Modeling biogeochemical processes in subterranean estuaries: The effect of flow dynamics and redox conditions on submarine groundwater discharge

Claudette Spiteri, Caroline P. Slomp, Kagan Tuncay and Christof Meile

Abstract  A 2D density dependent reactive transport model is used to investigate the fate of nutrients (NO$_3^-$, NH$_4^+$ and PO$_4^{3-}$) in idealized subterranean estuaries, representing four endmembers of oxic/anoxic aquifer and seawater redox conditions. The flow dynamics in a coastal aquifer are coupled with a reaction network, which takes into account some of the main biogeochemical pathways that remove/transform nutrients. The extent of groundwater nutrient removal prior to discharge into coastal waters and the resulting input of nitrogen and phosphorus species is largely determined by the prevalent flow characteristics and redox conditions in the freshwater seawater mixing zone. Denitrification, the key NO$_3^-$ removing process, prevails under anoxic conditions, resulting in dissolved inorganic nitrogen to phosphorus ratios (N:P ratios) of submarine groundwater discharge lower than that of dissolved organic matter (DOM). Both low fluid flow rates and high DOM reactivity enhance the depletion of NO$_3^-$ through denitrification. On the other hand, extremely high N:P ratios are predicted when anoxic groundwater meets oxic seawater, due to the localized P retention onto the Fe(OH)$_3$ that precipitate along the redox interface. Due to the occurrence of coupled nitrification-denitrification, the position of the NO$_3^-$ and NH$_4^+/PO_4^{3-}$ plumes, relative to the water table, is reversed compared to their original positions at the landward source.

Index Terms submarine groundwater discharge, subterranean estuaries, nutrients, nitrogen, phosphorus, reactive transport modeling

I. INTRODUCTION

Submarine groundwater discharge (SGD) is an important transport pathway for a variety of dissolved chemical species such as nutrients, heavy metals, radionuclides and organic compounds from land to coastal waters [1]. Although in most areas SGD rates are generally low compared to riverine inputs (worldwide range of 0.03 to 454 m yr$^{-1}$, most of which fall below 36 m yr$^{-1}$ and may consist of both freshwater and recirculated seawater; [2]), the high concentration of nutrients in freshwater SGD can significantly contribute “new” nutrients to the coastal zone, especially in areas strongly influenced by human activities. The discharge of nitrogen (N) and phosphorus (P)-contaminated groundwater, commonly originating from fertilizer/manure leachates and waste-water from septic systems, can trigger eutrophication and the growth of nuisance algal blooms, causing the degradation of coastal environments [3].

Most studies to date have focused on the identification of SGD hotspots and quantification of SGD rates [4]-[6]. However, the chemical composition of SGD is not only affected by the landward freshwater sources and discharge rates, but also by the reactions within the subterranean estuaries, the mixing zone of freshwater and seawater in coastal aquifers [7]. Nutrient dynamics in these coastal mixing zones, and hence SGD of nutrients, are strongly determined by the redox characteristics of freshwater and seawater ([8]-[12]). For this reason, redox processes in coastal aquifers, particularly within the subterranean estuaries, are now receiving more attention, although detailed studies on the biogeochemistry are still very limited.

In a review on nutrient inputs to the coastal ocean through SGD, [2] presented four hypothetical conceptual models which illustrate the fate of nutrients (NO$_3^-$, NH$_4^+$, PO$_4^{3-}$) in subterranean estuaries characterized by different redox conditions:

