemental Figure 1).[22, 23] Groundwater was collected with a push-point piezometer system modified for use within the subterranean estuary.[24] Dissolved oxygen, pH, oxidation reduction potential (ORP) and salinity were measured with a YSI™ sonde. Prior to field sampling, the probes were calibrated using Ricca™ pH, ORP and conductivity standards. Oxygen was calibrated in air according to a method described by YSI. ORP measures the tendency for electron transfer between an inert metal (platinum) electrode and a reference (glass) electrode within the same medium; ORP is a qualitative measure of the groundwater redox conditions since it measures the combined effects of all redox sensitive species in solution. As such, we use it to determine only if the groundwater is reducing (ORP < 0) or oxidizing (ORP > 0). Samples were collected for salinity and nutrients (passed through a 0.45 μm filter for NO_3^-, $NH4^+$, PO_4^{-3}). PO_4^{-3} samples were acidified with 8 μL sulfuric acid per 15 mL upon collection. Nutrient samples were initially stored on ice and frozen within three hours of collection. Salinity was measured with a Guideline AutoSal conductivity meter. Nutrient concentrations were measured on a Lachat Instruments QuickChem 8000 flow injection analyzer using standard colorimetric techniques. Methods for dissolved and sediment oxide-bound phosphorous and manganese were previously reported by Gonneea et al.[25]

Hydrologic Model. We employed a numerical simulation model (USGS SEAWAT code) that was designed to represent conditions within coastal permeable sand aquifers such as at Waquoit Bay.[26] Results from this model have been reported previously and are included here to help interpret both the hydrologic influence on nutrient cycling and to determine nutrient fluxes associated with groundwater discharge.[21] Briefly, this model simulates variable-density flow within a two-dimensional cross-section of an unconfined aquifer below a sloping beach (0.08 m/m) where the domain measures 130 m long and 10 m deep. The upland boundary was set as the groundwater head at a coastal monitoring well (50 m from MSL), while the marine boundary was the average monthly sea level from NOAA's Woods Hole tidal station (data available at http://tidesandcurrents.noaa.gov). This model does not incorporate short-time scale sea level oscillations (i.e. tides or waves) as the region of the subterranean estuary discussed here does not vary on this time scale.[21] Groundwater discharge to the bay and marine water intrusion into the aquifer were calculated across the entire model domain from January 2005 to June 2007. Further details on the model can be found in Mulligan et al.[27] and Gonneea et al.[21].

Results and Discussion

Model-derived Rates of Submarine Groundwater Discharge. During the period from January 2005 to May 2007, terrestrial groundwater fluxes were 3.4 ± 0.46 m^3 m^{-1} day^{-1} and marine groundwater discharge ranged between 0.39 (winter) and 4.7 (summer) m^3 m^{-1} day^{-1}. Here we separate terrestrial and marine groundwater into separate pools, but note that discharge from the subterranean estuary consists of varying mixtures of these two water sources. The terrestrial discharge rates are similar to previous independent estimates from the same location: 1.6-1.8 m^3 m^{-1} day^{-1} (recharge method[28]), 3.5 m^3 m^{-1} day^{-1} (seepage meters[22]) and 4.0 m^3 m^{-1} day^{-1} (Darcy method[23]). Abarca et al.[17] report a much lower terrestrial groundwater discharge of 0.25 m^3 m^{-1} day^{-1} (hydrologic model TRANSDENS) likely due to the much lower hydraulic conductivity used in that model (15 m d^{-1}) compared to other modeling studies at this location (43-54 m d^{-1}).[18, 23, 27] Marine groundwater discharge (and recharge) estimates are more variable with values ranging from 0.6 m^3 m^{-1} day^{-1} (radium isotopes July 2003[23]) to 6.9-15.0 m^3 m^{-1} day^{-1} (seepage meters July 1999 and August 2000[22]). The results of the hydrologic model demonstrate that SGD in Waquoit Bay was seasonally dynamic; in particular the amount of marine intrusion into the aquifer varied seasonally from 10% of total SGD in winter to a summer peak of 70%.

