Tidal Controls on Denitrification in Coastal Streambeds

THESIS

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By

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Abstract

In coastal rivers, tidal pumping enhances the exchange of oxygen-rich river water across sediment-water interfaces, controlling nitrogen cycling in suboxic riverbed sediments. I developed a one-dimensional, coupled fluid flow and solute transport model that quantifies the influence of tidal pumping on redox zonation and nitrate removal in the hyporheic zones of coastal rivers, and applied it to the tidal freshwater zone (TFZ) of White Clay Creek (Delaware, USA). At high tide when oxygen-rich river water infiltrates into the bed, denitrification rates decrease by ~20% relative to low tide when nitrate-rich anoxic groundwater discharges to the channel. Tidal pumping deepens the aerobic zone by a factor of 6, decreasing denitrification rates by 10%. Therefore, along TFZs nitrate removal rates decrease as tidal amplitude increases due to enhanced oxygen exchange across the sediment-water interface. Sensitivity analyses suggest that denitrification hot spots in TFZs will occur in less permeable, organic-rich sediment under lower tidal ranges and higher rates of ambient groundwater discharge. Tidal pumping is not efficient at removing surface water nitrate but removes up to 81% of groundwater nitrate that would discharge to White Clay Creek. Given the high population densities of coastal watersheds and thus the tendency towards high nitrate inputs from groundwater to rivers, the hyporheic zones of TFZs play a critical role in mitigating new nitrogen loads to coasts.
Acknowledgments

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Chapter 1: Introduction

Aquatic ecosystem productivity requires biologically available forms of nitrogen (N), such as nitrate (NO₃⁻) and ammonium (NH₄⁺). Historically, reactive N limits primary productivity within estuarine and marine ecosystems. Increases in the supply of NO₃⁻ to the coast, due to anthropogenic activities such as agriculture and the burning of fossil fuels [Howarth, 1998; Galloway et al., 2008], in recent decades has led to declines in coastal water quality. Estuaries are especially sensitive to NO₃⁻ loading, with excess NO₃⁻ tied to reductions in biodiversity [Nixon, 1995; Howarth, 1998; Boesch, 2002, Howarth 2007, hypoxia [Smith 2003; Howarth, 2007; Diaz and Rosenberg, 2008], and changes to local vegetation [Turner and Rabalais, 1994; Coops et al., 1999] that increase vulnerability to storm erosion [Edmonds and Slingerland, 2010; Ericson et al., 2006].

Denitrification in river networks mitigates NO₃⁻ loads to coasts [Mulholland et al., 2008]. Shallow riverbed sediments are often high in organic carbon and low in dissolved oxygen (DO) and therefore act as preferential zones for denitrification [Duff and Triska, 1990]. Whether shallow sediment is a net source or sink of NO₃⁻ is typically influenced by the Damkohler number, defined as the ratio of reaction rate to pore water residence time [Ocampo et al., 2006; Zarnetske et al., 2012]. Thus, high rates of denitrification can occur where residence times are long or biogeochemical reactions are rapid [Gu et al., 2007].
Tidal pumping in coastal rivers may lead to unsteady transformation of NO$_3^-$ sourced from surface water or upwelling groundwater. Tidal pumping causes NO$_3^-$ rich river water to infiltrate into the bed where it may be removed by denitrification (Figure 1) before subsequent discharge during falling tide. Groundwater residence times may increase with rising tide and longer residence times at high tide may provide an opportunity for increased removal of groundwater-borne NO$_3^-$ [Rocha et al., 2009]. Alternatively, tidal pumping may limit denitrification by enhancing the supply of dissolved oxygen from surface water [Rocha et al., 2009] (Figure 1).

Figure 1. Conceptual model for aerobic respiration and denitrification. Aerobic respiration and denitrification in upwelling groundwater for (a) rising and (b) falling tides. Arrows indicate flow direction.

Tidal influence often extends inland for tens to hundreds of kilometers in unregulated rivers. TFZs are fresh river reaches influenced by a substantial tidal regime [Odum, 1988; Muylaert, 1997]. Found worldwide, TFZs are usually associated with larger rivers such as the Delaware, Hudson, and Thames [Odum et al., 1988]. They are
often unmonitored for water and solute fluxes because of their complex hydrodynamics [Odum, 1988; Muylaert, 1997; Destouni et al., 2008].

TFZs are important to estuarine ecology and may play a significant role in removal of nutrients and other contaminants. However, few studies have examined surface water-groundwater interaction and contaminant transport within TFZs. Bianchin et al. [2010] showed that tidal pumping in the TFZ of the Fraser River (British Columbia, Canada) increased the depth of hyporheic exchange up to 1 m. Schuchardt et al. [1993] found that hyporheic zone residence times were prolonged in the TFZ of the Weser Estuary (Germany). They showed that longer residence times facilitated greater nitrification over shorter reaches compared to non-tidal reaches. Ensign et al. [2008] observed oxidation-reduction (redox) potential and developed an empirical model of denitrification in the floodplain of the Newport River, North Carolina. They suggested that denitrification in TFZ floodplains promotes NO₃⁻ attenuation and reduces NO₃⁻ delivery to the coast. Past work at the site showed that at least 11% of river water flows through near stream storage zones [Musial et al., 2015]. These studies illustrate that TFZs are regions of enhanced surface water-groundwater interaction and N processing. Although TFZs may play a critical role in modulating nutrient loads to the coast, N transport dynamics and removal efficiencies in TFZs are still uncertain.