Case 1): oxic groundwater meeting oxic seawater
Case 2): oxic groundwater meeting anoxic seawater
Case 3): anoxic groundwater meeting oxic seawater
Case 4): anoxic groundwater meeting anoxic seawater
For each case, the authors discussed the effect of the prevailing biogeochemical reactions on the discharge of N and P. Here, we use a 2D density-dependent reactive transport model to simulate the water flow and biogeochemical processes affecting N and P in the four scenarios outlined above, using a model coastal aquifer with a typical freshwater/seawater wedge. The fresh groundwater is assumed to be contaminated with a NO\textsubscript{3}/NH\textsubscript{4}/PO\textsubscript{4} plume, which typically originates from sewage effluents or agriculture activities along the coast. We first perform four baseline simulations to assess the impact of prevalent redox conditions on nutrient distributions and the subsequent dissolved inorganic nitrogen to phosphorus ratios (N:P ratios) of the freshwater and recirculated components of SGD. Then we extend our study to test the effect of a) higher transverse dispersivity ($\alpha_z$) on the N:P ratios of SGD in Case 1, b) additional NO\textsubscript{3} removal through denitrification with Fe\textsuperscript{2+} as electron-donor in the oxic/anoxic redox interface of Case 2, c) higher freshwater discharge rates and d) higher DOM reactivity on NO\textsubscript{3} removal through denitrification in Case 3.

II. MODEL SETUP

A schematic diagram of the rectangular model domain, representing a 60 m x 20 m confined aquifer, including the set of typical aquifer parameters used in the simulations, is given in Fig. 1.

The list of chemical constituents included in the model are NO\textsubscript{3}, NH\textsubscript{4}, PO\textsubscript{4}, PO\textsubscript{4}(ads), O\textsubscript{2}, DOM, Fe\textsuperscript{2+}, Fe(OH)\textsubscript{3}(s) and Ca\textsuperscript{2+} and salt. Table 1 provides the concentrations in the different parts of the aquifers assumed in the four scenarios. In each case, the aquifer is contaminated by a freshwater NO\textsubscript{3}, NH\textsubscript{4} or PO\textsubscript{4} plume of constant composition, depending on the groundwater redox conditions. Both oxic and anoxic aquifers are considered to be impacted by a NO\textsubscript{3} plume. Anoxic aquifers (Cases 3 and 4) contain NH\textsubscript{4}, while in the scenarios with oxic groundwater (Cases 1 and 2), it is assumed that the NH\textsubscript{4} plume has been converted to NO\textsubscript{3}. A PO\textsubscript{4} plume is considered in all cases, but with a much lower concentration in the oxic groundwater (Cases 1 and 2). The extended reaction network, comprising 6 kinetic reactions, is given in Table 2, while Table 3 contains the list of reaction parameter values. The rate laws for dissolved organic matter (DOM) degradation (Table 2) allow a smooth transition from aerobic degradation to denitrification to Fe(OH)\textsubscript{3} reduction, assuming a first order rate with respect to the electron donor, DOM, and a pseudo Michaelis-Menton type relationship with respect to the electron acceptor [13]. Nitrification, Fe\textsuperscript{2+} reoxidation and Fe\textsuperscript{2+} denitrification are described by bimolecular rate laws. PO\textsubscript{4} removal is assumed to occur through adsorption of dissolved PO\textsubscript{4}, leading to the instantaneous redistribution of total PO\textsubscript{4} into dissolved and sorbed P, PO\textsubscript{4}(ads). Sorption is represented by a sorption isotherm, in which the adsorption coefficient ($K_d$) is a function of the concentration of Fe(OH)\textsubscript{3}.

\[ K\cdot Fe(OH)_3\cdot \frac{\varphi}{(1-\varphi)} = \frac{[PO_{4(ads)}]}{[PO_{4(sat)}]} \]  

i.e. $K_d = K\cdot Fe(OH)_3$. The effects of variations in ionic strength and temperature between the freshwater and seawater are neglected.

Model calculations are performed for a saturated porous medium, using the classical Darcy flow approximation. In each time step, the pressure field is first calculated, taking into account density variations as a linear function of salinity. From the calculated pressure field, the velocity field is derived using the Darcy law, and the anisotropic dispersion tensor is obtained for the given longitudinal and transverse dispersivities [14]. Concentration fields are then computed by solving mass conservation equations for all species, considering diffusive/dispersive and advective transport for solutes. Reaction rates are evaluated from the previous concentration field for both solids and solutes (Table 2). We use a Galerkin finite element formulation for spatial discretization and a conjugate gradient approach to solve the linear set of equations at each time step [15], [16]. Boundary and initial conditions for the simulations are provided in Fig. 1 and Table 1.