As SGD varies, so does the residence time of groundwater within the subterranean estuary. Since the terrestrial flux lacks significant seasonal variability, we expect minimal change in residence time within this zone. However, marine intrusion and subsequent mixing and discharge varies seasonally by a factor of 10, thus the water residence time of marine groundwater and water within the mixing zone will be ~10 times longer in the winter compared to the summer.

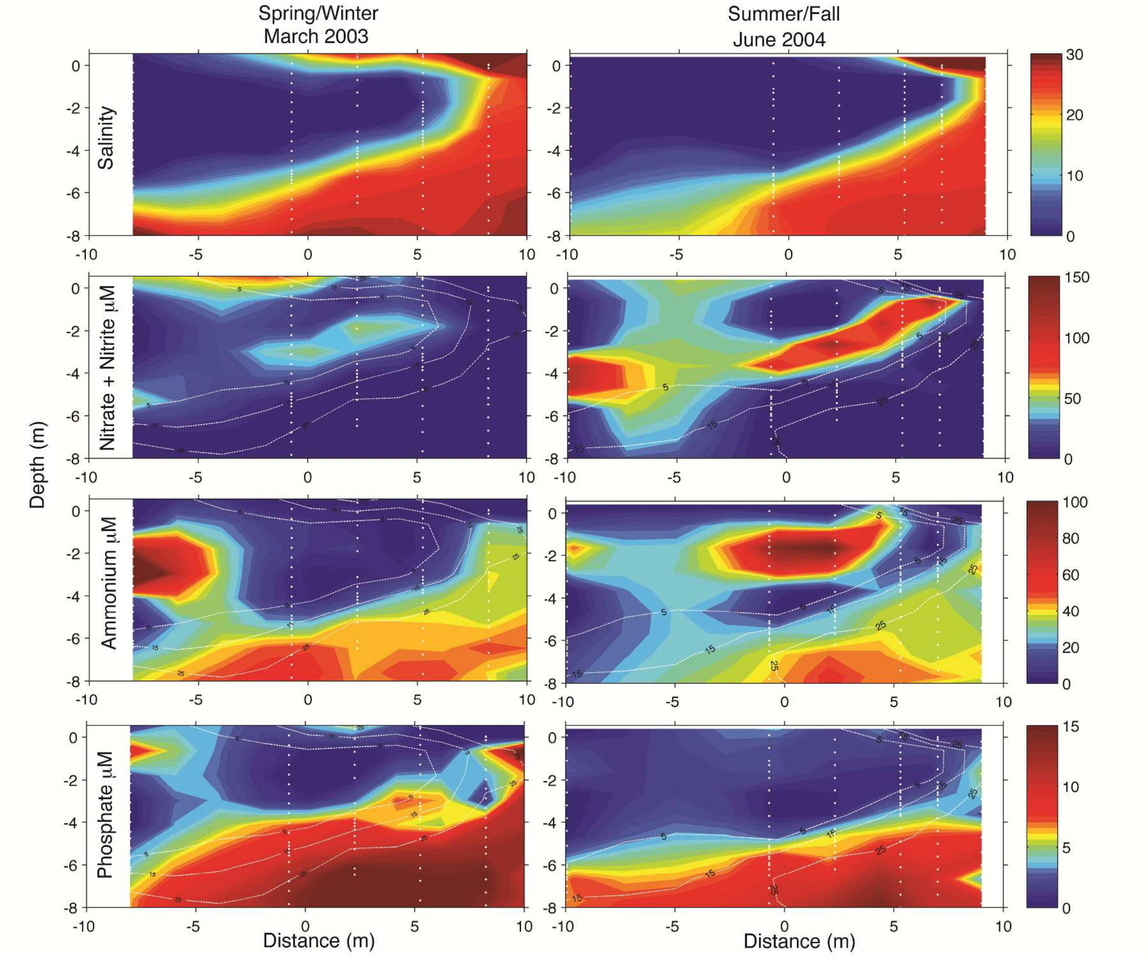


Figure 1: March 2003 and June 2004 salinity, nitrate, ammonium and phosphate concentrations across the Waquoit Bay subterranean estuary. During the summer of 2004, the salinity interface was further offshore and the nitrate plume had higher concentrations than in March 2003. The marine groundwater phosphate enrichment was similar between the two seasons. Horizontal distance is relative to the location of mean sea level.

Nutrient Distributions. Within the Waquoit Bay STE, terrestrial and marine nutrient associations persisted across the four transects (two winter/spring: March 2003 and April 2005, and two summer/fall: June 2004 and 2005). Terrestrial groundwater with high NH_4^+ (100-200 µM) overlies a region of elevated NO_3^- (up to 150 µM); NH_4^+ is the primary nitrogen species carried by marine groundwater (30-50 µM, Figure 1). The mixing zone, which is also a redox boundary, occurs over small spatial scales (~1 meter vertical extent). Previous work at this site reported both complete removal of terrestrially-sourced NO_3^- across the top of the mixing zone and largely conservative behavior of marine NH_4^+ to the top of the mixing zone where dissolved inorganic nitrogen (DIN, the sum of NO_3^- and NH_4^+) concentrations were low (<1 µmol L^{-1}).[11] Additionally, PO_4^{3-} was elevated in marine groundwater above bay water levels (8-12 compared to 1-2 µmol L^{-1} respectively) and in the reduced core of the terrestrial groundwater (up to 8 µmol L^{-1}).

