Simulating the Influence of Saltwater Intrusion on Coupled Element Cycles in Coastal Plain Wetlands

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Biogeochemistry of salt water intrusion
Biogeochemistry of salt water intrusion

Sulfate concentration (mg/L)

0 100 200 300 400 500 600
10/06 02/08 07/09 11/10 04/12 08/13
How do increases in sulfate concentrations associated with sea water influence the distribution of microbial pathways? (Trace gas production)
Redox Ladder as Organizing Concept
Connections in elemental cycles often lead to multi-dimensional, non-linear feedbacks both on the cycle of interest and other cycles.
Redox Ladder as Organizing Concept
Measured distribution from 5 years of surface and piezometer samples from coastal North Carolina wetland.
Michaelis-Menten Uptake: \( U_c = \frac{[C] \times \mu_{\text{max}}}{([C]+K_s)} \)

Average \( \mu_{\text{max}} \) and \( K_s \) from Piel and Gaudy, 1971, Appl. Microbiol., 21 pp. 253–256
Model Structure

Dissolved solutes

Available solutes

Uptake & release

\[
\begin{align*}
\text{O}_2 & \quad \text{CH}_4 \\
\text{C} & \quad \text{N} \\
\text{NH}_4^+ & \quad \text{NO}_3^- \\
\text{SO}_4^{2+} & \quad \text{Fe}^{2+} \\
\text{N}_2 & \quad \text{H}_2\text{S}
\end{align*}
\]
<table>
<thead>
<tr>
<th>Microbial Process</th>
<th>Reaction</th>
<th>$\Delta G_0'$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic organic carbon oxidation</td>
<td>$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$</td>
<td>-502</td>
</tr>
<tr>
<td>Denitrification:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrate reduction</td>
<td>$\text{CH}_2\text{O} + 2\text{NO}_3^- \rightarrow \text{CO}_2 + 2\text{NO}_2^- + \text{H}_2\text{O}$</td>
<td>-354</td>
</tr>
<tr>
<td>Nitrite reduction</td>
<td>$\text{CH}_2\text{O} + 2\text{NO}_2^- + 2\text{H}^+ \rightarrow \text{CO}_2 + \text{N}_2\text{O} + 2\text{H}_2\text{O}$</td>
<td>-481</td>
</tr>
<tr>
<td>Nitrous oxide reduction</td>
<td>$\text{CH}_2\text{O} + 2\text{N}_2\text{O} \rightarrow \text{CO}_2 + 2\text{N}_2 + \text{H}_2\text{O}$</td>
<td>-710</td>
</tr>
<tr>
<td>Nitrification:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium oxidation</td>
<td>$\text{O}_2 + \frac{2}{3}\text{NH}_4^+ \rightarrow \frac{2}{3}\text{NO}_2^- + \frac{4}{3}\text{H}^+ + \frac{2}{3}\text{H}_2\text{O}$</td>
<td>-183</td>
</tr>
<tr>
<td>Nitrite oxidation</td>
<td>$\text{O}_2 + 2\text{NO}_2^- \rightarrow 2\text{NO}_3^-$</td>
<td>-148</td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>$\text{CH}_2\text{O} \rightarrow \frac{1}{2}\text{CO}_2 + \frac{1}{2}\text{CH}_4$</td>
<td>-93</td>
</tr>
<tr>
<td>Methane oxidation</td>
<td>$\text{O}_2 + \frac{1}{2}\text{CH}_4 \rightarrow \frac{1}{2}\text{CO}_2 + \text{H}_2\text{O}$</td>
<td>-409</td>
</tr>
<tr>
<td>Dissimilatory nitrite reduction to ammonium</td>
<td>$\text{CH}_2\text{O} + 2\text{NO}_3^- + \frac{4}{3}\text{H}^+ \rightarrow \text{CO}_2 + 2\text{NH}_4^+ + \frac{1}{3}\text{H}_2\text{O}$</td>
<td>-319</td>
</tr>
<tr>
<td>Anaerobic ammonium oxidation</td>
<td>$\text{NH}_4^+ + \text{NO}_2^- \rightarrow 2\text{H}_2\text{O} + \text{N}_2$</td>
<td>-358</td>
</tr>
<tr>
<td>Sulfate reduction</td>
<td>$\text{CH}_2\text{O} + \frac{1}{2}\text{SO}_4^{2-} + \frac{1}{2}\text{H}^+ \rightarrow \frac{1}{2}\text{HS}^- + \text{CO}_2 + \text{H}_2\text{O}$</td>
<td>-104</td>
</tr>
<tr>
<td>Sulfide oxidation</td>
<td>$\text{O}_2 + \frac{1}{2}\text{HS}^- \rightarrow \frac{1}{2}\text{SO}_4^{2-} + \frac{1}{2}\text{H}^+$</td>
<td>-398</td>
</tr>
<tr>
<td>Iron reduction</td>
<td>$\text{CH}_2\text{O} + 4\text{Fe(OH)}_3 + 8\text{H}^+ \rightarrow 4\text{Fe}^{2+} + \text{CO}_2 + 11\text{H}_2\text{O}$</td>
<td>-232</td>
</tr>
<tr>
<td>Iron oxidation</td>
<td>$\text{O}_2 + 4\text{Fe}^{2+} + 6\text{H}_2\text{O} \rightarrow 4\text{FeOOH} + 8\text{H}^+$</td>
<td>-429</td>
</tr>
</tbody>
</table>
Important Assumptions:
Microbial assemblages will use the suite of metabolic pathways that maximize microbial growth.
Model Simulations

