Stable Isotope Constraints on N Deposition and Cycling in Lake Tahoe

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Isotope Notation

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

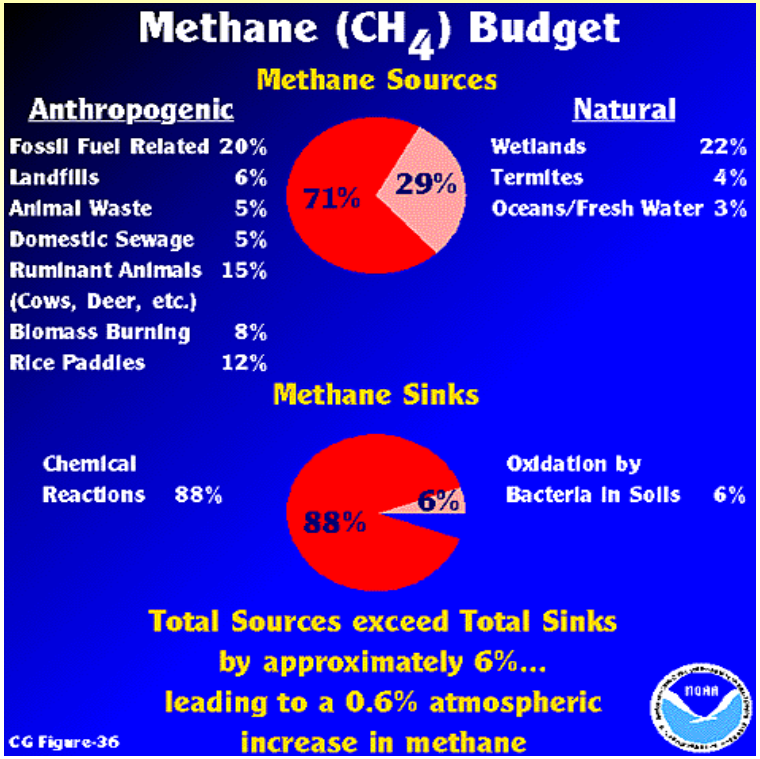
$$R=\frac{^{18}O}{^{16}O}$$

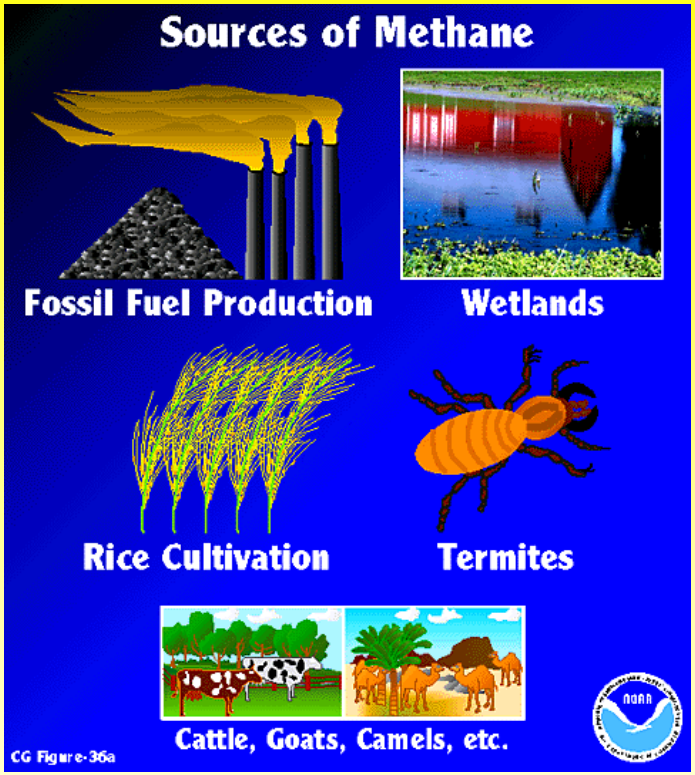
Oxygen Standard is Standard Mean Ocean Water (SMOW)

Stable Isotopes in Determining Biochemical Budgets:

Mass Balance

$$\delta^{13}C_{(atm)} = a\delta^{13}C_{(fuel)} + b\delta^{13}C_{(wet)} + c\delta^{13}C_{(rice)} + d\delta^{13}C_{(ter)} + e\delta^{13}C_{(cattle)}$$