III. RESULTS

A. Baseline Simulations

Fig. 2 shows the steady-state salt wedge and SGD velocities at the seaward boundary (60 m) representing average flow conditions, not taking into account the effect of tidal pumping or seasonal variation in freshwater discharge. Concentration distributions for NO\textsubscript{3}, NH\textsubscript{4} and PO\textsubscript{4} for Cases 1-4 at steady-state are shown in Fig. 3. A set of analogous simulations are also performed in which all reactions are turned off, referred to as the “conservative” runs. For comparison, Fig. 4 shows the concentration profiles of the most important solute species at the seaward boundary, together with their respective “conservative” ones.

Due to the absence of reactive DOM (Table 1), the results for the completely oxic model submarine estuary show very limited transformation or removal of all species, Case 1 (Figs. 3a-c, 4a-e). The propagation of the NO\textsubscript{3} plume towards the sea is virtually conservative. A drop in the peak discharge concentration relative to the source concentration is observed due to dispersion. The concentrations of NH\textsubscript{4} and PO\textsubscript{4} are relatively low, even though PO\textsubscript{4} removal through adsorption is not possible, since no “in situ” formation of Fe(OH)\textsubscript{3} occurs.

The trend in the NH\textsubscript{4} profile in the oxic groundwater/anoxic seawater case, Case 2 (Fig. 4g), indicates a redistribution relative to the “conservative” profile, resulting in lower concentrations in the freshwater part due to nitrification and higher concentrations in the seawater as a result of DOM degradation. The NH\textsubscript{4} transported in the anoxic seawater is nitrified to NO\textsubscript{3}, slightly increasing the NO\textsubscript{3} concentrations along the interface (Fig. 4f).

\[ K\cdot Fe(OH)_3\cdot \frac{\varphi}{(1-\varphi)} = \frac{[PO_{4(ads)}]}{[PO_{4(sat)}]} \]
Fig. 1. Schematic diagram of the model setup, showing the model domain, boundary conditions, aquifer parameters used in the baseline simulations and depths of the nutrient source plumes.

Fig. 2. Steady-state Ghyben-Herzberg type saltwedge formed in the model coastal aquifer.

### Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration in oxic groundwater</th>
<th>Concentration in anoxic groundwater</th>
<th>Concentration in oxic seawater</th>
<th>Concentration in anoxic seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$</td>
<td>0.25 (a)**</td>
<td>0.25 (a)**</td>
<td>0.02 (b)</td>
<td>-</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>-</td>
<td>0.2 (c) **</td>
<td>0.001 (b)</td>
<td>0.01 (c)</td>
</tr>
<tr>
<td>PO$_4$</td>
<td>0.001 (a) **</td>
<td>0.05 (a)**</td>
<td>0.001 (b)</td>
<td>0.3 (c)</td>
</tr>
<tr>
<td>PO$_4$(ads) (s)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.05 (a)</td>
<td>0.0</td>
<td>0.2 (b)</td>
<td>0.0</td>
</tr>
<tr>
<td>DOM</td>
<td>-</td>
<td>0.75 (c)</td>
<td>-</td>
<td>0.33 (c)</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>-</td>
<td>0.1 (d)</td>
<td>-</td>
<td>0.1 (d)</td>
</tr>
<tr>
<td>Fe(OH)$_3$ (s)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>-</td>
<td>1.0 (c)</td>
<td>10.5 (b)</td>
<td>6.7 (c)</td>
</tr>
<tr>
<td>Salt</td>
<td>0.28 (d)</td>
<td>0.28 (d)</td>
<td>27.0 (d)</td>
<td>27.0 (d)</td>
</tr>
</tbody>
</table>