In this study I quantified the effects of tidal pumping on NO₃⁻ removal in the hyporheic zone of a TFZ. I hypothesized that tidal pumping creates a deep zone of aerobic respiration that shifts over tidal time-scales. As tidal range increases with spring tides, or with proximity to the coast, the aerobic-anaerobic interface deepens and
denitrification rates decrease. I tested these hypotheses using a numerical reactive transport model developed from observations of fluid fluxes and pore water chemistry in the bed of White Clay Creek Delaware, USA (Figure 2). I present observed and modeled fluid flow and NO$_3^-$ dynamics at the field site and use sensitivity studies to explore spatial and temporal variations in NO$_3^-$ removal along a generalized TFZ. My analysis suggests that riverbed sediments within TFZs are efficient at reducing groundwater sources of NO$_3^-$ to coastal rivers, but tidal pumping may inhibit denitrification rates by increasing the size of the aerobic zone.
Chapter 2: Study Area

The study site (39.701172°, -75.649987°) is located on White Clay Creek, a fifth-order river within the Christina River Basin Critical Zone Observatory (CRB-CZO) Delaware (Figure 2). The CRB-CZO is one of ten national critical zone observatories that focus on the interaction of atmosphere, water, soil, and the Earth’s surface. Land use in the watershed is predominantly agricultural, forested and suburban [Newbold et al., 1997]. The study site is located within the TFZ, 17 km upstream of the Delaware Bay (Figure 2). The semidiurnal tidal range is approximately 0.9 m. Like many coastal rivers, White Clay Creek is deeply incised [Dellapenna, et al., 1997; Woolfe et al., 1998] and therefore the floodplain is not inundated at high tide (Figure 3), and sandy point bars are common along the channel.
Figure 2. Study Site.
(a) Field site (green dot) lies 17 km from the Delaware Bay on White Clay Creek. Stage was also monitored in 2015 at yellow and gray dots and at USGS stations 01480120 (black star) and 1480065 (blue star). (b) Stage data from August 19 to August 20, 2015. Colors correspond to locations in (a). (c) Interpolated tidal ranges along White Clay Creek with respect to distance from the coast.
Riverbed deposits at the study site generally consist of a lower sequence of alternating silty sand and sandy silt overlain by a sand unit approximately 25 cm thick (Figure 3) [Musial et al. 2015]. Macroscopic organic matter occurs sporadically throughout the lower silty sand and sandy silt unit. Porosity is approximately 0.45, and the vertical effective hydraulic conductivity is $4.0 \times 10^{-4}$ m s$^{-1}$ [Musial et al., 2015]. As part of a broader study to characterize surface water-groundwater exchange, a series of wells and piezometer nests were installed in June 2014 along a channel-perpendicular transect on the eastern bank of the river and within the riverbed [Musial et al., 2015]. For the current study, I focus on location B (Figure 3), which was inundated throughout most of the tidal cycle. Location B includes 5 sample ports at depths of 12, 25, 50, and 100 cm below the riverbed (Figure 3). Sample ports were constructed out of 0.635 cm outer diameter polypropylene tubes perforated over a 2-cm interval and attached to a PVC riser. The screen length for the sampling ports was 2 cm.

Figure 3. Stratigraphic cross section of study site on White Clay Creek. The study site is represented by the green dot in (Figure 2). River flow direction is out from page. Vertical Exaggeration =1.67. Modified from Musial et al. [2015]
Chapter 3: Methods

3.1 Field Sampling

Surface water and pore water chemistry were monitored over two consecutive days. On June 16, 2014, specific conductivity, temperature, pH, oxidation reduction potential, and dissolved oxygen (DO) were measured in surface water and all ports over low and high tides using a Thermo Orion Star A3229 multiparameter probe. On June 17, 2014, pore water samples were collected for anions, nutrients, and dissolved organic carbon (DOC) at approximately 2 hour intervals over one tidal cycle using a peristaltic pump at a rate of ~50 mL min⁻¹. One tubing volume (~60 mL⁻¹) was discarded before sample collection. Samples were filtered (0.45 µm), immediately placed on ice, and frozen until analysis. Samples were analyzed for DOC using high temperature combustion with a Shimadzu Total Organic Carbon analyzer. Duplicate samples, instrument replication, reference standards and blanks were used to ensure analysis quality. NO₃⁻ and NH₄⁺ were measured using a Skalar flow-injection nutrient analyzer, and their respective concentrations are reported as NO₃⁻-N and NH₄⁺-N.

To measure surface water-groundwater interaction, vertical head gradients (VHG) between the deepest port (1 meter below ground) and the river were measured every 15 minutes for the duration of one tidal period on June 18, 2014 using a manometer board. I assume that tidal dynamics were the same during pore water sampling and VHG measurements. VHG data were used to calculate the exchange rate across the riverbed.
using Darcy's law, assuming a vertical hydraulic conductivity of $4.0 \times 10^{-4} \text{ m s}^{-1}$ [Musial et al., 2015]. VHG measurements were accurate to ±2 mm, resulting in a seepage rate accuracy of ±0.16 m d$^{-1}$.

I measured river discharge rates and collected surface water samples in order to evaluate downstream NO$_3^-$ fluxes in the channel for comparison with NO$_3^-$ fluxes across the riverbed. River discharge was measured every 60 minutes with an acoustic Doppler current profiler (Teledyne RDI StreamPro) on June 18, 2014, and river water samples were collected simultaneously. Instantaneous riverine NO$_3^-$ loads were calculated as the product of river discharge and river NO$_3^-$ concentration.

To measure variations in tidal amplitude along the TFZ, pressure sensors were installed in a stilling well at the study site and at two locations downstream. Tidal fluctuations at all stations were recorded every 10 minutes between August 18, 2015 and August 21, 2015.

3.2 Fluid Flow and Reactive Transport Modeling

Unsteady fluid flow and reactive transport were simulated in one dimension within a vertical sediment column (Figure 1). Subsurface flow was first solved using the transient groundwater flow equation with a source term to represent the poroelastic response to rising and falling tide [Wang and Davis, 1996, Wilson and Gardner, 2006]:

$$S_s \frac{\partial h}{\partial t} = K \left[ \frac{\partial^2 h}{\partial x^2} \right] + \gamma \frac{\partial h(0,t)}{\partial t}$$

where, $S_s$ is specific storage, $h$ is hydraulic head, $t$ is time, $K$ is hydraulic conductivity, $x$ is depth below the sediment-water interface, and $\gamma$ is the loading efficiency of sediments (Table 1). A constant upward flux of 4.27 cm d$^{-1}$ was designated at the lower boundary of
the domain, representing net groundwater discharge. A fluctuating hydraulic head signal, \( h(0,t) \) was specified at the upper boundary to represent semidiurnal tides. For steady (non-tidal) conditions, the fluctuating hydraulic head condition was replaced with a constant hydraulic head condition. The upper 1 cm of the domain was assigned a high \( K \) (10^{-3} \text{ m s}^{-1}) to replicate surface water and allow downward dispersion of solute across the sediment water interface.

