Hydrogeologic Controls of Surface Water-Groundwater Nitrogen Dynamics Within a Tidal Freshwater Zone

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Abstract Microbial processing of reactive nitrogen in stream sediments and connected aquifers can remove and transform nitrogen prior to its discharge into coastal waters, decreasing the likelihood of harmful algal blooms and low oxygen levels in estuaries. Canonical wisdom points to the decreased capacity of rivers to retain nitrogen as they flow toward the coast. However, how tidal freshwater zones, which often extend hundreds of kilometers inland, process and remove nitrogen remains unknown. Using geochemical measurements and numerical models, we show that tidal pumping results in the rapid cycling of nitrogen within distinct zones throughout the riparian aquifer. Near the fluctuating water table nitrification dominates, with high nitrate concentrations (>10 mg N/L) and consistent isotopic composition. Beneath this zone, isotopes reveal that nitrate is both denitrified and added over the tidal cycle, maintaining nitrate concentrations >3–4 mg N/L. In most of the riparian aquifer and streambed, nitrate concentrations are <0.5 mg N/L, suggesting denitrification dominates. Model results reveal that oxygen delivery to groundwater from the overlying unsaturated soil fuels mineralization and nitrification, with subsequent denitrification in low-oxygen, high organic matter regions. Depending on flow paths, tidal freshwater zones could be sources of nitrate in regions with permeable sediment and low organic matter content.

Plain Language Summary Human activities related to energy and food production add large amounts of reactive nitrogen to the landscape. Rain and snow wash some of that nitrogen into rivers and eventually to the coast. The addition of excess nitrogen to coastal ecosystems can cause excessive algal growth and low-oxygen conditions, which can lead to fish kills. As nitrogen travels to the coast, microbes in the sediment beneath and near the river process and remove large portions of this nitrogen. It is unclear how daily tidal fluctuations within the freshwater tidal zone alter these processes. Geochemical measurements of pore water beneath the stream and within the stream bank reveal that there are different zones of nitrogen processing, where differences in sediment type and water exchange control the supply of reactants. Zones of nitrate production exist within the stream bank aquifer, but conditions favoring nitrate removal dominate the aquifer. Therefore, depending on how water moves through the subsurface, it is possible that tidal freshwater zones could act as a source of nitrate to the stream channel, exacerbating coastal management challenges.

1. Introduction

Eutrophic conditions in many coastal waterways persist due to the export of excess nutrients; resulting algal blooms have a myriad of consequences on the ecology and economy of these regions (Bricker et al., 1999; Paerl et al., 2011). Given that nitrogen (N) is often a limiting nutrient in coastal waters, it is critical that we understand the fate and transport of N within rivers. Anthropogenic N loading tends to increase downstream in river networks as population density increases and solutes accumulate (Caraco & Cole, 1999; Mulholland et al., 2008), but removal efficiency is thought to generally decrease (Alexander et al., 2000; Mulholland et al., 2008; Seitzinger et al., 2006). Decreased removal and retention of N in larger rivers is expected due to a decline in river-groundwater connectivity and hyporheic storage from headwater streams to coasts (Battin et al., 2008; Wondzell, 2011). This decline in connectivity is thought to reduce the ability of hyporheic storage zones to remove and retain N. However, it remains largely uncertain whether this is true near the river network terminus below head-of-tides, that is, in the tidal freshwater zone (TFZ), where tidal pumping promotes solute exchange across the sediment-water interface, in and out of storage zones.
Few studies have explored hyporheic exchange and N transport in TFZs, but studies in nontidal rivers have demonstrated that stage fluctuations associated with storms (Gu et al., 2012), dam releases (Sawyer et al., 2009), and snowmelt cycles (Loheide & Lundquist, 2009) increase exchange rates and biogeochemical transformations. Given that TFZs have large, semidiurnal or diurnal stage fluctuations year-round and accommodate strong hyporheic mixing (Bianchin et al., 2011), they should serve as regions for enhanced biogeochemical transformations and thus as potential ecosystem control points (Bernhardt et al., 2017). For example, daily tidal inundation of floodplain marsh sediments resulted in the estimated removal of 15% of riverine NO$_3^–$ flux via denitrification (Ensign et al., 2008). Even in supratidal floodplains, groundwater recharge across the banks (bank storage) can promote additional nitrate removal (Gu et al., 2012). However, the same saturation dynamics can also aerate hyporheic zones (Knights et al., 2017) and riparian aquifers (Wallace et al., 2018) reducing denitrification and the N removal potential of TFZs. Thus, it remains unclear if TFZs are net sinks or sources of reactive nitrogen to coastal waters.

Here, we show that the riparian aquifers of tidal rivers are engines for coupled nitrification-denitrification. Tidal pumping extends zones of surface water-groundwater interaction and biogeochemical activity, particularly near the fluctuating water table. We present geochemical observations from a transect at White Clay Creek (Delaware, USA), where nitrate concentrations vary by more than 10 mg N/L, with highest nitrate concentrations in the upper 0.5 m of the aquifer, while nitrate in the streambed and deeper portions of the riparian aquifer was below detection. Temporal trends in nitrate isotopes and concentrations suggest that denitrification occurs throughout much of the aquifer, both within the streambed and the bank. Using box models, we show that nitrification near a fluctuating water table produces these nitrate concentrations, above zones of coupled nitrification-denitrification and denitrification. The characteristics of the sediment and soil within the aquifer in large part control the zonation of dominant nitrogen processes, acting as both the source of organic matter (OM) and a control on water movement.