(a) [2]; (b) [23]; (c) [12]; (d) [24]
(-) low concentrations, assumed to be 0
* units for solutes are in mmol dm$^{-3}$ pore water, denoted as mM; solids (s) are in mmol dm$^{-3}$ solids, denoted as mmol dm$^{-3}$; units for salt are ‰.
However, the net removal of NO$_3^-$ is only marginal, mainly because denitrification is hindered by the presence of O$_2$ in the oxic groundwater. These results are in qualitative agreement with field observations by Uchiyama and co-workers [9] who report the occurrence of high NO$_3^-$ concentrations near the shore of Hasaki Beach in Japan, which they attribute to nitrification in the inland aerobic aquifer. Towards the shoreline, dissolved N in the freshwater part mixes with N supplied from the mineralization of organic matter from the seabottom, analogous to our modeled NH$_4^+$-rich seawater endmember. A net removal of modeled PO$_4^{3-}$ is observed since PO$_4^{3-}$ is absorbed on the iron oxides that form on the oxic/anoxic interface. This results in the retention and restricted landward penetration of the seawater PO$_4^{3-}$ front (Fig. 3f).

The nutrient distributions and species profiles obtained in Case 3, where anoxic groundwater meets oxic seawater, are given in Fig. 3g-i and Fig. 4k-o. Here, significant NO$_3^-$ removal through denitrification is observed in the anoxic aquifer (Fig 3g), which however, is not enough to consume the DOM completely (Fig. 4o). This implies that denitrification is either limited by the low reactivity of the DOM or by the high water flow velocity. Comparison of the NO$_3^-$ and NH$_4^+$ profiles with the “conservative” ones indicate the occurrence of coupled nitrification-denitrification at the redox interface. Denitrification lowers the peak NO$_3^-$ concentration from ~0.06 mM to ~0.02 mM at a depth of 1 m, while a new NO$_3^-$ peak develops at a depth of ~3 m as a result of nitrification. The upward shift in the NH$_4^+$ plume also reflects the occurrence of coupled nitrification-denitrification, with a depletion of NH$_4^+$ at a depth of ~3 m and production at ~1 m. It is interesting to note that, as a result of coupled nitrification-denitrification and PO$_4^{3-}$ adsorption, the depths of the NO$_3^-$ and NH$_4^+$/PO$_4^{3-}$ peaks at the seaward boundary are reversed relative to their original position at the landward source side. The PO$_4^{3-}$ plume is attenuated through sorption to concentrations as low as 0.005 mM prior to discharge. Such a phenomenon occurs in the subterranean estuary of Waquoit Bay, MA, where the formation of an “Iron Curtain” scavenges the freshwater NO$_3^-$ prior to discharge into the coastal zone [10], [17]. The freshwater NO$_3^-$ at the same site travels as a plume and apparently discharges to the bay within the intertidal zone [18] without major denitrification, possibly due to the lack of labile DOM or high water flow rates.

In a completely anoxic subterranean estuary, Fig. 3j-l and Fig. 4p-t, most of the anthropogenic NO$_3^-$ is consumed, causing the plume maximum to drop from ~0.05 mM to 0.01 mM in the anoxic groundwater. Yet, the shape of the profile is distinct from Case 3, since there is no additional NO$_3^-$ production from nitrification. Our model postulates an increase in the NH$_4^+$ peak due to DOM degradation, but virtually no PO$_4^{3-}$ removal due to the absence of Fe(OH)$_3$. Nevertheless, the calculated saturation indices for hydroxyapatite, assuming a constant pH of 7.0 (not shown) indicate that PO$_4^{3-}$ removal through hydroxyapatite precipitation may play a role, especially in carbonate aquifers. This was reported for an anoxic, saline Floridian aquifer where almost complete removal of dissolved wastewater phosphorus through the formation crystalline calcium phosphate occurs [19].