Resulting pore water velocities were used as inputs to the advection-dispersion reaction equations for dissolved oxygen (DO), nitrate (NO_3^{-}), ammonium (NH_4^{+}) and dissolved organic carbon (DOC):

\[
\frac{\partial O_2}{\partial t} = D \frac{\partial^2 O_2}{\partial x^2} - \frac{\partial v O_2}{\partial x} - V_{ar}X \beta_{ar}O_2 \left( \frac{\text{DOC}}{K_{\text{DOC}}+\text{DOC}} \right) \left( \frac{O_2}{K_{O_2}+O_2} \right) - V_{nit}X \beta_{nit,O_2} \left( \frac{\text{NH}_4}{K_{\text{NH}_4}+\text{NH}_4} \right) \left( \frac{O_2}{K_{O_2}+O_2} \right),
\]

(1)

\[
\frac{\partial \text{NO}_3}{\partial t} = D \frac{\partial^2 \text{NO}_3}{\partial x^2} - \frac{\partial v \text{NO}_3}{\partial x} + V_{nit}X \left( \frac{\text{NH}_4}{K_{\text{NH}_4}+\text{NH}_4} \right) \left( \frac{O_2}{K_{O_2}+O_2} \right) - X \beta_{den,O_2} I \left( \frac{\text{DOC}}{K_{\text{DOC}}+\text{DOC}} \right) \left( \frac{\text{NO}_3}{K_{\text{NO}_3}+\text{NO}_3} \right),
\]

(2)

\[
\frac{\partial \text{NH}_4}{\partial t} = D \frac{\partial^2 \text{NH}_4}{\partial x^2} - \frac{\partial v \text{NH}_4}{\partial x} - V_{nit}X \left( \frac{\text{NH}_4}{K_{\text{NH}_4}+\text{NH}_4} \right) \left( \frac{O_2}{K_{O_2}+O_2} \right) + V_{ar}X \beta_{ar,NH}_4 \left( \frac{\text{DOC}}{K_{\text{DOC}}+\text{DOC}} \right) \left( \frac{O_2}{K_{O_2}+O_2} \right) +
\]

\[
V_{den}X \beta_{den,NH}_4 I \left( \frac{\text{DOC}}{K_{\text{DOC}}+\text{DOC}} \right) \left( \frac{\text{NO}_3}{K_{\text{NO}_3}+\text{NO}_3} \right),
\]

(4)

\[
\frac{\partial \text{DOC}}{\partial t} = D \frac{\partial^2 \text{DOC}}{\partial x^2} - \frac{\partial v \text{DOC}}{\partial x} + \alpha (OM - k_d \text{DOC}) - V_{ar}X \left( \frac{\text{DOC}}{K_{\text{DOC}}+\text{DOC}} \right) \left( \frac{O_2}{K_{O_2}+O_2} \right) -
\]

\[
V_{den}X I \left( \frac{\text{DOC}}{K_{\text{DOC}}+\text{DOC}} \right) \left( \frac{\text{NO}_3}{K_{\text{NO}_3}+\text{NO}_3} \right),
\]

(5)

where \( v \) is the pore water velocity, \( V_k \) is the maximum microbial process reaction rate for the \( k \)th reaction and \( X \) is the biomass of the functional microbial group. \( \beta_{ar,O_2}, \beta_{nit,O_2}, \beta_{den,NO}_3, \beta_{ar,NH}_4 \) and \( \beta_{den,NH}_4 \) are stoichiometric coefficients [Doussan et al., 1997;
Canavan et al., 2006; Gu et al., 2007]. $K_j$ is the half saturation constant for reactant $j$. $OM$ is organic matter content. $DOC$ derived from $OM$ is represented as a first-order reversible kinetic reaction with mass transfer coefficient $\alpha$ that is intended to represent the combined effects of dissolution and desorption [Jardine et al., 1992; Gu et al. 2007; Zarnetske et al., 2012]. Denitrification occurs under anoxic conditions. I therefore include $I$ in Equations 3 and 4 to represent non-competitive inhibition of denitrification by DO [Widdowson, et al., 1988]:

$$I = \frac{K_i}{K_i + O_2},$$

where $K_i$ is the inhibition constant.

The hydrodynamic dispersion coefficient ($D$) is:

$$D = D_m + \alpha_i \nu,$$

where, $D_m$ is the molecular diffusion coefficient in porous media, and $\alpha_i$ is dispersivity (Table 1).