2. Materials and Methods

2.1. Site Description

Located within the fifth-order TFZ of White Clay Creek (30.701172°, −75.649987°), the study site is within the Christina River Critical Zone Observatory (Delaware, USA). The site is instrumented ~17 river kilometers upstream from Delaware Bay, where it drains 277 km$^2$ of forested, suburban, and agricultural land (Newbold et al., 1997). Channel morphology at the site is similar to other large coastal rivers such as the Fraser River, British Columbia (Bianchin et al., 2011) (deeply incised, the banks rarely inundated) and unlike first-order tidal creeks in coastal marshes (Ensign et al., 2008; Moffett et al., 2012; Wilson & Gardner, 2006). Sandy point bars are common within the channel. The fully fresh site experiences a semidiurnal 0.9-m tide.

Previous hydrostratigraphic work illustrates that the stream sediment and aquifer materials consist of a lower sandy unit with alternating silt and sand layers above (Figure 1; Musial et al., 2016). The various lithological units have similar porosities (0.42 to 0.49) with hydraulic conductivities varying by two orders of magnitude ($1.5 \times 10^{-3}$ m/s in sand to $1.46 \times 10^{-15}$ m/s in silt units; Musial et al., 2016).

2.2. Field Methods

The eastern stream channel and bank were instrumented with a perpendicular transect of wells and sampling ports (Figure 1) in June 2014 (Knights et al., 2017; Musial et al., 2016). Pressure sensors (In-situ Aqua Troll 200 s and Schlumberger Divers) installed in three wells in the bank (E–G, Figure 1), constructed out of polyvinyl chloride and screened throughout the zone of water table fluctuations, and a stilling well in the channel, monitored water levels. During well installation, eight sediment and soil cores (2.54 cm o.d.) were collected (six in the floodplain and two in the river) using an AMS Sand Sludge Sediment Probe (Musial et al., 2016). Sample ports for streambed pore water chemistry (Wells A–C) are located at 10, 25, 50, and 100 cm below the sediment-water interface. The five stream bank locations (Wells D–H) have sample ports at 2.2, 2.5, and 3 m below the land surface (Knights et al., 2017; Musial et al., 2016).

Surface water and pore water chemistry were monitored regularly over one 12-hr tidal cycle in August 2015. On 19 August 2015, pore water samples were collected for anions, cations, dissolved OM, and nitrate isotope ($\delta^{15}$N and $\delta^{18}$O-NO$_3^–$) analyses at approximately 60- to 90-min intervals over one tidal cycle. Samples were collected using a peristaltic pump (<50 ml/min), with one tubing volume discarded before pore water was
filtered (0.45 μm) and stored on ice. Samples for anions, cations, and isotopes were frozen until analyses, samples for dissolved OM analyses were kept cool (4 °C) and analyzed within 2 weeks of sampling. QA/QC was ensured and assessed with duplicates and blanks taken in the field. Dissolved oxygen was measured at low and high tides using a Thermo Orion Star A3229 multiparameter instrument.

2.3. Laboratory Analyses

Anions and cations were measured on a Dionex ICS-5000 IC, with measurement error of ≤0.05 mg/L for Cl\(^{-}\), NO\(_3\)\(^{-}\), and NH\(_4\)\(^{+}\). Dissolved organic carbon (DOC) and total dissolved nitrogen were measured on a Shimadzu TOC-L/TNM-L analyzer, with a measurement error of 0.05 and 0.02 mg/L, respectively. All nitrogen constituents (NO\(_3\)\(^{-}\), NH\(_4\)\(^{+}\), and DON) are reported in mg N/L. QA/QC was ensured and assessed with blanks, replicates, and standards.

For samples with nitrate concentrations great enough (20 nmoles N) for isotopic analyses, δ\(^{15}\)N-NO\(_3\)\(^{-}\) and δ\(^{18}\)O-NO\(_3\)\(^{-}\) were determined using denitrifying bacteria (Pseudomonas aureofaciens) that lack the nitrous oxide (N\(_2\)O) reductase enzyme, reducing NO\(_3\) to N\(_2\)O, which is then measured on a gas chromatograph isotope ratio mass spectrometer (Casciotti et al., 2002; Sigman et al., 2001). Isotope ratios for masses 44, 45, and 46 are obtained and converted to delta notation (δ\(^{15}\)N-NO\(_3\) and δ\(^{18}\)O-NO\(_3\)) using (R\(_{\text{sample}}\)/R\(_{\text{reference}}\) - 1) * 1,000‰ (Casciotti et al., 2002; Sigman et al., 2001), where R\(_{\text{reference}}\) is atmospheric N\(_2\) gas (δ\(^{15}\)N) and Vienna Standard Mean Ocean Water (δ\(^{18}\)O). All analyses include corrections based upon NO\(_3\)\(^{-}\) (USGS-34, USGS-35, and IAEA-N3) reference materials (Kaiser et al., 2007). Typical reproducibility for δ\(^{15}\)N, δ\(^{18}\)O is ±0.2‰ and ±0.5‰, respectively, and quantified by repeated runs of samples and standards.