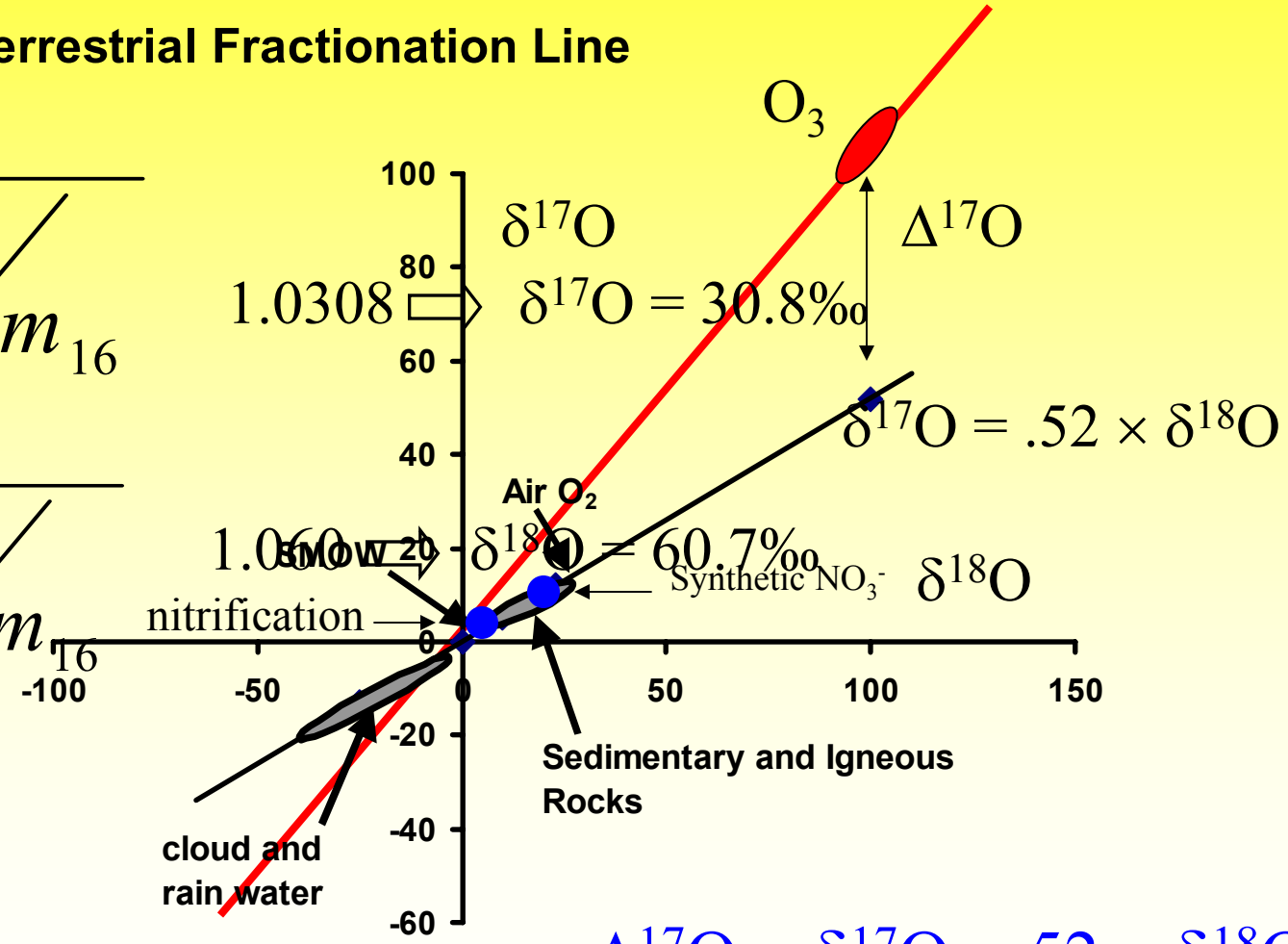




3 Isotope System: Oxygen (16,17,18)

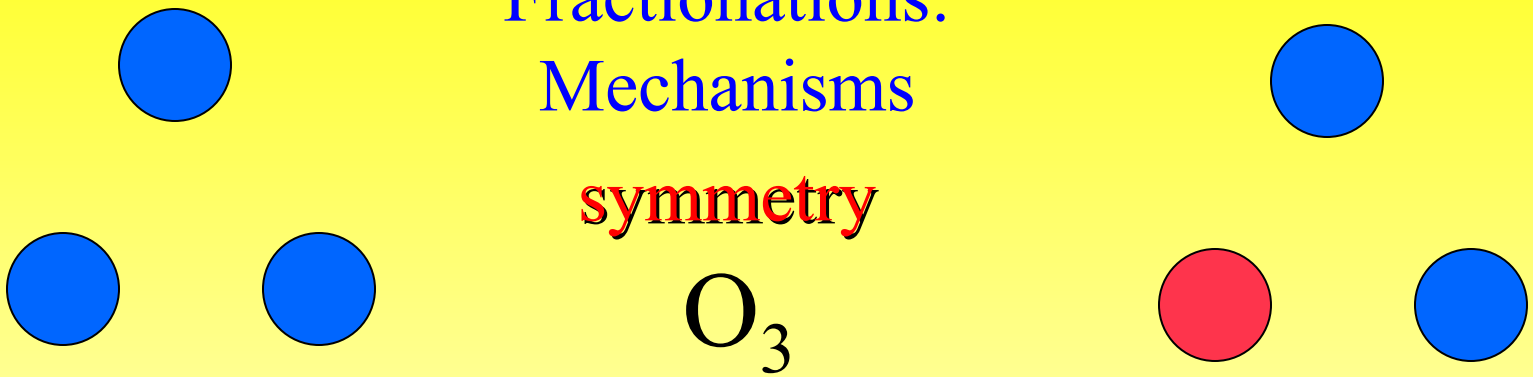
$$\sqrt{m_{17}/m_{16}}$$

$$\sqrt{m_{18}/m_{16}}$$



$$\Delta^{17}O = \delta^{17}O - .52 \times \delta^{18}O$$

Mass-independent Isotope Fractionations: Mechanisms



Mass Transfer

$S(IV) + {}^{\Delta}O_3 \rightarrow {}^{\Delta}SO_4^{-2}$ (Savarino et al., *JGR* 2000)

$CO_2 + {}^{\Delta}O^1D \rightarrow CO_3^* \rightarrow {}^{\Delta}CO_2 + O$