Concentrations of $NO_3^-$, $NH_4^+$, DO, and DOC in surface water and groundwater end-members were assigned to the upper and lower boundaries based on field observations (Table 1). OM content was estimated by fitting the modeled and measured DOC profiles. Reaction kinetics were constrained from the literature [Molz et al, 1986; Gu et al., 2007; Zarnetske et al., 2011, Marzadri et al., 2012, Sawyer, 2015] and adjusted by fitting measured concentration data (Table 1). Models were run until fluid fluxes and solute concentrations approached quasi-steady state (~130 days). The maximum element size was 1.5 cm. The groundwater flow equation was solved for a larger domain (100 m), while the advection dispersion reaction equation was solved for the upper 2 m only.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical Parameters</td>
<td></td>
</tr>
<tr>
<td>( n ) (porosity)</td>
<td>0.45</td>
</tr>
<tr>
<td>( q_{gw} ) (ambient groundwater flux at lower boundary)</td>
<td>( 4.95 \times 10^{-7} \text{ m s}^{-1} )*</td>
</tr>
<tr>
<td>( A ) (tidal amplitude)</td>
<td>0.45 \text{ m} )*</td>
</tr>
<tr>
<td>( K ) (hydraulic conductivity)</td>
<td>( 4.0 \times 10^{-4} \text{ m s}^{-1} )*</td>
</tr>
<tr>
<td>( S_s ) (specific storage)</td>
<td>( 2.5 \times 10^{-6} \text{ [1/Pa]} )</td>
</tr>
<tr>
<td>( \gamma ) (loading efficiency source term)</td>
<td>0.90</td>
</tr>
<tr>
<td>( \lambda ) (tidal period)</td>
<td>12 \text{ [h]}</td>
</tr>
<tr>
<td>Reaction Parameters</td>
<td></td>
</tr>
<tr>
<td>C:N:P (redfield ratio)</td>
<td>112:20:1**</td>
</tr>
<tr>
<td>( \alpha_L ) (dispersivity)</td>
<td>0.01 \text{ [m]}</td>
</tr>
<tr>
<td>OM(_0)</td>
<td>0.2</td>
</tr>
<tr>
<td>( D_m ) (molecular diffusion)</td>
<td>( 5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} )</td>
</tr>
<tr>
<td>( X ) (microbial biomass)</td>
<td>0.000142 \text{ [kg m}^3\text{]}</td>
</tr>
<tr>
<td>( V_{ar} ) (maximum specific O(_2) reaction rate)</td>
<td>1.97 \text{ [h}^{-1}\text{]}</td>
</tr>
<tr>
<td>( V_{nit} ) (maximum specific NH(_4^+) reaction rate)</td>
<td>1.08\text{[h}^{-1}\text{]}</td>
</tr>
<tr>
<td>( V_{den} ) (maximum specific NO(_3^-) reaction rate)</td>
<td>3.98\text{[h}^{-1}\text{]}</td>
</tr>
<tr>
<td>( \beta_{ar,O_2} ) (stoichiometric coefficient for aerobic respiration)</td>
<td>2.67</td>
</tr>
<tr>
<td>( \beta_{nit,O_2} ) (stoichiometric coefficient for nitrification)</td>
<td>4.57</td>
</tr>
<tr>
<td>( \beta_{den,NO_3} ) (stoichiometric coefficient for denitrification)</td>
<td>0.933</td>
</tr>
<tr>
<td>( \beta_{ar,NH_4} ) (stoichiometric coefficient for aerobic ammonification)</td>
<td>0.21</td>
</tr>
<tr>
<td>( \beta_{den,NH_4} ) (stoichiometric coefficient for anaerobic ammonification)</td>
<td>0.21</td>
</tr>
<tr>
<td>( K_{DOC} ) (half saturation constant for DOC)</td>
<td>8.68 \text{ [mg L}^{-1}\text{]}</td>
</tr>
<tr>
<td>( K_{O_2} ) (half saturation constant for DO)</td>
<td>5.28 \text{ [mg L}^{-1}\text{]}</td>
</tr>
<tr>
<td>( K_{NO_3} ) (half saturation constant for NO(_3^-))</td>
<td>1.65 \text{ [mg L}^{-1}\text{]}</td>
</tr>
<tr>
<td>( K_{NH_4} ) (half saturation constant for NH(_4^+))</td>
<td>0.43 \text{ [mg L}^{-1}\text{]}</td>
</tr>
<tr>
<td>( K_{i} ) (oxygen inhibition)</td>
<td>0.24 \text{ [mg L}^{-1}\text{]}</td>
</tr>
<tr>
<td>( \alpha ) (mass transfer coefficient for OM to DOC)</td>
<td>( 5 \times 10^{-5} \text{ [h}^{-1}\text{]} )</td>
</tr>
<tr>
<td>( K_d ) (distribution coefficient)</td>
<td>50 \text{ [m}^3\text{ kg}^{-1}\text{]}</td>
</tr>
</tbody>
</table>

Table 1. White Cay Creek model parameters

a, b and c represent the C:N:P ratio.

* Values used in White Clay Creek simulation

**Canavan et al. 2007

(continued)
To explore potential downstream trends in N transformation along a generalized TFZ, I varied tidal amplitude from 0.1 m to 1 m. I also varied net groundwater discharge rates from 0.43 cm d\(^{-1}\) to 8.6 cm d\(^{-1}\) in order to explore the sensitivity of the model to changes in base flow. I tested four end-member water quality scenarios: (1) high NO\(_3^-\) in groundwater (10 mg L\(^{-1}\), denoted HG), (2) high NO\(_3^-\) in surface water (8 mg L\(^{-1}\), denoted HS), (3) low NO\(_3^-\) in groundwater (2 mg L\(^{-1}\), denoted LG) and (4) low NO\(_3^-\) in surface water (1 mg L\(^{-1}\), denoted LS) (Table 2). I also examined the influence of sediment properties by varying \(K\) from 4.0\(\times\)10\(^{-6}\) (silty sand) to 9.0\(\times\)10\(^{-4}\) m s\(^{-1}\) (clean sand) [Freeze and Cherry, 1979]. For this sensitivity study, I assumed an exponential OM profile:

\[
OM(x) = (OM_0 e^{bx}),
\]  

(8)
where, \( OM_0 \) is 0.2 and \( b \) is 9. Modeled organic matter concentrations thus range from 20% at the sediment water interface to 0.0025% at 1 m depth with an average concentration of 4.1%.

3.4 Long-term simulations

To capture long-term dynamics in nitrogen cycling, tidal pumping was simulated using river stage data from USGS monitoring station 1480065 at Newport, DE between July 14, 2015 and August 17, 2015. The station lies 8 km downstream from the study site. The time range was chosen to include both spring and neap tides and encompasses several storm events. Stage data were used as the boundary condition for hydraulic head at the sediment-water interface, while all other parameters remained unchanged from the model scenario for White Clay Creek at location B (Table 1).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>HG (High Groundwater)</td>
<td>10 mg L(^{-1})</td>
</tr>
<tr>
<td>LG (Low Groundwater)</td>
<td>2 mg L(^{-1})</td>
</tr>
<tr>
<td>HS (High Surface Water)</td>
<td>8 mg L(^{-1})</td>
</tr>
<tr>
<td>LS (Low Surface Water)</td>
<td>1 mg L(^{-1})</td>
</tr>
</tbody>
</table>

Table 2. Surface water and groundwater end members. NO\(_3^-\) concentrations for surface water and groundwater end members in sensitivity analysis.
Chapter 4: Results