Sediment cores taken at the time of infrastructure installation (Musial et al., 2016) were sectioned into 2-cm sections, dried in an oven for 24 hr at 50–60 °C, and then ground with a mortar and pestle. All samples were fumigated with concentrated HCl for 12 hr, allowed to vent, and subsequently redried in an oven to remove inorganic C contents. For samples where grain size was also determined, half of the core was reserved for chemical analyses. Ground sediment was analyzed for C and N contents on a ThermoQuest NC2100 elemental analyzer, with a subset of three cores analyzed at Stroud Water Research Center on a Costech Elemental Analyzer. Across both instruments, standard reference material and duplicate sample analysis indicate good precision, with an average coefficient of variation of 0.03% for C and N measurements.
Equation No. | Equation
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(2) | \[
\frac{\partial O_2}{\partial t} = \alpha_{\text{in}, U} \left( O_2 \, \text{Sat} - O_2 \, (U) \right) - \beta_{\text{in}, O_2} V_{\text{in}} X \left( \frac{\text{DOC}_{(U)}}{K_{\text{DOC}} + \text{DOC}_{(U)}} \right) \left( \frac{O_2 \, (U)}{K_{O_2} + O_2 \, (U)} \right) - \beta_{\text{in}, O_2} V_{\text{in}} X \left( \frac{\text{NH}_4 \, (U)}{K_{\text{NO}_3} + \text{NH}_4 \, (U)} \right) \left( \frac{O_2 \, (U)}{K_{O_2} + O_2 \, (U)} \right) - \alpha_{U} \left( O_2 \, (U) - O_2 \, (L) \right)
\]
(3) | \[
\frac{\partial O_2}{\partial t} = -\beta_{\text{in}, O_2} V_{\text{in}} X \left( \frac{\text{DOC}_{(U)}}{K_{\text{DOC}} + \text{DOC}_{(U)}} \right) \left( \frac{O_2 \, (U)}{K_{O_2} + O_2 \, (U)} \right) - \beta_{\text{in}, O_2} V_{\text{in}} X \left( \frac{\text{NH}_4 \, (U)}{K_{\text{NO}_3} + \text{NH}_4 \, (U)} \right) \left( \frac{O_2 \, (U)}{K_{O_2} + O_2 \, (U)} \right) + \alpha_{U} \left( O_2 \, (U) - O_2 \, (L) \right)
\]
(4) | \[
\frac{\partial \text{NO}_3 \, (L)}{\partial t} = \beta_{\text{in}, \text{NO}_3} V_{\text{in}} X \left( \frac{\text{NH}_4 \, (U)}{K_{\text{NH}_4} + \text{NH}_4 \, (U)} \right) \left( \frac{O_2 \, (U)}{K_{O_2} + O_2 \, (U)} \right) - \beta_{\text{den}, \text{NO}_3} V_{\text{den}} X \left( \frac{\text{DOC}_{(U)}}{K_{\text{DOC}} + \text{DOC}_{(U)}} \right) \left( \frac{\text{NO}_3 \, (U)}{K_{\text{NO}_3} + \text{NO}_3 \, (U)} \right) + \alpha_{U} \left( \text{NO}_3 \, (U) - \text{NO}_3 \, (L) \right)
\]
(5) | \[
\frac{\partial \text{NH}_4 \, (U)}{\partial t} = -\beta_{\text{in}, \text{NH}_4} V_{\text{in}} X \left( \frac{\text{NH}_4 \, (U)}{K_{\text{NH}_4} + \text{NH}_4 \, (U)} \right) \left( \frac{O_2 \, (U)}{K_{O_2} + O_2 \, (U)} \right) - \beta_{\text{in}, \text{NH}_4} V_{\text{in}} X \left( \frac{\text{DOC}_{(U)}}{K_{\text{DOC}} + \text{DOC}_{(U)}} \right) \left( \frac{\text{NH}_4 \, (U)}{K_{\text{NH}_4} + \text{NH}_4 \, (U)} \right) \left( \frac{O_2 \, (U)}{K_{O_2} + O_2 \, (U)} \right) + \beta_{\text{den}, \text{NH}_4} V_{\text{den}} X \left( \frac{\text{DOC}_{(U)}}{K_{\text{DOC}} + \text{DOC}_{(U)}} \right) \left( \frac{\text{NO}_3 \, (L)}{K_{\text{NO}_3} + \text{NO}_3 \, (L)} \right) - \alpha_{U} \left( \text{NH}_4 \, (U) - \text{NH}_4 \, (L) \right)
\]
(6) | \[
\frac{\partial \text{DOC}_{(U)}}{\partial t} = \beta_{\text{in}, \text{DOC}} V_{\text{in}} X \left( \frac{\text{DOC}_{(U)}}{K_{\text{DOC}} \text{DOC}_{(U)}} \right) \left( \frac{O_2 \, (U)}{K_{O_2} + O_2 \, (U)} \right) - \beta_{\text{DOC}} V_{\text{DOC}} X \left( \frac{\text{DOC}_{(U)}}{K_{\text{DOC}} \text{DOC}_{(U)}} \right) \left( \frac{O_2 \, (U)}{K_{O_2} + O_2 \, (U)} \right) - \alpha_{U} \left( \text{DOC}_{(U)} - \text{DOC}_{(L)} \right)
\]

Note. Equations (2) and (3) track the changes in O2 concentrations in the upper and lower box, respectively. Equations (4)–(6) are for the upper box and parallel equations for changes in NO3 (4), NH4 (5), and DOC (6) exist for the lower box. DOC = dissolved organic carbon.