The overall effect of the reactions on N and P inputs into the coastal ocean via SGD is illustrated in Fig. 5a-d, which shows the N:P profiles at the seawater boundary compared to the corresponding “conservative” ones. The N:P ratio of SGD in Case 1 decreases from a maximum of 600 in the freshwater part, down to ~20 in the recirculated SGD, representing the marine endmember (Table 1, Fig. 5a) These relatively high values of N:P ratios (greater than twice the N:P ratio on the landward domain boundary) in the freshwater discharge zone are the result of the converging flow in the freshwater part, rather than of reaction. Comparison of the N:P profile obtained in Case 2 with the “conservative” counterpart shows an significant increase in the N:P ratio of the freshwater SGD due to PO$_4^{3-}$ adsorption (Fig. 5b). Nitrification has no major effect on the N:P ratios since it is merely the interconversion of N from one species, NH$_4^+$, to another NO$_3^-$. In Case 3 (Fig. 5c), the N:P of the freshwater SGD increases drastically primarily due to localized retention of PO$_4$ on Fe(OH)$_3$ at the interface. On the contrary, in Case 4, the N:P of SGD is close to the Redfield ratio due to the lack of PO$_4$ retention in the anoxic subterranean estuary. The N:P ratios for the four cases are plotted together in Fig. 5e, to highlight the variety in the possible range resulting from different redox conditions. Cases 1 and 4 show a smooth decline with depth, whereas the profiles in Cases 2 and 3 reflect localized sorption of PO$_4$.

**B. Sensitivity Analysis**

A sensitivity analysis is performed to investigate factors that are poorly known and are expected to have a significant impact on the baseline model results. We specifically focus on the role of dispersion, denitrification pathways, flow rate and DOM reactivity (Table 4). Doubling the value of $\alpha$ in Case 1, the most conservative scenario with minimal feedbacks to and from reactions, we observe a broadening of the freshwater-seawater interface, an increased overlap between the freshwater and seawater species and an increased transverse dispersion of the NO$_3^-$ plume (Fig. 6a). The broadening of the NO$_3^-$ plume alone causes a decrease in the maximum N:P ratio to ~400 (Fig. 6b).

An alternative pathway for NO$_3^-$ reduction is its reaction with Fe$^{2+}$ as an electron-donor. Although field evidence of NO$_3^-$ reduction by Fe$^{2+}$ has been presented by [20], the exact reaction mechanism is still not fully understood [21], [22]. However, the inclusion of Fe$^{2+}$ denitrification, which is assumed to follow a bimolecular rate law in our model, leads to little additional NO$_3^-$ removal (Fig. 7a). In contrast, the removal of PO$_4^{3-}$ is enhanced substantially through sorption on the additional Fe(OH)$_3$ produced through the oxidation of Fe$^{2+}$ (Fig. 7b, c).

Comparison of Fig. 8a and b show that high groundwater flow rates reduce the efficiency of NO$_3^-$ removal through denitrification from the core of the plume. As suggested by Capone and Slater [8], intermediate groundwater flow rates are a prerequisite for denitrification to occur. High rates will result in dominance of advective transport over reaction,
whereas low rates will limit denitrification due to a limited NO$_3^-$ supply. The second sensitivity analysis run for Case 3, (Fig. 9) shows that the reactivity of the DOM is another important factor which determines the extent of NO$_3^-$ removal. On increasing the rate of DOM degradation by one order of magnitude, near complete removal of NO$_3^-$ is obtained close to its freshwater source (Fig. 9b).

IV. CONCLUSIONS

This study demonstrates that subterranean estuaries are biogeochemically active environments, characterized by complex nutrient dynamics. The results from the four baseline simulations show that the fate of N and P strongly depends on the redox conditions along the freshwater seawater continuum. However, the extent of freshwater and seawater mixing, assessed by changing the transverse dispersivity and flow rates, also plays a role on the degree of nutrient transformation/removal.

Denitrification and P sorption are the two key processes that determine the extent of nutrient removal. Denitrification is coupled not only to the reactivity of DOM, but also to the flow dynamics, since more efficient removal of NO$_3^-$ is observed at lower rates of water flow. P sorption is mainly important in Cases 2 and 3, where a redox interface is formed when groundwater and seawater with different redox conditions interact. The overall effect of the various redox processes occurring within each subterranean estuary is reflected in the molar N:P ratio of the SGD. The different behaviors exhibited by N and P lead to a wide range of N:P ratios of SGD, spanning from ~0.03 to 30000.

