Evaluating Anthropogenic Impacts to the Nitrogen Cycle Based on the Isotopes of Nitrate

Meredith G. Hastings

Environmental Change Initiative
Department of Geological Sciences
Brown University
Lots of folks to acknowledge!

- Eric Steig and Julia Jarvis (Univ of Washington)
- IsoLab at UW (Shelley Kunasek, Peter Neff, Andy Schauer)
- Jack Dibb (UNH)
- VECO Summit crew and Bella Bergeron (ICDS)
- Danny Sigman and the Sigman Lab (Princeton)

- JISAO and UW Atmospheric Sciences
- NSF Office of Polar Programs

And thank you for your attention!
Talk Overview

- Motivation and interest in studying atmospheric nitrate
- Using isotopes of nitrate to elucidate sources and chemistry
- Variations in the isotopes of nitrate in a 100-meter ice core from Summit, Greenland
  ⇒ evidence of fossil fuel emissions impact on nitrate record
- Conclusions/Implications
NOx from soils

Ozone, OH

Nitrogen oxides

NOx

Nitric Acid/Nitrate

HNO3

Wet + Dry Deposition
Oxidizing Capacity of the Atmosphere

NO\textsubscript{x}, NO\textsubscript{y}, O\textsubscript{3}, OH

Biogeochemical Cycling

Ecosystem Impacts

Watershed Impacts

Nutrient cycling

Climate

Chemistry

Air Quality

Human Health

Acid Rain

Natural and Anthropogenic Source Emissions

Biogeochemical Cycling

Climate

↓↑

Chemistry
Sources of NOx (and therefore NO₃⁻):

- Fossil fuel burning: ~25.6 Tg N/yr*
- Biogenic soil emissions: 8.9*
- Biomass burning: 5.8*
- Lightning: 5.0
- Aircraft: 0.6
- N₂O oxidation in strat.: 0.6

* e.g., Jaeglé et al., 2005
### NO$_x$ Chemistry

#### (daytime or high-latitude summer)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO + O$_3$</td>
<td>NO$_2$ + O$_2$</td>
</tr>
<tr>
<td>NO$_2$ + $hv$</td>
<td>NO + O</td>
</tr>
<tr>
<td>NO$_2$ + OH $^M$</td>
<td>HNO$_3$</td>
</tr>
</tbody>
</table>

#### (nighttime or high-latitude winter)

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<tbody>
<tr>
<td>NO$_2$ + O$_3$</td>
<td>NO$_3$ + O$_2$</td>
</tr>
<tr>
<td>NO$_3$ + NO$_2$ $^M$</td>
<td>N$_2$O$_5$</td>
</tr>
<tr>
<td>N$_2$O$_5$ + H$_2$O $^{aerosol}$</td>
<td>2HNO$_3$</td>
</tr>
</tbody>
</table>

Isotopes of NO$_3^-$ reflect NO$_x$ sources and chemistry.
Overview on Isotopes

• denote isotopes in form $^{14}\text{N}$ where 14 is the mass number, or neutrons+protons

\[
\begin{align*}
\text{N} : & \quad ^{14}\text{N} \ 99.64\% \quad ^{15}\text{N} \ 0.36\% \\
\text{O} : & \quad ^{16}\text{O} \ 99.763\% \quad ^{17}\text{O} \ 0.0375\% \quad ^{18}\text{O} \ 0.1995\%
\end{align*}
\]

• definition of delta ($\delta$) units:

\[
\delta^{15}\text{N} = \left[ \frac{^{15}\text{N} / ^{14}\text{N}_{\text{sample}}}{^{15}\text{N} / ^{14}\text{N}_{\text{std}}} - 1 \right] \times 1000 \quad \text{(per mil ‰ units)}
\]

std for N is atmospheric N$_2$
Summit, Greenland

Summit (GISP2)
72.6°N 38.5°W
3200 m.a.s.l.
A clear (negative) trend is found in $\delta^{15}\text{N}$ of NO$_3^-$ in recent ice

Hastings et al., 2009
A clear (negative) trend is found in $\delta^{15}\text{N}$ of NO$_3^-$ in recent ice.

This trend closely follows estimates of fossil fuel burning over the last 250 years.

Hastings et al., Science, 2009
Seasonal changes in $\delta^{15}\text{N}$ of $\text{NO}_3^-$ in Greenland ice

- Recent ice (11-14 m depth) shows similar seasonality to modern snow studies:
  - $\delta^{15}\text{N}$ in **summer**
  - $\delta^{15}\text{N}$ in **winter**

- Limited measurements on pre-industrial ice show no clear seasonality in $\delta^{15}\text{N}$

Hastings et al., *Science*, 2009
A clear (negative) trend is found in $\delta^{15}\text{N}$ of NO$_3^-$ in recent ice.

This trend closely follows estimates of fossil fuel burning over the last 250 years.

Can we quantitatively interpret changes in NOx sources?

Hastings et al., *Science*, 2009
\[ \delta^{15}N \text{ of atmospheric } NO_3^-: \]

**NO\textsubscript{x}** Source Signatures?

- **NO\textsubscript{x}** from fossil fuels combustion has not been measured recently and there is no published data in N. America

- \( \delta^{15}N \) of NO\textsubscript{x} from biomass burning ??

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**Graph Details:**
- **Snow emissions** (photolyzed nitrate)
- **Lightning** (electric sparks)
- **Soils** (fertilized)
- **Vehicles**
- **Coal**
- **Precipitation Nitrate**

**Data Sources:**
- Moore, 1977
- Heaton, 1990
- Amman et al., 1997
- Li and Wang, 2007
- Hoering, 1957
- Savarino et al., 2007
- Morin et al., 2008
- Kendall et al., 2007

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**Diagram Axes:**
- \( \delta^{15}N \) (%)
- Precipitation Nitrate
- Snow emissions (photolyzed nitrate)
- Lightning (electric sparks)
- Soils (fertilized)
- Vehicles
- Coal
- Stratosphere (calculated)
Conclusions/Implications

- $\delta^{15}N$ of atmospheric NO$_3^-$ shows a clear decrease (-12‰) since 1750 based on results from a Greenland ice core.

- The change in $\delta^{15}N$ is best explained by a significant change in the source of NO$_3^-$, namely the addition of nitrogen oxides (NOx) from fossil fuel combustion.

- To use the $\delta^{15}N$ of NO$_3^-$ in ice to quantify NOx source changes we need to know the isotopic source signatures of all NOx sources.

- The relatively short lifetime of NOx/NO$_3^-$ should allow us to develop regional pictures of source and chemistry variations over both recent and climate-relevant timescales.

- Interpretation of other isotopic records that are impacted by atmospheric NO$_3^-$ should account for variations over time in the isotopic composition of NO$_3^-$. 