### 2.4. Numerical Modeling

A transient “box model” simulated the evolution of O2, NH4+, NO3-, and DOC concentrations in saturated aquifer materials adjacent to a tidal river (Figure 1). The goal of these reduced-complexity models was to understand conditions that promote the accumulation of excess nitrate near the water table and depletion at depth in a tidal riparian aquifer. Here, we define “accumulation” as concentrations greater than those observed in surface water or groundwater far from the stream. We define “depletion” as concentrations less than those observed in surface water or groundwater far from the stream.

Box models have been widely used to represent complex natural systems ranging from carbon in the ocean-atmosphere system (Cui & Kump, 2015 and references therein) to the geochemical evolution of groundwater along flow paths in floodplains (Frei et al., 2012). Their reduced complexity allows rapid analysis of a wide range of controlling parameters, facilitating first-order insights into any multidimensional problem that can be simplified as a system of connected reservoirs. Though more complex, spatially explicit transient fluid flow and reactive transport simulations (i.e., Dwivedi et al., 2018; Shuai et al., 2017; Wallace, 2019) are better suited to replicate the full spatial structure of nitrogen transport and reactions in riparian aquifers, these models require longer run times and greater parameterization and therefore limit analysis of the conditions under which excess nitrate accumulates and is removed in tidal aquifers.

Here, we idealize saturated groundwater in the riparian aquifer as a vertically stratified system of shallow and deeper groundwater that predominantly flows in the lateral direction toward the channel (Figure 1). The upper reservoir, denoted with subscript (U), represents saturated sediments immediately beneath the fluctuating water table. Vertical oxygen exchange occurs across the water table between the vadose zone and upper reservoir. The lower reservoir, denoted with subscript (L), is disconnected from the vadose zone but experiences vertical solute mixing with the upper reservoir. Aerobic respiration, nitrification, denitrification, and ammonium uptake follow Monod kinetics (Tables 1 and 2). DOC is supplied from OM in sediments according to fast equilibrium sorption kinetics (e.g., Gu et al., 2007; Jardine et al., 1989) given the multiple lines of evidence illustrating sediment sources of DOC within riparian aquifers (Hill et al., 2004; Kolbjørn Jensen et al., 2017; Robertson & Cherry, 1995).

We represent vertical solute transfer as a Fickian process. Within the saturated aquifer, vertical mixing between the upper and lower reservoirs equals the concentration difference multiplied by a first-order rate constant, \( \alpha_{U,L} \).
verse dispersion, lower reservoir is primarily horizontal toward the river and vertical solute mixing is primarily due to transverse dispersion. Thus, we assumed the first-order transfer coefficient, \( \alpha_{fl} \), is transverse dispersivity and \( v \) is seepage velocity. Here, we assume \( \alpha_{fl} \) is \( \sim 0.05 \text{ m} \) to represent the effects of mechanical dispersion at scales ranging from small floodplain layers to macropores. If average groundwater flow in the saturated lower reservoir primarily horizontal toward the river and vertical solute mixing is primarily due to transverse dispersion, \( D \) equals \( \alpha_{fl} v \), where \( \alpha_{fl} \) is transverse dispersivity and \( v \) is seepage velocity. Here, we assume \( \alpha_{fl} \) is \( -0.05 \text{ m} \) to represent the effects of mechanical dispersion at scales ranging from small floodplain layers to macropores. The average measured seepage velocity toward the river is \( 5 \text{ m/day} \) (Musial et al., 2016).

If average groundwater flow in the saturated lower reservoir is primarily horizontal toward the river and vertical solute mixing is primarily due to transverse dispersion, \( D \) equals \( \alpha_{fl} v \), where \( \alpha_{fl} \) is transverse dispersivity and \( v \) is seepage velocity. Here, we assume \( \alpha_{fl} \) is \( -0.05 \text{ m} \) to represent the effects of mechanical dispersion at scales ranging from small floodplain layers to macropores. The average measured seepage velocity toward the river is \( 5 \text{ m/day} \) (Musial et al., 2016). Thus, \( \alpha_{fl} \) is \( \sim 10^{-2} \text{ hr}^{-1} \) at our field site (Table 3). It is important to note that additional transport processes such as oscillatory, small-scale advection and associated mixing are not necessarily excluded from the vertical solute transfer term in equation (1), as they can be represented through an enhanced dispersion coefficient (e.g., Cirpka & Attinger, 2003; Dentz & Carrera, 2005). By testing a range of vertical solute transfer coefficients (Table 3), we essentially relax the assumption that traditional, transverse mechanical dispersion dominates vertical solute mixing.

We represent transport of dissolved oxygen (DO) across the water table between the external vadose zone (where oxygen is assumed to be saturated) and the upper reservoir using a similar first-order transfer coefficient, \( \alpha_{ext,U} \). If the primary vertical transport process near the water table is transverse dispersion along primarily horizontal groundwater flow paths or enhanced dispersion associated with oscillatory flow, \( \alpha_{ext,U} \) and \( \alpha_{fl} \) are likely similar in magnitude. However, \( \alpha_{ext,U} \) may be greater due to additional processes such as imbibition or groundwater recharge (Sinko et al., 1998; Williams & Oostrom, 2000). Haberer et al. (2012) showed that transverse dispersion can account for much of the vertical oxygen transfer near a fluctuating water table when a significant component of horizontal flow is present. We therefore explore values of \( \alpha_{ext,U} \) ranging from a lower limit of 1 up to 100.

