Nitrogen Biogeochemistry

Summary: Year 2

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Karst Environmental
Pete Butt, et al.
Objectives

1. Characterize sources of N and potential denitrification loss in soils of major land uses

2. Determine the impact of denitrification within the Surficial/Floridan Aquifer Systems on N loading to Silver Springs

3. Identify hot spots and hot moments of N delivery and attenuation within the Silver Springs springshed
Aquifers

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PC1</th>
<th>PC2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved CH₄</td>
<td>-0.42</td>
<td>0.04</td>
</tr>
<tr>
<td>(DO)</td>
<td>0.36</td>
<td>-0.32</td>
</tr>
<tr>
<td>Water Temperature</td>
<td>0.39</td>
<td>-0.06</td>
</tr>
<tr>
<td>Ca-T</td>
<td>0.12</td>
<td>0.38</td>
</tr>
<tr>
<td>Cu-T</td>
<td>0.35</td>
<td>0.34</td>
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<tr>
<td>Fe-T</td>
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<td>0.45</td>
</tr>
<tr>
<td>Cl</td>
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<td>0.46</td>
</tr>
<tr>
<td>SO₄²⁻-T</td>
<td>0.30</td>
<td>0.40</td>
</tr>
<tr>
<td>NH₄⁺-T</td>
<td>-0.42</td>
<td>0.20</td>
</tr>
<tr>
<td>TOC</td>
<td>-0.35</td>
<td>0.15</td>
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</tbody>
</table>
$\text{NO}_3^-$ Stable isotopes ($\delta^{18}\text{O}$ and $\delta^{15}\text{N}$)

- Water extractable solution

Schematic of typical ranges of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate from various sources as well as the isotopic effect of denitrification. (Adapted from http://wwwrcamnl.wr.usgs.gov/isoig/isopubs/Fig16-9.jpg)
Mixed nursery/pasture (L. Weir)
Dissolved gases

- Dissolved \(N_2\)
  - Soluble \((P_{N2})\)
  - Produced by denitrification
- Dissolved noble gases (Ar, Ne, ...)
  - Recharge temperature
  - Excess air
Denitrification Progression

A chart showing the progression of a variable, labeled $\delta^{15}$N-NO$_3$ (%), on the y-axis, against $f(\text{NO}_3)_R$ on the x-axis. Different data points are color-coded to represent various environments: Agriculture, Urban, Forest, Wetlands, East vent, and West vent. The data points are scattered across the chart, indicating the progression of denitrification in these environments.
Source ID
Sources: Conclusions/Next steps

• Springshed sources
  • Ag and Urban, West (mostly-unconfined)
  • Highest in 10yr capture zone

• Source ID
  • Most wells/vents, $\delta^{15}$N=7‰, $\delta^{18}$O=5‰
  • Evidence for both organic (Ag) and inorganic sources (Urban)

• Additional vents
  • Source, denitrification, chemical composition

• Boron and B isotopes to separate soil N and manure/urban?
Hotspots

Goldscheider et al. (2006)
Denitrification

Residential

Nursery/Residential

Sprayfield/Cattle

Horse Farm

Relic marine layers
Soil Denitrification
Soil Denitrification

Denitrification (20°C and 35% WFPS) by Land Use

![Bar chart showing N2O emissions (nmol/dw/hr) by land use and nitrogen application rate.]

- Septic
- LD
- HD
- Crop
- Turf

Legend:
- *4 kg/ha N
- *30 kg/ha N
- *50 kg/ha N
Soil Denitrification

LD Pasture: %WFPS vs Denitrification

- 25°C, $R^2 = 0.9996$
- 20°C, $R^2 = 0.989$
- 15°C, $R^2 = 1$

N2O (nmol/dw/hr) vs WFPS (%)
N Processes, Controls

\[
\text{CH}_4 + 4\text{NO}_3^- \rightarrow \text{CO}_2 + 4\text{NO}_2^- + 2\text{H}_2\text{O}
\]

\[
3\text{CH}_4 + 8\text{NO}_2^- + 8\text{H}^+ \rightarrow 3\text{CO}_2 + 4\text{N}_2 + 10\text{H}_2\text{O}
\]

\[
\text{CH}_4 + \text{NO}_3^- + 2\text{H}^+ \rightarrow \text{CO}_2 + \text{NH}_4^+ + \text{H}_2\text{O}
\]

![Graphs showing dissolved N\textsubscript{2}O and dissolved N\textsubscript{2}O against NO\textsubscript{X}-N and NH\textsubscript{4}-N concentrations.]

- High DO, high dissolved N\textsubscript{2}O nitrification??
- Low NH\textsubscript{4}-N, high dissolved N\textsubscript{2}O, nitrification??

![Graph showing dissolved N\textsubscript{2}O against Dissolved O\textsubscript{2} and Dissolved N\textsubscript{2} against Dissolved N\textsubscript{2}O.]

- High dissolved N\textsubscript{2}, low dissolved N\textsubscript{2}O
Hot Moments?

- Seasonal
  - Wet/Dry season changes
  - Growth cycles, Land use activities
- Events
  - Storm events, stormwater discharges

![Graph showing discharge and nitrate concentrations over time with highlighted months and events such as TS Fay.]

**East Mammoth**

**West Mammoth**

- Discharge
- E. Vent
- W. Vent
- Nitrate (mg/L N)
- Year range: 2004 to 2014
Dry/Wet Seasonality

*Graph showing dissolved N2 and N2:Ar concentrations for both dry and wet seasons across various samples labeled M-0771 to M-0787.*
- $\text{N}_2\text{O}$ highest in dry season

- $\text{CH}_4$ highest in wet season
Conclusions/Next steps

- Improved soil model:
  - N loading/level, moisture (rainfall), temperature
- Significant N loss (soils and aquifer)
  - Highest rates in Forest/Wetland/Ag
  - Highest levels in >100yr CZ (also 2yr CZ)
  - Highest rates from Estimate ~35% NO₃ in Silver Spring
- Seasonality/variability
  - Denitrification (CH₄/DO)
  - Sources (N₂O/NO₃)
- Potential for non-C-based nitrate attenuation pathways
  - N₂O-source indicator?
  - CH₄-hotspots?
- Age dating to estimate rates?