In March 2003 the mixing zone was located further offshore than in June 2004 and 2005, coincident with an increase in the hydraulic gradient.[21] While the April 2005 transect was the only one completed at site "B", it is likely that the STE under the entire 610 m seepage face responds to the same physical forcings (i.e. seasonally variable hydraulic gradient). The terrestrial and marine nutrient plumes migrated landward during the winter/spring season. Also, during March 2003 the NO_3^- concentration was reduced to ~50-70 µM compared to 100-150 µM in June 2004 and 2005, while NH_4^+ was 250 µM. This could be due to the main NO_3^- core migrating further inland outside the sampling domain or to removal of NO_3^- from the plume at this time. Since the mixing zone only migrated inland 3 m, and the transect captured 10 m of the NO_3^- plume, the observed reduction is unlikely to be an artifact of sampling location. The terrestrial DIN plume follows the salinity (and density) contours within the subterranean estuary, terminating at the top of the salinity mixing zone. There is a region of elevated NO_3^- above the main plume at shallow depths (<50 cm) in June 2005 and April 2004. Nutrient transformations that may occur on scales <50 cm in the discharge zone were not a focus of this study and therefore are not captured in the spatial resolution of the samples reported here.

Redox Zones. Dissolved oxygen levels within groundwater were typically <100 μM and commonly reached ~30 μM in the reduced core of the terrestrial groundwater and in the mixing zone, with the exception of April 2005 (higher terrestrial groundwater flow site) when O_2 reached 400 μM in terrestrial groundwater (Supplemental Figure 2). There are regions of elevated O_2 at depth during the other time periods, which do not appear to be related to other variables (i.e. salinity, temperature) and may indicate oxygen contamination during groundwater sampling. pH is low (5-6) in terrestrial groundwater, and rises to 8-8.5 in marine groundwater. The mixing zone has a pH gradient from 6.5 to 7.5 in each transect (Figure 1). Terrestrial groundwater is largely oxidizing, except within the reducing core of the NH_4^+ plume, while marine groundwater is reducing. However, H_2S has never been detected in this system, so sulfate is likely not acting as an electron acceptor.