Given the wide range of both solute transport and kinetic rates observed across field and laboratory studies, we ran Monte Carlo experiments in which we randomly varied the following parameters: solute transfer coefficients \( \alpha_{ext,U} \) and \( \alpha_{fl} \), maximum specific uptake rates for aerobic respiration, nitrification, and denitrification, C:N ratio, and OM content (Table 3). All equations for both reservoirs were solved in Matlab using an explicit Runge-Kutta solver. The initial concentrations, based on our observations, were chosen to represent oxic groundwater with \( 8 \text{ mg/L dissolved O}_2 \), \( 2 \text{ mg/L NO}_3^- \), \( 0.05 \text{ mg/L NH}_4^+ \), and \( 2 \text{ mg/L DOC} \). The 10,000 simulations were run until they reached steady state (less than 8,000 hr) or demonstrated an unbounded increase in \( \text{NO}_3^- \) concentration.

### 3. Results

#### 3.1. Geochemistry

Pore water sampling over the 12-hr tidal cycle revealed temporal variability in \( \text{Cl}^- \) concentrations in the streambed, while in the stream bank there was greater variation in \( \text{Cl}^- \) in space rather than time.

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**Table 2**

**General Stoichiometry of Microbially Mediated Reactions Represented in Box Model**

| Reaction processes | Chemical equations |
|--------------------|--------------------|
| Aerobic respiration | \( [(\text{CH}_2\text{O})_4(\text{NH}_3)_2] + Y\text{O}_2 \rightarrow 2\text{NH}_4^+ + 3\text{CO}_2 + Y\text{H}_2\text{O} \) |
| Denitrification    | \( [(\text{CH}_2\text{O})_4(\text{NH}_3)_2] + 0.8Y\text{NO}_3^- \rightarrow 2\text{NH}_4^+ + 0.4N_2 + (0.2Y - 2)\text{CO}_2 + (0.8Y + 2)\text{HCO}_3^- + (0.6Y - 2)\text{H}_2\text{O} \) |
| Nitrification     | \( \text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{CO}_2 + \text{H}_2\text{O} \) |
| Microbial \( \text{NH}_4^+ \) uptake\(^a\) | \( [(\text{CH}_2\text{O})_4(\text{NH}_3)_2] + \text{HCO}_3^- + \text{NH}_4^+ \rightarrow \text{C}_5\text{H}_7\text{NO}_2 + 4\text{H}_2\text{O} + \text{CO}_2 \) |

Note. Adapted from Stumm and Morgan (1996) and Hedin et al. (1998).

\(^a\)Cell synthesis (as \( \text{C}_5\text{H}_7\text{NO}_2 \)) with \( \text{NH}_4^+ \) as the \( \text{N} \) source.

\[ \alpha_{U,L} = -\frac{D A}{\Delta z V} \]  
(1)


| Parameter | Parameter description | Value | Source |
|-----------|-----------------------|-------|--------|
| $K_d$     | Distribution coefficient for DOC | 0.005 L/mg | Zarnetske et al. (2012) and Knights et al. (2017) |
| $K_{DOC}$ | Half-saturation constant for DOC | 3.7 mg/L | Zarnetske et al. (2012) |
| $k_I$     | Half-saturation constant for oxygen inhibition | 0.2 mg/L | Zarnetske et al. (2012) |
| $K_{NO3}$ | Half-saturation constant for NO$_3^-$ | 3.1 mg/L | Zarnetske et al. (2012) |
| $K_{NH4}$ | Half-saturation constant for NH$_4^+$ | 0.1 mg/L | Zarnetske et al. (2012) |
| $K_O2$    | Half-saturation constant for DO | 0.2 mg/L | Zarnetske et al. (2012) |
| $n$       | Porosity | 0.4 | Musial et al. (2016) |

| OM(U)     | Sediment organic matter upper reservoir | 0.1–1% | this study |
| OM(L)     | Sediment organic matter lower reservoir | 1–5% | this study |
| $O_2$(sat) | Dissolved oxygen concentration in vadose zone | 9.7 mg/L | Zarnetske et al. (2012) |
| $V_{ar}$  | Maximum specific aerobic respiration rate | 2–10 hr$^{-1}$ | Zarnetske et al. (2012) |
| $V_{nit}$ | Maximum specific nitrification reaction rate | 1–4 hr$^{-1}$ | Zarnetske et al. (2012) |
| $V_{den}$ | Maximum specific denitrification reaction rate | 0.2–2 hr$^{-1}$ | Zarnetske et al. (2012) |
| $V_{up}$  | Maximum specific ammonium uptake rate | 1.5 $V_{nit}$ | Zarnetske et al. (2012) |
| $X$       | Microbial biomass | 0.142 mg/L | Gu et al. (2007) |
| $z/y$     | C:N ratio in organic matter | 10:1–25:1 | this study |
| $α_{DOC}$ | Mass transfer coefficient for DOC | $10^{-3}$–$10^{-4}$ hr$^{-1}$ | Zarnetske et al. (2012) |
| $α_{ext,U}$ | External oxygen transfer rate | $(10^5$–$10^7)$x$α_{UL}$ | Equation (1) |
| $α_{UL}$  | Solute transfer rate | $10^{-3}$–$10^{-4}$ hr$^{-1}$ | this study |
| $β_{NO3}$ | Stoichiometric coefficient for aerobic respiration (O$_2$) | 32/2 | Table S3 |
| $β_{NH4}$ | Stoichiometric coefficient for nitrification (O$_2$) | 16/7 | Table S3 |
| $β_{NH4N}$ | Stoichiometric coefficient for nitrification (NO$_3^-$) | 1 | Table S3 |
| $β_{NH4N}$ | Stoichiometric coefficient for denitrification (NO$_3^-$) | 14/15 | Table S3 |
| $β_{NH4}$ | Stoichiometric coefficient for nitrification (NH$_4^+$) | 1 | Table S3 |
| $β_{NH4}$ | Stoichiometric coefficient for uptake (NH$_4^+$) | 1 | Table S3 |
| $β_{NO3}$ | Stoichiometric coefficient for aerobic respiration (NH$_4^+$) | 14/12y | Table S3 |
| $β_{NO3}$ | Stoichiometric coefficient for denitrification (NH$_4^+$) | 14/12y | Table S3 |
| $β_{arDOC}$ | Stoichiometric coefficient for aerobic respiration (DOC) | 1 | Table S3 |
| $β_{denDOC}$ | Stoichiometric coefficient for denitrification (DOC) | 1 | Table S3 |
| $β_{b}$   | Bulk density | 1.96 kg/L | Musial et al. (2016) |

