In-stream Denitrification: Pilot Studies and Site Characteristics on a Headwater Stream

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Goal of this study

- Does the constant rate injection method have the **resolution** necessary to evaluate in-stream N removal rates in the settings and conditions found within lower-order streams in southern New England?
- How sensitive is this method to **seasonal variation**?
- What is the extent of **intra-seasonal variation**?
Study site

- 500 meter reach of a first/second order tributary
- Red maple swamp riparian area
- Located on sandy outwash with glaciofluvial deposits
- Forested watershed with some agricultural land use
- Representative of many streams in southern New England
Overview of Constant Rate Injection Method

- Isotopically enriched nitrate ($^{15}$N-KNO$_3$)
- Couple with gas tracer (SF$_6$) and a solute tracer (Br$^-$)
- Inject the solution into stream at steady, slow pace to create a plateau of concentration
- Comparison of downstream concentrations relative to tracer and measurement of $^{15}$N indicate N removal
Using the constant rate injection method

- Whole reach study (series of sampling stations along 500 m reach)
- In-stream cycling and groundwater N inputs
- Transport and removal processes
- Does not artificially elevate ambient NO$_3$-N...1$^{st}$ order kinetics
Replication and Sampling

- 3 replicate trials in the summer (August)
- 3 replicate trials in the fall (November)
- Sample prior to dosing and twice during the plateau
- At first and last stations, took samples every 5 min
  - assess rising and falling concentrations
  - quantify hydrologic processes with USGS model (dispersion, storage in the hyporheic zone or in slow moving pockets)
Stream Solute Transport Model (OTIS)

- **One dimensional** Transport with **Inflow** and **Storage**
- Downstream Br⁻ data
- Estimates where the solute/water is being held up
SPARROW model

- **SPAtially Referenced Regressions On Watershed attributes**
- Utilizes physical stream properties (flow & depth)
- Predicts:
  - uptake length (average distance traveled by a nitrate molecule before it is denitrified in a stream reach)
  - fraction of N delivery downstream
Results: Ambient characteristics

<table>
<thead>
<tr>
<th></th>
<th>Upstream Discharge (L s(^{-1}))</th>
<th>Downstream Discharge (L s(^{-1}))</th>
<th>Mean Stream Depth (m)</th>
<th>Time of Travel (hours)</th>
<th>Average Reach Velocity (m s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer 2006</td>
<td>4.3 (0.37)</td>
<td>5.3 (0.48)</td>
<td>0.06 (0.42)</td>
<td>1.30 (0.01)</td>
<td>0.11 (0.01)</td>
</tr>
<tr>
<td>Fall 2006</td>
<td>28 (1.48)</td>
<td>49 (8.26)</td>
<td>0.14 (0.48)</td>
<td>1.24 (0.01)</td>
<td>0.11 (0.01)</td>
</tr>
</tbody>
</table>

Data is mean for all three trials (SE)
Denitrification rate calculation

1. NO$_3^-$ disappearance (Downstream NO$_3^-$-N : Br$^-$ ratios)

2. $^{15}$N gas flux (corrected for evasion using SF$_6$)

3. $^{15}$NO$_3^-$-N mass balance (corrected using Br$^-$)
<table>
<thead>
<tr>
<th>Date</th>
<th>Mass Removal g day(^{-1})</th>
<th>Mass Removal µmoles/m(^2)/hr</th>
<th>Percent Removal</th>
<th>Uptake lengths (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8/7/2006</td>
<td>0.12 (0.08)</td>
<td>0.7</td>
<td>&lt; 0.1</td>
<td>2510</td>
</tr>
<tr>
<td>8/9/2006</td>
<td>0.03 (0.01)</td>
<td>0.2</td>
<td>&lt; 0.1</td>
<td>9030</td>
</tr>
<tr>
<td>8/11/2006</td>
<td>1.82 (1.33)(^a)</td>
<td>10.8</td>
<td>&lt; 0.1</td>
<td>180</td>
</tr>
<tr>
<td>Fall</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11/7/2006</td>
<td>0.08 (0.01)</td>
<td>0.5</td>
<td>&lt; 0.1</td>
<td>7340</td>
</tr>
<tr>
<td>11/10/2006</td>
<td>1.31 (0.91)</td>
<td>7.8</td>
<td>&lt; 0.1</td>
<td>340</td>
</tr>
<tr>
<td>11/15/2006</td>
<td>1.41 (0.71)</td>
<td>8.4</td>
<td>&lt; 0.1</td>
<td>340</td>
</tr>
</tbody>
</table>