REFERENCES


Fig 3 Simulated 2D steady-state distributions for NO$_3^-$, NH$_4^+$ and PO$_4$ obtained for Case 1 (oxic groundwater-oxic seawater), Case 2 (oxic groundwater-anoxic seawater), Case 3 (anoxic groundwater-oxic seawater) and Case 4 (anoxic groundwater-anoxic seawater)
Case 1 (Oxic groundwater/Oxic seawater)

Case 2 (Oxic groundwater/Anoxic seawater)
Fig. 4. NO$_3$, NH$_4^+$, PO$_4$, O$_2$ and DOM concentration profiles at the seaward boundary for the top 10 m depth (solid lines), compared with their respective conservative profiles (dashed lines). The horizontal dotted line indicates the freshwater-seawater interface, based on the modeled salinity.
**Fig. 5.** Simulated N:P profiles for Cases 1-4 (solid lines, panels a-d), together with the respective profiles obtained in conservative runs (dashed lines) over the top 10 m. Note that the x-axis of panel e) is on a logarithmic scale. The horizontal dotted line indicates the freshwater-seawater interface, based on the modeled salinity.

**Fig. 6.** Profiles of NO$_3^-$ (a) and N:P ratio (b) over the top 10 m on the seawater boundary obtained with $\alpha T = 0.1$ m, compared to the baseline profiles with an $\alpha T = 0.05$ m (Case 1). The horizontal dotted line indicates the freshwater-seawater interface, based on the modeled salinity.

**Fig. 7.** Profiles of NO$_3^-$ (a), PO$_4$ (b) and Fe(OH)$_3$ (c) over the top 10 m, obtained when Fe$^{2+}$ denitrification is included in the reaction network (solid lines), compared to the baseline profiles (dashed lines) (Case 2). The horizontal dotted line indicates the freshwater-seawater interface, based on the modeled salinity.
Fig. 8. Difference in NO$_3$ concentrations for Case 3 (mM) (a) between baseline and conservative run, with a groundwater head of 0.4 m and (b) sensitivity run 3 and corresponding conservative run with a groundwater head of 0.8 m, simulating higher water flow velocity.

Fig. 9. Difference in NO$_3$ concentrations (mM) for Case 3 (a) between baseline and conservative run (identical to Fig. 8a above but plotted on a different scale) and (b) sensitivity run 4 ($k_{so} = 3.0 \times 10^{-5}$ m/s; Table 4) and corresponding conservative run.
### Table 2
THE REACTION NETWORK AND KINETIC FORMULATIONS USED IN THE MODEL

<table>
<thead>
<tr>
<th>Name</th>
<th>Reaction</th>
<th>Kinetic formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reaction network used in “Base simulations”</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxic degradation</td>
<td>CH$_4$O$^2$ + xO$_2$ + (-y + 2z)HCO$_3$ $\rightarrow$ (x - y + 2z)CO$_2$ + yNH$_4$ + zHPO$_4^{2-}$ + (x - y + 2z)H$_2$O</td>
<td>If O$<em>2$ &gt; kmo2; Rate = $k</em>{f1}$[CH$_4$O] $\frac{O_2}{kmO2}$</td>
</tr>
<tr>
<td>Denitrification</td>
<td>CH$_4$O + 0.8xNO$_3$ $\rightarrow$ 0.4xN$_2$ + 0.2x + y - 2z)HCO$_3$ + (0.8x + y - 2z)CO$_2$ + yNH$_4$ + zHPO$_4^{2-}$ + (0.6x - y + 2z)H$_2$O</td>
<td>If O$<em>2$ &lt; kmo2; Rate = $k</em>{f1}$[CH$_4$O] $\frac{O_2}{kmO2}$</td>
</tr>
<tr>
<td>Fe(OH)$_3$ reduction</td>
<td>CH$_4$O + 4xFe(OH)$_3$ + (7x + y - 2z)HCO$_3$ $\rightarrow$ 4xFe$^2+$ + (8x + y - 2z)CO$_2$ + yNH$_4$ + zHPO$_4^{2-}$ + (3x - y + 2z)H$_2$O</td>
<td>If NO$_3$ &gt; kmno3; Rate = 0</td>
</tr>
<tr>
<td>Nitrification</td>
<td>NH$_4$ + 2O$_2$ + 2HCO$_3$ $\rightarrow$ NO$_3$ + 2CO$_2$ + 3H$_2$O</td>
<td>If NO$_3$ &lt; kmno3 and Fe(OH)$<em>3$ &gt; kmfe; Rate = $k</em>{f1}$[CH$_4$O] $\frac{1 - \frac{NO_3}{kmO2}}{kmO2}$</td>
</tr>
<tr>
<td>Fe$^{2+}$ reoxidation</td>
<td>Fe$^{2+}$ + 0.25O$_2$ + 2HCO$_3$ + 0.5H$_2$O $\rightarrow$ Fe(OH)$_3$ + 2CO$_2$</td>
<td>If NO$_3$ &lt; kmno3 and Fe(OH)$<em>3$ &lt; kmfe; Rate = $k</em>{f1}$[CH$_4$O] $\frac{1 - \frac{NO_3}{kmO2}}{kmO2}$</td>
</tr>
</tbody>
</table>