Note. Sensitivity parameters are in bold. DOC = dissolved organic carbon; OM = organic matter.

(Figure 2 and Table S1 in the supporting information.) Generally, Cl$^-$ concentrations were highest in the stream (~60 mg/L) and upper streamed ports and lowest in the riparian aquifer farthest from the channel (~10 mg/L). These are assumed to represent end-member waters that mix within the riparian aquifer and hyporheic zone. Cl$^-$ concentrations varied more over the tidal cycle in the streamed than stream bank. For example, in the upper port (10 cm) of Well A, Cl$^-$ varies 25 mg/L while at ports in Well G, Cl$^-$ varies by less than 1 mg/L over the same period (Figure 2 and Table S1). Nitrate concentrations varied from below detection levels in streambed sediments and the deeper portions of the aquifer to greater than 10 mg/L near the fluctuating water table (Figure 2 and Table S1). In most streamed and bank well locations, NO$_3^-$ varied by less than 1 mg N/L over the tidal cycle; however, within the upper 0.5-m portion of the aquifer (sampled by Wells D, E, F, and G) NO$_3^-$ concentrations varied by up to 8 mg N/L over the 12-hr cycle. DOC concentrations were also dynamic and varied from 0.5 mg/L to greater than 10 mg/L, with the majority of measurements ranging from 1–5 mg/L and varying by 1–2 mg C/L over the tidal cycle at most ports (Table S1). The NO$_3^-$ concentrations of the assumed end-members of the system differed and varied little over the tidal cycle; the average NO$_3^-$ concentration in stream water was 3.4 mg N/L, while distant groundwater averaged 0.01 mg N/L. Ammonium concentrations were low, below detection, or less than 0.1 mg N/L at the majority of well ports throughout the tidal cycle. The remainder of ports were less than 0.5 mg N/L and varied by less than 10% over 12 hr, with the exception of Well G at 3 m (2.3 ± 0.1 mg N/L; Table S1).

Pore water DO concentrations responded to tidal fluctuations, increasing with the rise in tide in shallow streamed and upper streambank ports. Oxygen concentrations were consistent within the streamed (~0.5 mg/L) with the exception of the portions exposed to the atmosphere at low tide (i.e., upper ports at Well C; Table S1). In the stream bank, DO concentrations are greatest at the fluctuating groundwater.
surface (~2–5 mg/L), while the remainder of the ports display hypoxic conditions (<0.5 mg/L). The shallowest ports in the stream bank aquifer had the greatest variability in DO over the tidal cycle (Table S1). Examining the Cl\(^-\) concentrations at each well port over the tidal cycle relative to two end-members (stream water and relatively distant groundwater) provides a way to assess the contribution of mixing source waters versus the processing of reactive elements within the pore space. Locations with consistently high Cl\(^-\) indicate a consistent source of stream water, locations with consistently low Cl\(^-\) indicate a consistent source of groundwater, and locations with fluctuating Cl\(^-\) indicate dynamic sources (Figure 2). Significant, dynamic mixing occurs in all ports within the streambed (e.g., Location B in Figure 2; Wells A and C in Table S1). Within the stream bank, the contribution of stream water decreases with distance from stream, and the amount of dynamic mixing also decreases (i.e., there is a decline in the average Cl\(^-\) concentration as well as the magnitude of fluctuations, Figure 2). It is important to note that this is a conservative estimate of mixing. There is likely an additional water source with an unknown, but likely low, Cl\(^-\) concentration (e.g., infiltrating precipitation) to the riparian system.

By comparing reactive solute concentrations (i.e., NO\(_3^+\), NH\(_4^+\), and DOC) with conservative solutes (i.e., Cl\(^-\)) over the tidal cycle, estimates of net production or consumption at each time point are determined (Figure 3). Stream wells (A–C) generally show net consumption of NO\(_3^-\) and net production of DOC. Within the stream bank the patterns are variable in the well closest to the stream (e.g., Well D), with NO\(_3^-\) removal dominating in the upper ports and NO\(_3^-\) production occurring in the lower port. When compared to the conservative solute, NO\(_3^-\) concentrations indicate net production through the top ~1 m of aquifer sampled at Wells D-F and the upper 20–50 cm of aquifer at Wells G and H (Figure 3). There is net

![Figure 2](image-url)
production of DOC in Wells E–G but net removal of DOC in most of the ports at the nearest (~5 m) and furthest (~30 m) Wells D and H, respectively (Figure 3).