4.1. Fluid Flow and Nitrogen Dynamics at White Clay Creek

Tides drive reversals in fluid flow across the sediment-water interface. River water infiltrates into the bed during rising tide and discharges during falling tide (Figure 4). Measured vertical seepage rates fluctuated between $-0.66 \pm 0.16 \text{ m d}^{-1}$ (infiltration) and $0.38 \pm 0.16 \text{ m d}^{-1}$ (discharge) over the tidal cycle [Musial et al., 2015]. Net flux was calculated as $-0.09 \pm 0.16 \text{ m d}^{-1}$ at location B. However, overall net flux was $0.98 \text{ m d}^{-1}$ along the entire transect (Figure 3), indicating net discharge of groundwater to the channel [Musial et al., 2015]. Simulated vertical seepage rates fluctuate between $-14.7 \text{ m d}^{-1}$ (infiltration) and $19.5 \text{ m d}^{-1}$ (discharge) over the tidal cycle (Figure 4a). The modeled vertical head gradient (VHG) generally agrees with measured VHG but has a slightly greater range (Figure 4b).
DOC concentrations in surface water and pore water were relatively stable over the tidal cycle and ranged from 2 to 4 mg L\(^{-1}\) (Figure 5a). NO\(_3^-\) concentrations were also stable (Figure 5b), pore water NO\(_3^-\) concentration was highest (4.22 mg L\(^{-1}\)) at 1 m depth but negligible between 0.75 and 0.25 m depths (Figure 5b). Surface water NO\(_3^-\) concentrations were consistently high (~4 mg L\(^{-1}\)) over the tidal cycle (0 m depth, Figure 5b). Groundwater NH\(_4^+\) concentrations increased steadily from 0 to ~1 mg L\(^{-1}\) between depths of 1 and 0.25 m (Figure 5c). NH\(_4^+\) in surface water was negligible. DO concentrations were low and mostly negligible at all sampling depths in the subsurface (Figure 5d). The only exception was at 0.5 m depth, where DO concentrations were ~1.5
and ~0.5 mg L$^{-1}$ at high and low tide respectively. Surface water DO concentrations were consistently high (~8 mg L$^{-1}$) over the tidal cycle.

The modeled concentration profiles for DOC, NO$_3^-$, NH$_4^+$ and DO generally agree with the measured data (Figure 5). The model accurately predicts a zone of negligible NO$_3^-$ between 0.25 and 0.75 m and higher NO$_3^-$ at 1 m (Figure 5b). The model also predicts elevated NH$_4^+$ concentrations in the zone of depleted NO$_3^-$ (0.25 to 0.75 m) but particularly overestimates concentrations at ~0.75 m. The simulated DO profile shows good agreement with measured data and indicates an aerobic zone that extends from the sediment-water interface to 0.08 m at low tide and 0.12 m at high tide (Figure 5).

![Figure 5. Concentration profiles.](image)

Concentration profiles of (a) DOC (precision: 1.6%), (b) NO$_3^-$ (precision: 0.8%), (c) NH$_4^+$ (precision: 5.3%) and (d) DO (precision: 14%) from measurement and models at nest B. Black and white dots on figure 4a correspond with sample times at high and low tide.

Modeled NO$_3^-$ removal rates fluctuate over tidal timescales (Figure 6a). During low tide, rates of denitrification and NO$_3^-$ removal (aggregate effect of denitrification and nitrification) steadily increase. When tide begins to rise, denitrification and NO$_3^-$ removal
rates reach a maximum of 160 mg m\(^{-2}\) d\(^{-1}\) and 150 mg m\(^{-2}\) d\(^{-1}\) respectively (Figure 6a). Denitrification and NO\(_3\)\(^-\) removal rates then decrease by \(\sim 25\%\) and 40\% to 120 mg cm\(^{-2}\) d\(^{-1}\) and 90 mg cm\(^{-2}\) d\(^{-1}\), respectively, shortly after high tide (Figure 6a). The NO\(_3\)\(^-\) removal rate is consistently lower than the denitrification rate, indicating coupled nitrification-denitrification throughout the tidal cycle.

Simulated DO and NO\(_3\)\(^-\) fluxes across the bed are positive at low tide, indicating transport from sediments to surface water (Figure 6b). As tide rises, fluxes become negative, indicating transport from the surface water to sediments. NO\(_3\)\(^-\) flux across the sediment-water interface ranges from -1300 to 750 mg m\(^{-2}\) d\(^{-1}\), and DO flux ranges from -520 to 690 mg m\(^{-2}\) d\(^{-1}\), respectively (Figure 6b). The timing of downstream NO\(_3\)\(^-\) transport is similar to flux across the bed. The measured riverine NO\(_3\)\(^-\) load was lowest (523 kg d\(^{-1}\)) approximately two hours before high tide, at a period when water infiltrates hyporheic storage zones. The measured riverine NO\(_3\)\(^-\) load was highest (2200 kg d\(^{-1}\)) one hour after high tide (Figure 6c). As tide falls, hyporheic water comes out of storage, and the downstream transport rate increases. The riverine NO\(_3\)\(^-\) load was proportional to river discharge (Figure 6c).
4.2 Sensitivity Study

As simulated tidal amplitude increases from 0 to 1 m along an idealized TFZ, tidal pumping exchanges more dissolved oxygen across the sediment-water interface, causing a steady increase in the aerobic respiration rate (Figure 7a). Because oxygen increases nitrification and inhibits denitrification, the NO$_3^-$ removal rate decreases (Figure 7b). For the HG/HS scenario (representative of low water quality in surface and groundwater), NO$_3^-$ removal is 165 mg m$^{-2}$ d$^{-1}$ under low tidal amplitude (amplitude of 0.1
m). However, NO$_3^-$ removal decreases to 46 mg m$^{-1}$ d$^{-1}$ at a tidal amplitude of 1 m (Figure 7b). This shift is primarily due to a decrease in denitrification (Figure 7c) and, to a lesser extent, an increase in nitrification (Figure 7d). The nitrification rate increases steadily from 3.1 mg m$^{-2}$ d$^{-1}$ at 0.1 m tidal amplitude to 36 mg m$^{-2}$ d$^{-1}$ at 1 m.

