Stable Isotope Constraints on N Deposition and Cycling in Lake Tahoe

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Isotope Notation

\[ \delta \left( \%_{oo} \right) = \left( \frac{R_{\text{Sample}}}{R_{\text{Std}}} - 1 \right) \times 1000 \]

\[ R = \frac{^{18}O}{^{16}O} \]

Oxygen Standard is Standard Mean Ocean Water (SMOW)
Stable Isotopes in Determining Biochemical Budgets:

**Mass Balance**

\[
\delta^{13}C_{(atm)} = a\delta^{13}C_{(fuel)} + b\delta^{13}C_{(wet)} + c\delta^{13}C_{(rice)} + d\delta^{13}C_{(ter)} + e\delta^{13}C_{(cattle)}
\]
3 Isotope System: Oxygen (16, 17, 18)

\[ \Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O \]

Terrestrial Fractionation Line

- Cloud and rain water
- SMOW
- Air O₂
- Sedimentary and Igneous Rocks

\[ \sqrt{m^{17}} / m^{16} \]

\[ \sqrt{m^{18}} / m^{16} \]

\[ \delta^{17}O = 60.7\% \]

\[ \delta^{17}O = 30.8\% \]

\[ \delta^{17}O = 0.52 \times \delta^{18}O \]
Mass-independent Isotope Fractionations: Mechanisms

\[ \text{Mass Transfer} \]

\[ \text{S(IV)} + \Delta \text{O}_3 \rightarrow \Delta \text{SO}_4^{2-} \ (\text{Savarino et al., } JGR \ 2000) \]

\[ \text{CO}_2 + \Delta \text{O}^1\text{D} \rightarrow \text{CO}_3^* \rightarrow \Delta \text{CO}_2 + \text{O} \]

(Thiemens et al., Science, 1995; Yung, GRL, 1991)
Nitrate Oxygen Isotopic Analysis

\[ \text{NO}_3^-, \text{SO}_4^{2-}, \text{CO}_3^{2-}, \text{Cl}^-, \text{DOC, Particulate matter} \]

.2 micron filtered, activated carbon

\[ \text{NO}_3^-, \text{SO}_4^{2-}, \text{CO}_3^{2-}, \text{Cl}^-, (\text{DOC}) \]

BaCl\(_2\), HCl

\[ \text{NO}_3^-, \text{Cl}^-, (\text{DOC}) \]

Cation exchange

Anion exchange

C18 Resin

\[ \text{NO}_3^-, \text{Cl}^- (\text{in column}) \]

Elute HCl

\[ \text{HNO}_3, \text{HCl} \]

\[ \text{HCl} + \text{HNO}_3 + \text{Ag}_2\text{O} \rightarrow \text{AgNO}_3 + \text{AgCl}_2 \]

\[ \text{AgNO}_3 \xrightarrow{\Delta} \text{Ag}_2 + \frac{1}{2} \text{O}_2 + \text{NO}_2 \]

\[ \Delta^{17}\text{O}(\text{USGS}-35) \text{ vs. } \text{O}_2 \text{ Sample Size} \]

USGS-35

\[ \Delta^{17}\text{O Standard} \]

( Michalski et al., *Analytical Chemistry*, 2002 )
Seasonal Variation of Nitrate $\Delta^{17}O$ in La Jolla, Ca

$\Delta^{17}O = 21\%_o$

$\Delta^{17}O = 28\%_o$

Michalski et al. *GRL*, 2002
Atmospheric Nitrate $\Delta^{17}O$ from Multiple Environments

$\delta^{18}O$ vs $\delta^{17}O$ graph

Streamlines with markers for Bakersfield, Riverside, South Pole, and La Jolla.

$\Delta^{17}O$ values indicated with arrows:
- 20\%
- 30\%
Tracing Nitrate Source Using Stable Isotopes

Atmospheric Nitrate

Kinetic/equilibrium fractionations

Stable Isotopes in Catchment Hydrology
Carol Kendal, editor

Tracing Atmospheric Nitrate Using $\Delta^{17}O$

(Michalski et al., GRL, 2002)
NO$_3^-$ atm Detection using $\Delta^{17}$O

Michalski et al., Envi. Sci. and Tech, 2004
Quantifying $\text{NO}_3^-_{\text{atm}}$ using $\Delta^{17}\text{O}$

![Graph showing the relationship between $\% \text{NO}_3^-_{\text{atm}}$ and $\delta^{18}\text{O}$ with data points and error bars. The graph includes annotations for peak stream flow in October and March.](image-url)
Atmospheric Nitrate $\Delta^{17}O$ from Multiple Environments

$\delta^{17}O$ vs $\delta^{18}O$ plot with data points for Bakersfield, Riverside, South Pole, and La Jolla. The graph shows a trend with $\Delta^{17}O$ values ranging from 20‰ to 30‰.
FIGURE 5. Streamflow hydrograph for Devil Canyon (solid line), stream NO$_3^-$ concentration for site 2 (dotted line) and site 7 (dashed line), and $\Delta^{17}$O variations for site 2 (■) and site 7 (○) during November and March rainstorms in the Devil Canyon watershed. The November storm was preceded by an 8 month dry period. The March storm came at the end of the rainy season.
Lake Tahoe Water Column NO$_3^-$ $\Delta^{17}O$
Lake Tahoe Water Column Nitrate Dynamics