Nutrient Delivery to the Subterranean Estuary. We explore seasonal variability in nutrient delivery to the STE by coupling the hydrologic model flow results to nutrient inventories from repeat measurements of terrestrial and marine groundwater profiles (locations at -12 and 9 m in Supplemental Figure 1). Nutrient inventories were determined by integrating the DIN and PO_4^{3-} concentration profiles for the furthest onshore and offshore stations. To calculate fluxes, we computed the weighted average by dividing the inventory by the profile depth, and then multiplied this value by the modeled water flux. The terrestrial groundwater DIN inventory as recorded over numerous years and seasons was 290 ± 100 mmol m^{-2} (weighted average, 36 ± 12 mmol m^{-3} (n=9), Supplemental Table 1 and Supplemental Figure 3). The dataset is too limited to discern seasonal patterns, but if they do exist, they are likely not larger than the 35% standard deviation noted in Supplemental Table 1. Phosphate inventories were 8.3 ± 3.5 mmol m^{-2} (weighted average 1 ± 0.4 mmol m^{-3}, Supplemental Table 1 and Supplemental Figure 3).

There were fewer repeat profiles of the marine groundwater, but inventories were similar across three years (DIN: 290 ± 30 mmol m^{-2} and PO_4^{3-}: 64 ± 23 mmol m^{-2}, and a depth weighted average DIN: 37 ± 4 mmol m^{-3} and PO_4^{3-}: 8 ± 3 mmol m^{-3}). The N:P ratio was much higher in the terrestrial groundwater than the marine, typical of terrestrial systems where N fixation and anthropogenic nitrogen inputs may elevate N/P ratios.

We use these end members coupled with the modeled terrestrial and marine groundwater flow to determine total nutrient delivery to the STE during each sampling period. Since the end member is assumed constant, changing groundwater flow drives all variability in fluxes into the STE. Typical terrestrial nitrogen delivery was 109 ± 9 mmol m^{-1} d^{-1} in the summer and 130 ± 14 mmol m^{-1} d^{-1} in the winter, while marine rates were 115 ± 34 and 25 ± 19 mmol m^{-1} d^{-1} in the summer and winter respectively. Terrestrial phosphate fluxes were 3 ± 0.3 (summer) and 4 ± 0.4 (winter) mmol m^{-1} d^{-1}, while marine fluxes were 25 + 8 (summer) and 7 ± 7 (winter) mmol m^{-1} d^{-1}. Additional uncertainty in fluxes calculated this way is at least as great as the interannual variability during each season (terrestrial DIN: 35%, terrestrial PO_4^{3-}: 40%, marine DIN: 10% and marine PO_4^{3-}:

40%), while the uncertainty in water fluxes from the hydrologic model is harder to determine.

Nitrogen Attenuation in Terrestrial Groundwater. The terrestrial nitrogen attenuation in the subterranean estuary is the reduction in the DIN inventory during transit across the STE. The inventory was calculated for profiles that intersect the top of the mixing zone, thereby ensuring the entire terrestrial groundwater plume was captured. Terrestrial DIN removal was 12-13% in June 2004 and 2005, while removal was much greater in March 2003 (71%) and April 2005 (70%) (Figure 2).