\(^a\) Indicates significant increase.
Results: The Models

- SPARROW predicted that uptake length was > 170 km (agreeing with our observations)
- OTIS model indicates minimal stream storage zone area and hyporheic exchange in summer and fall
Results: GIS analysis of RI landscape

- Our stream’s features were representative of many RI streams
- Headwater streams account for 70% of RI drainage network
- 36% of streams in RI similar to study stream
- Average length of RI headwater streams is about 1.4 km (100 fold less than uptake length)
Results: Seasonal variation

- Removal rates remained consistent
- Discharge, DOC, temp...no affect on removal rates
- No major difference between seasons in ambient NO$_3$-N and stream reach retention times ($1^{st}$ order kinetics)
Results: Within-season variation

- Discharge variable in the fall
- Downstream ambient NO$_3$-N variable in the summer
- No notable impacts on removal rates
<table>
<thead>
<tr>
<th>Study Site</th>
<th>Mean Depth (m)</th>
<th>Ambient NO$_3$-N (mg l$^{-1}$)</th>
<th>Denitrification Uptake Length (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar Creek (Bohkle et al., 2007)</td>
<td>0.19</td>
<td>0.99</td>
<td>17,950</td>
</tr>
<tr>
<td>Walker Branch (Mulholland et al., 2000)</td>
<td>0.05</td>
<td>0.02</td>
<td>0.5</td>
</tr>
<tr>
<td>Walker Branch (Mulholland et al., 2004)</td>
<td>0.03</td>
<td>0.03</td>
<td>0.217</td>
</tr>
<tr>
<td>Illinois agricultural stream (Royer et al., 2004)</td>
<td>0.31</td>
<td>7.78</td>
<td>166- &gt;200</td>
</tr>
<tr>
<td>Rhode Island stream (Milliman)</td>
<td>0.10</td>
<td>0.90</td>
<td>176-9,030</td>
</tr>
</tbody>
</table>
“What-if scenarios” based on Mulholland et al. (2000) denitrification rates

<table>
<thead>
<tr>
<th></th>
<th>Ambient NO$_3$- N (mg l$^{-1}$)</th>
<th>Velocity (m s$^{-1}$)</th>
<th>Denitrification rate (μmoles/m$^2$/hr)</th>
<th>Denitrification Uptake length (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Summer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actual Upper Rate</td>
<td>1.1</td>
<td>0.11</td>
<td>10.8</td>
<td>176</td>
</tr>
<tr>
<td>Hypothetical</td>
<td>1.1</td>
<td>0.11</td>
<td>123.3</td>
<td>15</td>
</tr>
<tr>
<td><strong>Fall</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actual Upper Rate</td>
<td>0.7</td>
<td>0.11</td>
<td>8.4</td>
<td>338</td>
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<tr>
<td>Hypothetical</td>
<td>0.7</td>
<td>0.11</td>
<td>123.3</td>
<td>23</td>
</tr>
</tbody>
</table>
Take home messages

• Average headwater stream length in RI is substantially less than uptake lengths.
• Residence time and ambient NO$_3$-N conditions ($1^{st}$ order kinetics) important
• $^{15}$N enrichment studies are costly
Future work

- Focus on settings with extended retention times and benthic interactions
- Impoundments and streams connected to swamps and ponds
- Review constant rate injection method for these studies- high costs associated with long retention times