![Image of graphs showing aerobic respiration, NO$_3^-$ removal, denitrification, and nitrification rates along a continuum from low to high tidal influence.](image)

**Figure 7.** Spatial nitrate dynamics
(a) Rates of aerobic respiration, (b) NO$_3^-$ removal, (c) denitrification and (d) nitrification along a continuum from low to high tidal influence (inland to coast). Rates are less sensitive to surface water than groundwater NO$_3^-$ concentration, which indicates that denitrification mostly removes groundwater-sourced NO$_3^-$.

The other three water quality conditions (HG/LS, LG/HS and LG/LS) show similar trends in aerobic respiration and N transformations (Figure 7). Rates are nearly identical for both high groundwater NO$_3^-$ conditions (HG/HS and HG/LS) but differ from low groundwater NO$_3^-$ conditions (LG/HS and LG/LS). For example, denitrification rates tend to be higher for scenarios with high NO$_3^-$ concentration in groundwater (HG/HS and HG/LS), particularly at low tidal amplitudes (Figure 7c and Figure 8). NO$_3^-$ removal rates
scale nearly linearly with groundwater NO$_3^-$ concentration but are generally insensitive to surface water NO$_3^-$ concentrations (Figure 8).

Figure 8. Surface water-groundwater nitrate concentration
NO$_3^-$ removal generally increases with groundwater NO$_3^-$ concentration and is less sensitive to surface water NO$_3^-$ Star indicates White Clay Creek concentrations.

NO$_3^-$ removal rate also varies with sediment properties. The removal rate decreases as the hydraulic conductivity of sediment increases from values typical of silt to sand (Figure 9). NO$_3^-$ removal is lowest (in fact, net production occurs) when hydraulic conductivity and tidal pumping are high, both of which promote greater oxygen exchange across the sediment-water interface. The highest modeled NO$_3^-$ removal rate (110 mg m$^{-2}$ d$^{-1}$) occurs at a tidal amplitude of 0.1 m and hydraulic conductivity of $4.0 \times 10^{-6}$ m s$^{-1}$, typical of silty sand [Freeze and Cherry 1979]. Organic matter content also strongly controls denitrification rates. I increased the average OM content from 4.1 to 5.3% to test the effect on DOC supply and denitrification rates. Under these conditions, aerobic respiration and nitrification still increase (not shown) with tidal amplitude or proximity to the coast, while NO$_3^-$ removal rate decreases (Supplementary Figure). However, the NO$_3^-$
removal rate is between 1.7 and 3.5 times greater, between high and low amplitude as compared to the lower OM content scenario. A deeper organic matter profile (Supplementary Figure) supplies more DOC to facilitate faster oxygen consumption.

Figure 9. Tidal Amplitude on nitrate removal. NO$_3^-$ removal rate generally decreases with tidal amplitude and hydraulic conductivity. Negative values indicate net NO$_3^-$ production. The star indicates White Clay Creek conditions.

Net groundwater discharge is yet another control on the NO$_3^-$ removal rate. Wetter climates and better drained soils tend to have greater ambient groundwater discharge rates (or base flow). As this base flow contribution increases, the NO$_3^-$ removal rate increases (Figure 10). Faster rates of groundwater discharge inhibit oxygen transfer from river water into sediments and deliver more NO$_3^-$ from below to shallow, carbon-rich sediments where denitrification can occur.
4.3 Long-term tidal and storm dynamics

Four storm events increased river discharge in White Clay Creek between July 14, 2015 and August 13, 2015. During each storm event, stage rose ~0.5 m upstream of the TFZ (Figure 11a). Within the TFZ, the average stage and tidal amplitude fluctuated over the one-month interval, but fluctuations may have been more associated with spring-neap cycles than storm dynamics (Figure 11b). These dynamics drive complex changes in both the daily average denitrification rate and amplitude of denitrification rate (Figure 11c).

For example, on July 24 during base flow and neap tide, the average denitrification rate over a single tidal period was 160 mg m⁻² d⁻¹. That rate fell by 12.5% to 140 mg m⁻² d⁻¹ over the ensuing days as spring tides drove an increase in tidal amplitude. Around August 8 (a neap phase), the denitrification rate fell again even though the tidal amplitude decreased. The decline in the modeled denitrification rate is likely associated with an increase in the average stage, which would tend to temporarily increase infiltration of

Figure 10. Ambient Groundwater Discharge on nitrate removal. 
NO₃⁻ removal generally increases with groundwater discharge but decreases with tidal amplitude. Star indicates White Clay Creek conditions.
oxic river water into the bed and reduce ambient groundwater discharge. Both effects would tend to decrease denitrification rates.

Figure 11. Long Term nitrate dynamics. Stage data for (a) USGS station 1479000 along a non-tidal reach of the Christina River at Newark (black) and (b) USGS station 1480065 at Newport within the TFZ. Simulated denitrification rate (black) over 30 days using stage data collected from July to August, 2015 at USGS station 1480065 along the Christina River Newport, DE
Chapter 5: Discussion

5.1 Role of tidal pumping in riverbed denitrification

Riverbed sediments within TFZs are dynamic sites of denitrification characterized by both semidiurnal and episodic hot moments. Over a single tidal cycle at the study site, denitrification rates fluctuate as much as 20% between high and low tide due to expansion and contraction of the riverbed anaerobic zone (Figure 6). Hensley et al. [2015] observed similar tidal dynamics in N removal within a clear, spring-fed TFZ in Florida and attributed them to changes in the residence time of water within transient storage zones. Denitrification rates also fluctuate over weekly timescales in response to storm and spring-neap events. Between July 14 and August 13, 2015 modeled denitrification rates at White Clay Creek varied by 60% (Figure 11). Increases in average stage tend to coincide with decreases in average denitrification rates. These increases in average stage could be associated with storms, onshore winds, or even reservoir management. Increases in tidal amplitude, i.e. distance from coast, also decrease average denitrification rates and can occur during spring tides. These lower frequency fluctuations in denitrification rates are analogous to observed variations in carbon cycling over spring-neap cycles in mangrove systems [Call et al., 2015]. Future work is required to characterize dynamics in carbon cycling in TFZs.