**Extended reaction network used in “Sensitivity Analysis”**

Denitrification via Fe$^{2+}$ | 5Fe$^{2+}$ + NO$_3$ + 12H$_2$O $\rightarrow$ 5Fe(OH)$_3$ + 5H$^+$ + 8H$_2$O | Rate = $k_{f1}$[Fe$^{2+}$][NO$_3$] |

### Table 3
LIST OF SENSITIVITY ANALYSIS RUNS

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Case</th>
<th>Parameter changed/reaction added</th>
<th>Aim</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>$\alpha_T$ = 0.1 m</td>
<td>To assess the effect of $\alpha_T$ on the extent of freshwater/seawater mixing</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>Denitrification via Fe$^{2+}$</td>
<td>To assess the additional NO$_3^-$ removal potential using Fe(II) as the electron donor</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>Freshwater head = 0.8 m</td>
<td>To test the effect of flow rate on denitrification</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>kfox = 3.0 $\times$ 10$^8$ s$^{-1}$</td>
<td>To test the effect of DOM reactivity on NO$_3^-$ removal</td>
</tr>
</tbody>
</table>

### Table 4
REACTION PARAMETER VALUES USED IN THE MODEL

<table>
<thead>
<tr>
<th>Parameter (units)</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{f1}$ (s$^{-1}$)</td>
<td>Rate constant for decomposition of DOM</td>
<td>3.0 $\times$ 10$^{-9}$ a</td>
</tr>
<tr>
<td>$k_{N1}$ (mM$^{-1}$ s$^{-1}$)</td>
<td>Rate constant for nitrification</td>
<td>4.8 $\times$ 10$^{-4}$ a</td>
</tr>
<tr>
<td>$k_{fox}$ (mM$^{-1}$ s$^{-1}$)</td>
<td>Rate constant for Fe$^{2+}$ reoxidation</td>
<td>6.4 $\times$ 10$^{-2}$ a</td>
</tr>
<tr>
<td>$k_{feox}$ (mM$^{-1}$ s$^{-1}$)</td>
<td>Rate constant for Fe$^{2+}$ reoxidation</td>
<td>6.4 $\times$ 10$^{-2}$ b</td>
</tr>
<tr>
<td>kmo2 (mM)</td>
<td>Limiting concentration of O$_2$</td>
<td>0.008 a</td>
</tr>
<tr>
<td>kmno3 (mM)</td>
<td>Limiting concentration of NO$_3^-$</td>
<td>0.002 a</td>
</tr>
<tr>
<td>kmfe (mmol dm$^{-3}$)</td>
<td>Limiting concentration of Fe(OH)$_3$</td>
<td>18.95 a</td>
</tr>
<tr>
<td>K (dm$^3$ mmol$^{-1}$)</td>
<td>Adsorption coefficient for PO$_4$ adsorption</td>
<td>1545 c</td>
</tr>
</tbody>
</table>

*a [25]; b assumed to be equal to Fe$^{2+}$ reoxidation with O$_2$; c calculated assuming a Fe(OH)$_3$ concentration of 0.2 mmol dm$^{-3}$ and a dimensionless K$_d$ of 309 [26]*