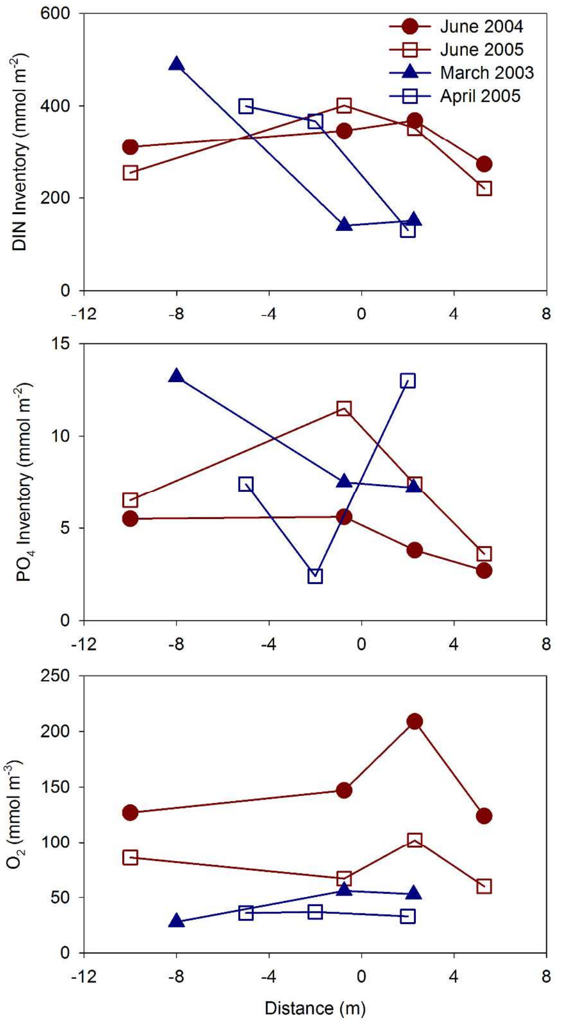


Figure 2: Spring/winter (blue) and summer/fall (red) dissolved inorganic nitrogen and phosphate inventories across the portion of the subterranean estuary dominated by terrestrial groundwater. The bottom panel indicates the average oxygen concentration of the mixing zone, which is a potential site for nutrient transformations including denitrification and nitrification.

Nutrient removal that may occur in the shallow tidally influenced mixing zone is not included in this approach, but may be important. For example, Santos et al.[30] reported production of NO_3^- within a shallow STE dominated by marine groundwater and tidal pumping, while Weinstein et al.[13] found near complete removal of NO_3^- the tidal circulation cell due to rapid denitrification. If removal processes in the discharge zone are important, then the nutrient attenuation rates reported below will underestimate the actual removal. As a result, the subsequent calculated nutrient fluxes into Waquoit Bay reported here would overestimate the actual nutrient load via SGD.

Recycled Marine Nitrogen in the Mixing Zone. In addition to terrestrial nitrogen mixing into the salinity transition zone, the marine NH_4^+ pool may be transformed along its flow path. Typical NH_4^+ concentrations were <1 µM in bay water, but marine groundwater had an elevated NH_4^+ load within the subterranean estuary, presumably due to organic matter degradation and ammonification potentially within organic matter rich sediments of the outer bay (the marine groundwater recharge zone; Supplemental Figure 3). Assuming that marine groundwater enters the STE fully saturated with dissolved oxygen, then initial O_2 concentrations would be in the range of 240 µM during the summer (salinity 28, temperature 20°C) and 330 µM in the winter (salinity 28, temperature 5°C). With observed marine groundwater O_2 concentrations of 30 µM or lower (Supplemental Figure 2), oxygen consumption in the marine groundwater of ~210-300 µM must be the result of O_2 consuming reactions such as organic matter remineralization and oxide/hydroxide formation.[29] Applying Redfield stoichiometric ratios (O_2:C:N:P of 106:106:16:1), this O_2 loss should result in a DIN production of 32 to 45 µM, which is consistent with the DIN concentrations found in the marine groundwater endmember of the STE.