- Model implemented in linear programming (LPSolve) with Monte Carlo wrapper (Java)
- 10,000 values for each solute based on distributions from coastal NC wetland across range of DO concentration (0 – 10 mg / L)
- >300,000 single time step model runs
Example of model simulation results

**Aerobic Processes**

- **Low Carbon**
  - Fe - Ox
  - Nitr.

- **High Carbon**
  - S - Ox
  - DOC - Ox

**Anaerobic Processes**

- Meth.
- Fe-Red
- Annamox
- S - Red
- DNRA
- Denit.
- DNRA
- Denit.
Model-derived trace gas production

![Graph showing trace gas production (N2O, CH4, or CO2 mol / mol C Biomass) vs. Dissolved Oxygen Concentration (mg / L) for Low Carbon and High Carbon scenarios.]

- **Low Carbon**
  - CO2
  - N2O X 1000
  - CH4

- **High Carbon**
  - CO2
  - CH4

The graph illustrates the model-derived trace gas production for different dissolved oxygen concentrations, comparing low and high carbon scenarios.
Trace gas production and sulfate loading: Model generated hypotheses

Redox Ladder Hypotheses:
1. CH$_4$ decreases because sulfate reducers outcompete methanogens.
2. CO$_2$ increases because sulfate provides new source of electron acceptors to sulfate reducers.
**Model**

![](image1.png)

**Field**

![](image2.png)

**Lab**

![](image3.png)
Summary

With increasing SO$_4$ concentrations:

1. CH$_4$: In the model, field, and lab CH$_4$ emissions decrease EXCEPT high salt concentrations in the lab increase CH$_4$ emissions.

2. CO$_2$: In the model, CO$_2$ emissions increase. Field results are inconclusive. Laboratory CO$_2$ emissions decrease.
**Additional drivers and next steps**

**Geochemical**
- $\text{NH}_4^+$ released from sediments
- DOC flocculation

**Hydrologic:** Wet v. Dry

**Biological**
- Actual free energy yield.
- Novel pathways (AOM, AOS).
- Carbon breakdown (fermentation).
- Competition for $\text{H}_2$ (hydrogenotrophic methanogenesis).
- Stress.
Field Measurements

Model Simulations

Lab Experiments
Model simulations

- **S1**: C, N, and O.
- **S2**: DNRA & Anammox.
- **S3**: S and Fe.