The isotopic composition of NO$_3^-$ ($\delta^{15}N$ and $\delta^{18}O$) provides insight as to the source and processing of NO$_3^-$ within a system (Kendall et al., 2007). Nitrate isotopes within the riparian aquifer pore water vary both spatially and temporally with a relatively enriched signal throughout the aquifer; $\delta^{15}N$-NO$_3^-$ ranges from 12‰ to 28‰ and $\delta^{18}O$-NO$_3^-$ from 5.5‰ to 14‰ (Table S1). The majority of ports exhibit ~1–2‰ variation over the 12-hr sampling period. However, in some instances, values change by 3–5‰ (Figure 4 and Table S1). There is limited isotopic data for the ports in the streambed due to low and nondetectable NO$_3^-$ concentrations.

To determine the likely biogeochemical processes underlying observed patterns, NO$_3^-$ isotopes are often compared to NO$_3^-$ concentrations (Kendall, 1998; Figure 4). For example, an inverse relationship between $\delta^{15}N$ and NO$_3^-$ is often indicative of denitrification, while a positive relationship suggests a mixing of sources. The concomitant shifts in $\delta^{15}N$- and $\delta^{18}O$-NO$_3^-$ also provide insights as to the combination of N processes affecting the NO$_3^-$ pool (Granger & Wankel, 2016). Examining these patterns (Figure 4) reveals three distinct regions of the bed and banks (Figure 1). The first region includes the shallowest stream bank port at locations E–G. These ports exhibit high NO$_3^-$ concentrations (>8 mg/L) and relatively stable NO$_3^-$ isotopic signals. The isotopic signals vary by less than 1‰ over the 12-hr tidal cycle (e.g., Well E at 2.5 m and Well G at 2.2 m; Figure 4), suggesting a source of NO$_3^-$ to the system. Beneath this shallow groundwater, a second region exhibits high NO$_3^-$ concentrations and a dynamic, inverse relationship between NO$_3^-$ concentrations and isotopes. For example, at 3 m in Well E, NO$_3^-$ concentrations changed by more than 3 mg N/L, with decreased concentrations corresponding to 4.9‰ and 4.2‰ increases in the $\delta^{15}N$- and $\delta^{18}O$-NO$_3^-$,
respectively (Figure 4 and Table S1); a pattern characteristic of denitrification (Mariotti et al., 1981). The slope of the relationship between $\delta^{15}$N and $\delta^{18}$O is indicative of the net processing of NO$_3^-$ within pore water. Specifically, when $\Delta \delta^{18}$O-$\Delta \delta^{15}$N deviates from the canonical denitrification slope of 1, it is due to concurrent NO$_3^-$ production via nitrification (slopes <1) or annamox (slopes >1; Granger & Wankel, 2016). Bank wells E-G are shown above, with the sampling depth indicated by shade. Darker shades correspond to greater depths. The range of stream/water table fluctuation (meters) is shown in parentheses next to each well name.

![Figure 4](image)

Figure 4. The relationships between nitrate concentration and isotopic composition (top row) and $\delta^{15}$N and $\delta^{18}$O (bottom row) provide diagnostic information (Kendall et al., 2007). Specifically, nitrate removal via denitrification results in the enrichment of both the $^{15}$N and $^{18}$O isotopes in the remaining pool and an inverse relationship between $\delta^{15}$N and NO$_3^-$ concentrations (i.e., patterns illustrated in both Well E at 3 m and Well G at 2.5 m). Bank wells E-G are shown above, with the sampling depth indicated by shade. Darker shades correspond to greater depths. The range of stream/water table fluctuation (meters) is shown in parentheses next to each well name.

3.2. Numerical Models

A shallow saturated zone that maintains greater oxygen concentrations than the deeper, more isolated zone characterizes all simulations, reflecting field observations. Oxygen exchange across the water table maintains this gradient (Figure 1). In the majority (75.5%) of all simulations, NO$_3^-$ concentration decreases in both zones (Figure S2), unlike field observations that show a shallow region of NO$_3^-$ accumulation. A small but significant number of simulations (19.9%) show high NO$_3^-$ concentrations in the shallow, more oxygenated reservoir, similar to observations (Figure S3). Equilibrium NO$_3^-$ concentrations range up to 21 mg/L, but most (88.2%) are below 4 mg/L (Figure S5). Denitrification removes nitrate that is transferred to the lower more isolated, less oxygenated reservoir, balancing out NO$_3^-$ production near the water table (note that this balance of nitrification and denitrification is a requirement in the 95.4% of simulations that reach steady state). In 4.6% of simulations, NO$_3^-$ production near the water table exceeds removal in the isolated reservoir, and NO$_3^-$ concentrations do not reach equilibrium (Figures S4 and S5).
In order for NO$_3^-$ to accumulate near the water table, fast N mineralization must occur in the presence of oxygen. These conditions tend to be met in simulations with relatively high maximum specific aerobic respiration rate ($V_{ar}$), low C:N ratio in OM (z:y), and high oxygen transfer rate across the water table ($\alpha_{ext, U}$; Figure 6 and Table S4). Simulations with large NO$_3^-$ accumulation also tend to have relatively large maximum specific nitrification rates ($V_{nit}$) and small maximum specific denitrification rates ($V_{den}$), but the inclusion of these parameters does not significantly alter the trend in Figure 6. It is worth noting that the traditional Damköhler number, which represents the balance between reaction and transport rates, is not a good predictor of equilibrium NO$_3^-$ concentrations near the water table, at least in its simplest form ($V_{nit}/\alpha_{ext, U, L}$), though it has been used in other modeling studies to describe general reactive nitrogen transport behavior (e.g., Marzadri et al., 2012; Newcomer et al., 2018; Zarnetske et al., 2012). In this box model framework, the Damköhler number most aptly describes the efficiency with which ammonium and oxygen are converted to NO$_3^-$ within the upper reservoir before export to the lower reservoir, rather than the equilibrium NO$_3^-$ concentration. In summary, NO$_3^-$ is most likely to accumulate where the potential oxygen supply rate ($\alpha_{ext, U}$) and potential N mineralization rate (z:y $V_{ar}$) are large (Figure 6), a result that may not have been evident from a select number of multidimensional, transient flow and reactive transport simulations.