Along the spatial continuum of the TFZ, increasing tidal amplitude favors aerobic respiration and limits denitrification rates (Figure 7). Previous studies have suggested that
Riverine denitrification rates are generally higher than estuarine [Seitzinger, 1988; Mulholland et al., 2008], and my models provide new insights into denitrification rates along the transition zone between these ecosystems. At the study site near the upstream limit of the TFZ in White Clay Creek, the modeled average denitrification rate is 140 mg m\(^{-2}\) d\(^{-1}\). This rate is slightly greater than measurements from five locations within the Delaware River’s TFZ (55-115 mg m\(^{-2}\) d\(^{-1}\)) and significantly greater than denitrification rates (0-90 mg m\(^{-2}\) d\(^{-1}\)) measured from \(\text{N}_2\) production of intact sediment cores in the fully tidal Delaware Bay [Seitzinger, 1988]. If interpreted along a gradient of tidal influence, these estimates support my finding that denitrification rates decrease along TFZs. In the absence of tides (upstream of the TFZ), groundwater flow and denitrification rates would be steady, and my model suggests that \(\text{NO}_3^-\) removal rates would increase by \(\sim 10\%\). The increased removal rate is due to a thinner aerobic zone. Tidal pumping associated with 1 m stage change, extends the aerobic zone to \(\sim 0.12\) m (Figure 5), while an absence of tidal pumping limits the aerobic zone to \(\sim 0.02\) m (not shown).

Riverbed sediments within TFZs are efficient at removing \(\text{NO}_3^-\) from upwelling groundwater, but tidal pumping does not enhance \(\text{NO}_3^-\) removal from surface water. The majority of \(\text{NO}_3^-\) removed originates from groundwater, as evidenced by the high sensitivity of \(\text{NO}_3^-\) removal rates to groundwater rather than surface water \(\text{NO}_3^-\) concentrations (Figures 7 and 8). Surface water \(\text{NO}_3^-\) is not removed as efficiently as groundwater \(\text{NO}_3^-\) because tidal pumping exchanges oxygen across the sediment water interface, inhibiting denitrification in shallow sediments. At the study site, \(\text{NO}_3^-\) from surface water travels \(\sim 0.03\) m into the bed by advection over one tidal cycle before the
flow reverses again towards the channel. That is, a particle of water travels 0.03 m into the bed before it flows out again. In comparison, the aerobic zone is 0.12 m deep due to enhanced dispersion of oxygen, which occurs over many tidal cycles. Thus, only a portion of the hyporheic zone is suitable for denitrification, as seen by other studies [Harvey et al., 2013]. Most NO$_3^-$ that enters the sediment during a given tidal cycle will return to the stream without exposure to anaerobic conditions, limiting the potential for NO$_3^-$ removal prior to discharge during falling tide.

In this model I assumed that dissolved oxygen inhibits denitrification and chose an inhibition constant similar to previous studies: denitrification is limited for DO concentrations greater than 0.24 mg L$^{-1}$ [Sheilby et al., 2003; Zarnteske et al., 2012]. However, field measurements have shown strong correlations between denitrification and high oxygen demand and the potential for high denitrification rates in shallow, aerobic riverbed sediments [Arango et al., 2007; O'Conner and Hondzo, 2008; Mulholland et al., 2008]. Therefore, an increase in tidal pumping and oxygen supply to shallow sediments may not limit denitrification as much as my models suggest. The persistence of anoxic sites in heterogeneous sediment can facilitate denitrification in bulk aerobic zones [Harvey et al. 2013, Sawyer, 2015; Briggs et al., 2015]. Heterogeneity in sediment type (both permeability and organic matter content) and microbial activity affect bulk rates of redox transformation in the hyporheic zone [Harvey et al., 2013; Sawyer, 2015].

In order to measure the sensitivity of my results to oxygen inhibition, I ran several models where the inhibition constant ranges from 0.05 to 2 mg L$^{-1}$. Over this range, the denitrification rate only changes by 7.8%. Changes in aerobic respiration rate and
nitrification rates are negligible. For small inhibition constants (less than 0.25 mg L\(^{-1}\)), there is a nearly linear increase in denitrification rate of about 0.17 mg m\(^{-2}\) d\(^{-1}\) for every mg L\(^{-1}\) increase in \(K_I\). For greater inhibition constants, there is a much smaller increase in the denitrification rate. This suggests that the presence of DO may not be the only factor limiting denitrification rates in my models. DOC availability may also strongly limit NO\(_3^-\) removal [Zarnetske et al., 2011], especially given the sensitivity of denitrification rates to OM content (Supplementary Figure). Field-scale observations are needed to confirm whether aerobic sediments within TFZs are better zones of denitrification than my models suggest.

Other mechanisms such as bedform-current interactions may be efficient at removing NO\(_3^-\) from surface water, even if tidal pumping is not. Notably, bedform-current interactions would be modulated by tidal changes in currents and water depths [Boano et al., 2013]. Bianchin et al. [2010] presented a conceptual model for the influence of tides on bedform-current interactions. At high tide when river flow is low, hyporheic exchange through bedforms tends to decrease. However, tidal pumping may counteract this effect by enhancing downward flow into the bed. As tide falls and river flow increases, hyporheic exchange through bedforms tends to increase, but groundwater discharge associated with tidal pumping again may counter this effect. My one-dimensional models do not fully capture the range of hyporheic mechanisms that drive N transport and removal in TFZs. Future field observations and models that include hyporheic exchange due to current-bedform interactions would more accurately constrain N removal in TFZs.
5.2 Implications for N export to coasts and TFZ management

Rivers and streams are substantial NO₃⁻ sinks and act as natural buffers that limit N transport to sensitive coastal environments [Wolheim et al. 2006; Mulholland et al., 2008; Kiel and Cardenas, 2014]. Several field and modeling studies have quantified denitrification rates within various river networks [Helton et al., 2010], but none of these studies have considered the tidally influenced portion of the network. For example, Wolheim et al. [2008] used a modeling approach to show that ~13-16% of N can be removed by rivers and streams on a network scale, thus mitigating N delivery to the coast. My study illustrates that at the downstream ends of river networks, TFZs may have a reduced capacity to remove river-borne N even though tidal pumping often enhances hyporheic exchange (Figure 7b).