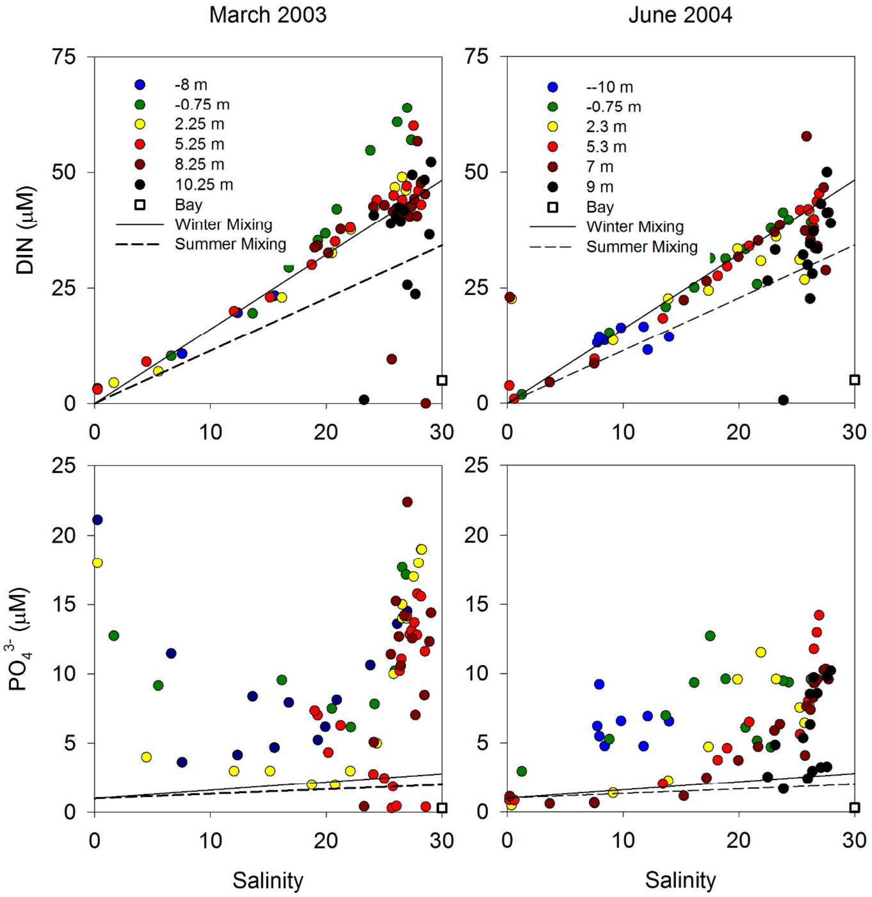


Figure 3: Salinity mixing plots for dissolved inorganic nitrogen and phosphate for March 2003 and June 2004 for groundwater samples collected from the mixing zone (i.e. the base of the terrestrial groundwater plume and below). The mixing lines indicate the expected production of DIN and P during oxic organic matter remineralization due to the observed consumption of oxygen as groundwater transits from bay intrusion to the mixing zone. The two seasons represent different oxygen saturation levels due to seasonal temperature changes of the surface water. Cool colors are located further up the beach from the bay. Note that profiles were collected at different distances along the same shore-perpendicular transect in different years.

The predominance of mixing zone samples for both winter/spring and summer/fall lie along the DIN mixing line using the higher wintertime (45 µM) predicted marine groundwater endmember, indicating no further production or removal of DIN within the STE (Figure 3). However, some marine groundwater samples from June 2004 intersect the predicted DIN concentration for summer-time recharge (32 μM), while some March 2003 samples fall above the predicted DIN concentration. Regardless, seasonally dependent oxygen concentrations in marine groundwater intrusion may play an important role in the delivery of recycled nutrients to the subterranean estuary.