Stable coupling of NO$_3^-$ production and removal requires solute exchange between relatively connected, oxygenated, and isolated, anoxic zones. As NO$_3^-$ accumulates near the water table, the concentration gradient between connected and isolated reservoirs increases, and the rate of NO$_3^-$ transfer to the isolated reservoir balances the production rate. Denitrification in the isolated reservoir maintains the concentration gradient. However, if the maximum specific denitrification rate is very low, NO$_3^-$ accumulates (Figure S3). Alternatively, if solute transfer between the reservoirs is very efficient, both reservoirs become

![Figure 5. Equilibrium concentrations of oxygen (a, b) and nitrate (c, d) in upper and lower reservoirs. Total number of simulations that reached steady state = 9543.](image)
nitrification-denitrification. Though we modeled these in a simplistic, vertically stratified way at the meter-scale based on our macroscopic observations, these dynamics likely exist at the pore scale too (Harvey, 1993). Nitrification likely dominates in macropores that intersect the water table, while denitrification dominates in adjacent, immobile pores (Briggs et al., 2015; Harvey et al., 2013). The same system of equations (Table 1) can represent N cycling at this smaller scale, but the solute transfer coefficient between reservoirs requires reevaluation. Given a pore-scale transverse dispersivity of approximately 500 $\mu$m and reservoir dimensions of $1 \text{ mm}^3$, the solute transfer coefficient would be about $10^{-5} \text{ hr}^{-1}$ instead of $10^{-2} \text{ hr}^{-1}$, at the upper limit of the range we tested in the Monte Carlo experiments (Table 3). Thus, many of our simulations are representative of coupled nitrification-denitrification at both macroscopic and pore scales, illustrating the power of simple but easily generalized box models. Models and observations suggest nitrate removal occurs in relatively organic-rich zones, where the combination of microbial processing and reduced exchange with surrounding regions are likely to deplete pore spaces of oxygen, promoting denitrification, similar to other studies (Arango et al., 2007; Briggs et al., 2015; Hill & Cardaci, 2004; Sawyer, 2015). Numerical simulations suggest that most tidally influenced riparian aquifers are more likely to be depleted in nitrate rather than enriched (Figure 5). In addition, observations of low to nondetect nitrate levels throughout much of the hyporheic and bank aquifers (Table S1), suggest that the nitrification occurring at the water table, likely does not contribute significant nitrate to riverine export. However, in instances which allow for fast oxygen transfer across the water table and fast mineralization of OM with low C:N (Figure 6), elevated nitrate can persist. This suggests that in regions where aquifer materials are porous, with N-rich OM, tidal fluctuations could stimulate nitrification, resulting in elevated nitrate concentrations, which could ultimately be transferred to coastal rivers and on to oceans.

5. Conclusions

Tidal freshwater zones often extend tens to hundreds of kilometers inland. Despite their extent, few studies have examined how TFZs process and transport nitrogen. Given that population centers are often near coasts, for example, 60% of the U.S. population resides in a coastal county (Beach, 2002), it is critical that we understand how these highly impacted systems function so that we can make better water resource
and nutrient management decisions. This work represents an important step toward linking the biogeochemical processing of nitrogen within riparian and hyporheic storage zones with tidal forcing. By isotopically characterizing the geochemical spatial and temporal variability within the bank aquifer, we were able to discern nitrogen processing over the 12-hr tidal cycle. Results from numerical box models support our findings, illustrating that nitrate can accumulate in regions of the aquifer that are highly porous and low in OM content. Similarly, sensitivity analyses illustrate that under most conditions denitrification acts to remove nitrate, due to oxygen consumption via decomposition-mineralization of OM. However, modeling results and in situ measurements illustrate the accumulation of nitrate under specific conditions, namely, combinations of low soil C:N ratios, large oxygen transport rates, and large potential aerobic respiration rates. Thus, depending on the advective flow paths that connect zones of elevated nitrate in the riparian aquifer with river channels, TFZs could be sources of nitrate to coastal ecosystems. Shifts in dominant nitrogen process will likely change with proximity to the coast, for example, aquatic systems with greater tidal amplitude will likely have greater nitrification and less denitrification, all things being equal. Thus, it is essential that we continue to examine these highly impacted and dynamic systems.

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