Paerl et al. *Limnology and Oceanography*, 1975
Lake Tahoe Water Column $\text{NO}_3^-$ $\Delta^{17}\text{O}$

- **Spring**
- **Summer**
- **Fall**

**Depth (m)**

- 0
- 1
- 2
- 3
- 4
- 5

**$\Delta^{17}\text{O}$ %**

- 0
- 1
- 2
- 3
- 4
- 5
A Simple Nitrate Isotopic Balance Model

- **NO₃⁻ In flow**
- **Atm** \( \Delta^{17}O = 23\%\)
- **Denitrification** \( N₂, N₂O \)
- **NO₃⁻ Out-flow** \( \Delta^{17}O \approx 3\% \)
- **Uptake** \( \Delta^{17}O = 0\% \)
Nitrate $\Delta^{17}O$ Mass Balance Calculation

\[
\Delta^{17}O_{\text{Lake}} = X \cdot \Delta^{17}O_{\text{ATM}} + (1-X) \cdot \Delta^{17}O_{\text{nitrif.}}
\]

\[
X = 13\% \quad (1-X) = 87\%
\]

$\text{NO}_3^-$ Deposition (wet and dry) = 26 $\mu$mol m$^2$ d$^{-1}$ = 0.13 g N m$^2$ yr$^{-1}$

Jassby et al., *Water Resources Research*, 1994

Nitrification $\text{NO}_3^-$ = 200 $\mu$mol m$^2$ d$^{-1}$ = 1.0 g N m$^2$ yr$^{-1}$

*IF we apply a lake wide $\text{NO}_3^-$ steady state approximation*

*e.g. Input + mineralization = uptake*

*Then algal uptake $\sim$ 1.13 g N m$^2$ yr$^{-1}$*

10 $\mu$g N-$\text{NO}_3^-$ L$^{-1}$ = (1000 L m$^{-3}$•100 m) = 1.0 g N m$^2$ yr$^{-1}$

Paerl et al. *Limnology and Oceanography*, 1975
Difficulties with the Study:

Analytical Interference by Organic Material!

\[ \text{AgNO}_3 + \text{C (organic)} \xrightarrow{\Delta} \text{CO}_2 + \text{CO} + \text{Ag}^{(s)} \]
A Bacterial Method for the Nitrogen Isotopic Analysis of Nitrate in Seawater and Freshwater

D. M. Sigman,* † K. L. Casciotti, † M. Andreani, ‡ C. Barford, § M. Galanter, † and J. K. Bohlke^†

*Anal. Chem. 2001, 73, 4145-4153

Sample size 20-100 nmol, No anion or DOC removal required
Isobaric interference inhibits accurate $\Delta^{17}$O measurements

High-Precision Isotopic Determination of the $^{18}$O/$^{16}$O and $^{17}$O/$^{16}$O Ratios in Nitrous Oxide

Steven S. Cliff and Mark H. Thiemens'

Coupled nitrogen and oxygen isotope fractionation of nitrate during assimilation by cultures of marine phytoplankton

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*Emiol. Oceanogr., 49(5), 2004, 1763–1773*
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Conclusions

• $\Delta^{17}O$ values in Lake Tahoe aerosols are similar to those previously measured.
• $\Delta^{17}O$ in Lake Nitrate is a sensitive tracer of atmospherically deposited $\text{NO}_3^-$.
• Lake nitrate $\Delta^{17}O$ variations over time and space will give new insights into lake mixing dynamics and nitrification rates.
• Simultaneous measurements of nitrate $\Delta^{17}O$, $\delta^{15}N$, $\delta^{18}O$ can help determine overall N cycle functionality in the Lake.
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Work in Progress

Continue Weekly Aerosol collections and begin wet deposition collections

Isotopically Characterize watershed NO$_3^-$

Include $\delta^{18}$O and $\delta^{15}$N using denitrifier method

Future Work

Utilize $\Delta^{17}$O, $\delta^{18}$O and $\delta^{15}$N at much higher temporal and spatial resolution
Lake Tahoe Objectives and Strategies

Atmospheric Component

• Characterize NO$_3^{-}$ atm $\Delta^{17}$O signature within the basin
• Characterize NO$_3^{-}$ atm $\Delta^{17}$O signature along transport gradient
• Measure NO$_3^{-}$ atm $\Delta^{17}$O during transport event

Lake and watershed component

• Sample and measure $\Delta^{17}$O,$\delta^{18}$O ($\delta^{15}$N) in NO$_3^{-}$ in Lake Tahoe
• Sample and measure $\Delta^{17}$O,$\delta^{18}$O ($\delta^{15}$N) in NO$_3^{-}$ in feed streams
• Sample and measure $\Delta^{17}$O,$\delta^{18}$O ($\delta^{15}$N) in NO$_3^{-}$ in soils
Lake Tahoe Facts

Surface area 500 km²
Volume 156 km³
Watershed area 800 km²
Oligotrophic
Annual Visitors > 23,000,000
Hybrid Cars 6