Phosphorous Cycling. Phosphate concentrations in the STE are elevated above values predicted due to organic matter remineralization and there is no clear seasonal trend (Figure 3). The excess PO_4^{3-} is likely due to the accumulation of P associated with iron- and manganese-rich sediments within the Waquoit Bay STE while the variability may be related to the competing influence of pH and salinity on PO_4^{3-} adsorption onto Fe-Mn oxides/ hydroxides.[8, 31-33] In laboratory experiments, 100% of the PO_4^{3-} is sorbed at pH<6, decreasing to 80% sorption at pH 7 and 65% at pH 8.[33] Phosphate sorption to Fe and Mn-oxides/hydroxides occurs as an inner-sphere complex and is enhanced at higher ionic strength.[33] Marine groundwater typically has a pH range of 7 to 8, while terrestrial water ranges from 5-7 within the Waquoit STE. Elevated dissolved PO_4^{3-} was observed where groundwater had a low salinity and pH ~7 (Supplemental Figure 4). Further evidence that PO_4^{3-} sorbed onto Mn-oxides/hydroxides is provided in the sediment oxide associated-PO_4^{3-} (sPO_4^{3-}) profile. Sediment bound PO_4^{3-} (sP) was elevated within the high Mn oxide region (sMn), which is coincident with groundwater of high ionic strength and pH of 7 to 8. This elevated sP was located below the iron oxide/hydroxide peak, which had very low sP. Molar ratios of sP:sMn in this region were 5-20, while throughout the remainder of the profile they were <1. Similarly, molar ratios of sP:sFe were quite high in this region. The dissolved dP:dMn ratio was low coincident with this region of high sorbed sP:sMn ratios, indicating preferential sorption of dissolved PO_4^{3-} onto sediments in contact with low pH, low salinity groundwater. The high sFe region at depth has low sP associated with it.

When all four transects are considered, there appears to be net removal of PO_4^{3-} within the STE; indeed the nitrogen to phosphorous ratio (N:P) of terrestrial inputs (39) was higher than water within the STE near the discharge point (12) (Figure 2). It is evident that P is actively cycling in the STE and while the presence of Fe and Mn oxides/hydroxides may enhance P sorption, the ability of the STE to act as a P sink has additional complexities. Additional P dynamics may occur within the shallow tidally-indiced mixing zone that is not considered in this study.

Nutrient fluxes out of the subterranean estuary Nutrient export from the STE to the bay is the difference between terrestrial and marine nutrient delivery to the STE and subsequent attenuation of these two pools upon transport through the STE; this is calculated as the product of the nutrient inputs (mol m^{-1} d^{-1}) times the fraction removed. In the case of marine-derived nutrients, we assume no attenuation across the mixing zone for nitrogen. Modeled groundwater discharge rates are available only for 2005, coinciding with the April and June 2005 transects. However, the seasonal trends in both groundwater discharge and nutrient attenuation were similar between the two transects within each season such that we can extrapolate the fluxes to March 2003 and June 2004. The total inorganic nitrogen load to the Bay was 65 mmol m^{-1} d^{-1} during the winter/spring, which was 60% terrestrial nitrogen and 210 mmol m^{-1} d^{-1} during the summer/fall (45% terrestrial). For phosphorus, the net winter/spring flux was 9 mmol m^{-1} d^{-1} and 32 mmol

m^{-1} d^{-1} during the summer/fall. The nutrient fluxes calculated in this study are five to seven times lower than reported for a STE with similar groundwater flow rates that was dominated by marine recirculation and marine nutrient sources.[30] Conversely, our nutrient fluxes are an order of magnitude larger than a sandy STE with a well developed denitrification zone that has discharge rates two to four times lower than we report.[13]

Hydrologic control on nutrient biogeochemistry The larger flux nitrogen via SGD in the summer is due to both increased input of recycled nutrients via marine groundwater, as predicted by the hydrologic model, and to low terrestrial nitrogen removal rates within the STE. Gonneea et al.[21] previously hypothesized that nutrient loading to the coastal ocean would be at a minimum during summer, with enhanced nutrient removal due to greater mixing as posited by Kroeger & Charette[11]. The authors based this hypothesis of enhanced nitrogen attenuation resulting from greater mixing on the near total drawdown of DIN at the salinity/redox mixing boundary. In this instance, the amount of nitrogen attenuation would be limited by the delivery rate of reactant pools to the mixing zone. Alternatively, the microbes that mediate removal processes may not be limited by reactant supply (including O_2, NH_4^+ and NO_3^-), but rather reaction kinetics. There are two lines of evidence that reaction kinetics are unlikely to explain the observed difference in nitrogen attenuation. First, the temperature gradient between summer and winter in the subterranean estuary is at most 5-15°C compared to 0-30°C for the bay. Second, we would anticipate reaction rates to slow during winter based on a metabolic response, yet this is when the greatest nitrogen removal occurred. However, little is known about microbial reaction rates within the subterranean estuary and how these populations may respond to moving redox and salinity boundaries.[34]