Based on my model results for White Clay Creek, I can evaluate the importance of riverbed denitrification on N export to the Delaware Bay through simple extrapolation. The cross sectional width of White Clay Creek at the study site is 26 m and the length of White Clay Creek’s TFZ is approximately 17 km. For simplicity, I assume a constant channel width and denitrification rate along the TFZ, though the channel width increases and the denitrification rate likely decreases in the downstream direction. The resulting NO₃⁻ removal rate for the entire riverbed area is 61 kg/d. This is only 4% of the measured riverine NO₃⁻ load near the upstream limit of the TFZ (1500 kg/d, Figure 6c). In other words, riverbed sediments within the TFZ of White Clay Creek are only able to remove 4% of the NO₃⁻ in river water that discharges to the coast. However, this removal rate is equivalent to 81% of the potential groundwater-borne NO₃⁻ load to the TFZ (~75 kg d⁻¹ if
The hyporheic zone of the TFZ therefore plays an important role in mitigating new NO$_3^-$ sources from groundwater that would otherwise discharge near the coast. This ecological service is particularly crucial, given the density of NO$_3^-$ sources to coastal aquifers from septic tanks and fertilizers. Groundwater-borne NO$_3^-$ loads to coastal rivers can constitute a sizeable fraction of the total NO$_3^-$ loads to estuaries. For example, in the Chesapeake Bay, base flow contributions of NO$_3^-$ to coastal rivers represent more than half (58 to 73%) the total estimated load [Miller et al., 2015]. Groundwater-borne NO$_3^-$ loads are only expected to increase into the future because the age distribution of groundwater that discharges to streams still includes a large fraction of older water that recharged prior to land use change or intensive fertilizer applications [Bohlke and Denver, 1995].

TFZs are rarely monitored for either river discharge or N loads due to their complex hydrodynamics [Destouni et al., 2008]. Most observations and models of N loads to coasts neglect TFZs, which may lead to underestimation of total N export. Relatively recent improvements in sensor technology have made it possible to monitor both river velocity and nitrate concentrations at sub-hourly timescales. I advocate for increased monitoring of water and solute fluxes in tidally influenced rivers in order to improve my understanding of ultimate chemical loads to coastal waters.

N fate in TFZs likely varies regionally due to both geologic and hydroclimatic controls. Denitrification rates in TFZs are influenced by hydraulic conductivity (Figure 9), organic matter (Supplementary Figure), and net groundwater discharge (Figure 10).
Sandier sediments typically have high hydraulic conductivity and low organic matter content, both of which correspond with lower denitrification rates, all other factors held constant. Sand-rich TFZs likely remove less groundwater-borne NO$_3^-$ than silt-rich TFZs, similar to findings in beach and estuary settings [Weinstein et al., 2011; Sawyer et al., 2014]. The net rate of groundwater discharge also influences NO$_3^-$ supply and thus the denitrification rate. For a given lithology or hydraulic conductivity, the rate of groundwater discharge to a stream depends on the recharge rate. Therefore, TFZs in wetter regions may remove more groundwater-borne NO$_3^-$ than TFZs in arid regions. Field observations from TFZs in other geologic settings and climates are essential for verifying these predictions.

My one dimensional model provides a useful framework for testing ideas about N removal in TFZs, however the model is relatively simple and has its limitations. For example, the behavior of flow and N transformation in the riverbanks likely differs from that of the riverbed. Gomez-Velez et al. [2015] reported that denitrification potential in the riverbed exceeds denitrification potential in the banks of non-tidal rivers. Also, Harvey et al. [2013] showed that denitrification rates can vary between channel thalweg and side cavities. In TFZs, the river bed and banks are likely to have even greater disparities in denitrification potential. Tidally driven water table fluctuations in the riparian aquifer aerate shallow groundwater. At White Clay Creek, 11% of tidal hyporheic exchange occurs in the banks [Musial et al., 2015] and it is unclear how tidal fluctuations and aeration affect N dynamics there. Also, heterogeneity in physical and biogeochemical properties (hydraulic conductivity, organic matter content and quality,
and microbial activity) play significant roles in denitrification rates [Sawyer et al., 2015] but are not included in my model. Future studies should incorporate higher dimensional modeling that includes reactive transport in the variably saturated floodplain aquifer. Denitrification occurs in tidally inundated floodplain soils [Ensign et al., 2008] and may also occur in bank storage zones within floodplains. High resolution field and modeling studies are still needed to refine estimates of nutrient transformation and dynamics in TFZs.
Chapter 6: Conclusions

TFZs are dynamic regions of coastal rivers where N cycling in riverbed sediments varies both temporally and longitudinally. At high tide, oxygenated river water infiltrates sediments and decreases denitrification rates. Along TFZs, NO$_3^-$ removal rates decrease with increasing tidal influence due to greater exchange of oxygen across the sediment-water interface. At my study site near the upstream limit of a TFZ, tides increase the depth of aerobic sediments by a factor of 6, resulting in a 10% reduction in NO$_3^-$ removal rates. Nevertheless, riverbed sediments within TFZs can still be tremendously effective at mitigating NO$_3^-$ loads from groundwater (base flow). Riverbed denitrification removes more than 80% of groundwater-borne NO$_3^-$ at my site.

Most efforts to monitor or model N loads from rivers to coasts are concentrated upstream of TFZs. As a result, N loads from some of my most densely populated coastal catchments go unmonitored. This research provides an important step in understanding N fate in TFZs. Future research should focus on reach scale sampling and modeling to accurately predict the N transformation potential of TFZs across a range of geologic, land use, and climate settings. These observations are essential to improving predictions of N export to coasts and informing best management practices for coastal rivers.


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Appendix A: Supplementary Figure

Figure 12. Modified DOC profile. (a) Simulated DOC concentration using a shallow organic matter profile (black) and deep organic matter profile (grey) (b) Simulated NO$_3^-$ removal rate using a shallow organic matter profile (black) compare with a deep organic matter profile (grey).