The seasonal variability shown here reveals additional complexity within STE nutrient cycling. During the winter, the model predicts greatly reduced marine groundwater intrusion, effectively increasing water residence time in this portion of the STE by a factor of 10. We observe lower oxygen concentrations in the mixing zone during the winter/spring (<50 μM) compared to summer/fall (50 - >200 μM) (Figure 2). We infer that NO_3^- removal occurs via denitrification and NH_4^+ removal occurred via nitrification[35], since ammonia oxidizing archaea are present within the mixing zone of the Waquoit Bay STE.[36] While denitrification is most commonly observed in anoxic sediments, this process has also been reported for oxic environments where anoxic microenvironments are thought to develop, typically associated with sediment or suspended particle surfaces and/or biofilms.[37-39] Indeed Gao et al.[37] observed denitrification in sediments with porewater oxygen concentrations up to 90 μM, well above the 30-50 μM we observe in the winter concurrent with the greatest nitrogen attenuation. Nitrification is not sensitive to oxygen levels, since the decrease in reaction rate under oxygen-limited conditions is countered by biomass increase, resulting in minimal net impact on overall nitrification.[35] Since there is no accumulation of NO_3^-, denitrification is likely closely coupled to nitrification.

An alternative mechanism for DIN removal is anaerobic ammonium oxidation (anammox), whereby NH_4^+ is oxidized with NO_2^-, ultimately resulting in the simultaneous loss of both NH_4^+ and NO_3^-. Anammox is thought to be strictly anaerobic and largely limited by the supply of NO_3^-.[40] There is some evidence, however, that anammox may occur in environments with up to 20 μM oxygen.[41] Sáenz et al.[42] found evidence of ammonia-oxidizing bacteria associated with sediments coincident with groundwater redox boundaries within the mixing zone of the Waquoit Bay subterranean estuary. If anammox does occur at the mixing zone boundary, reaction rates must be rapid relative to physical transport when NO_3^- and NH_4^+ do not co-occur within the STE.

Potential mechanisms to lower groundwater oxygen levels to allow denitrification and/or anammox to proceed include increasing organic matter respiration or Mn-Fe hydro/oxide precipitation. We suggest that the reduced residence time of the winter STE enhances oxygen consumption within the mixing zone and creates an environment favorable to nitrogen attenuation via denitrification and/or anammox. This hypothesis predicts that hydrology, via controls on water residence time and delivery of reactants, in part controls biologically mediated nutrient cycling within the subterranean estuary.

The timing of nutrient delivery to the coast has important implications for estuarine ecosystems. At this site, terrestrial (new nutrient) fluxes into the subterranean estuary are greatest in the winter, coincident with peak removal rates, while marine (recycled) nutrient inputs peak during the summer. Total nitrogen fluxes to Waquoit Bay thus peak in the summer, when maximal algal growth is possible due to warm temperatures and long daylight hours. Sea level fluctuations have been implicated for driving movement of the mixing zone and increasing marine groundwater recharge and mixing during the summer. Enhanced seasonal variability in mean sea level has been observed in some locations[43], which we hypothesize may enhance marine groundwater intrusion during summer months, reducing the nitrogen attenuation capacity of the STE and further exacerbating summer eutrophication in the coastal zone. Finally, the close interplay between the physical mixing of the salinity transition zone and the biological response hypothesized here may have important implications for future applications of engineered solutions to coastal groundwater nitrogen such as permeable reactive barriers.

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