(Thiemens et al., *Science*, 1995; Yung, *GRL*, 1991)

Nitrate Oxygen Isotopic Analysis

NO_3^-, SO_4^{-2}, CO_3^{-2}, Cl^-,
DOC, Particulate matter

.2 micron filtered,
activated carbon ↓

NO_3^-, SO_4^{-2}, CO_3^{-2}, Cl^-, (DOC)

$BaCl_2$, HCl ↓

NO_3^-, Cl^-, (DOC)

Cation exchange
Anion exchange
C18 Resin ↓

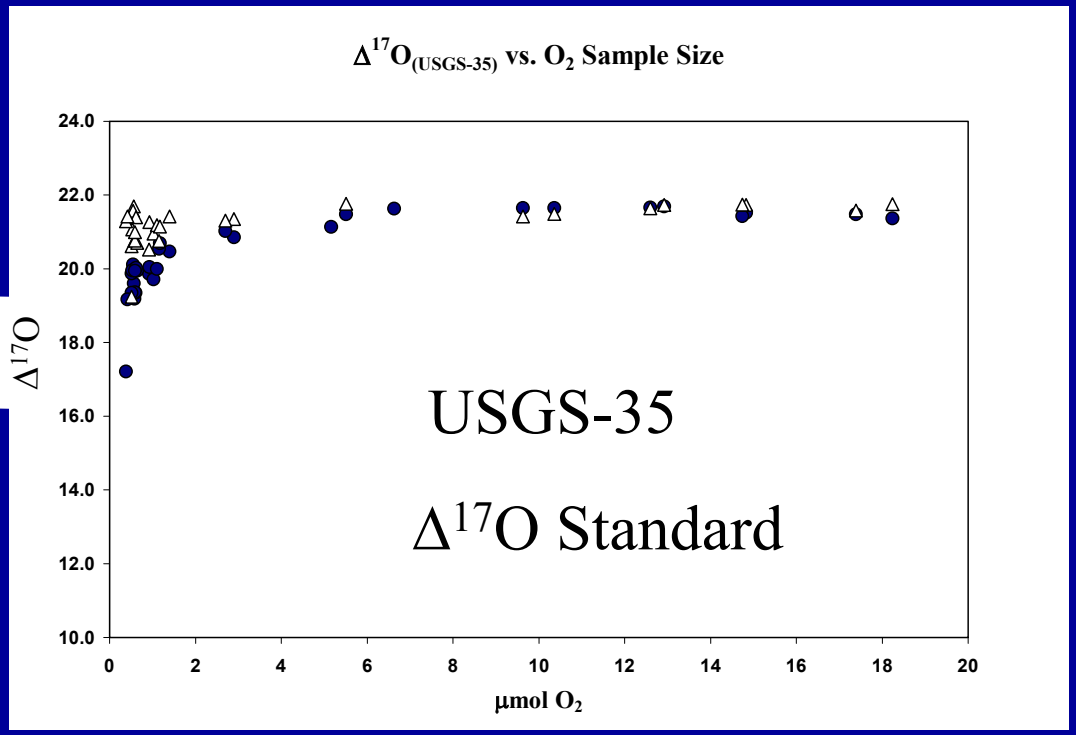
NO_3^-, Cl^- (in column)

Elute HCl ↓

HNO_3, HCl

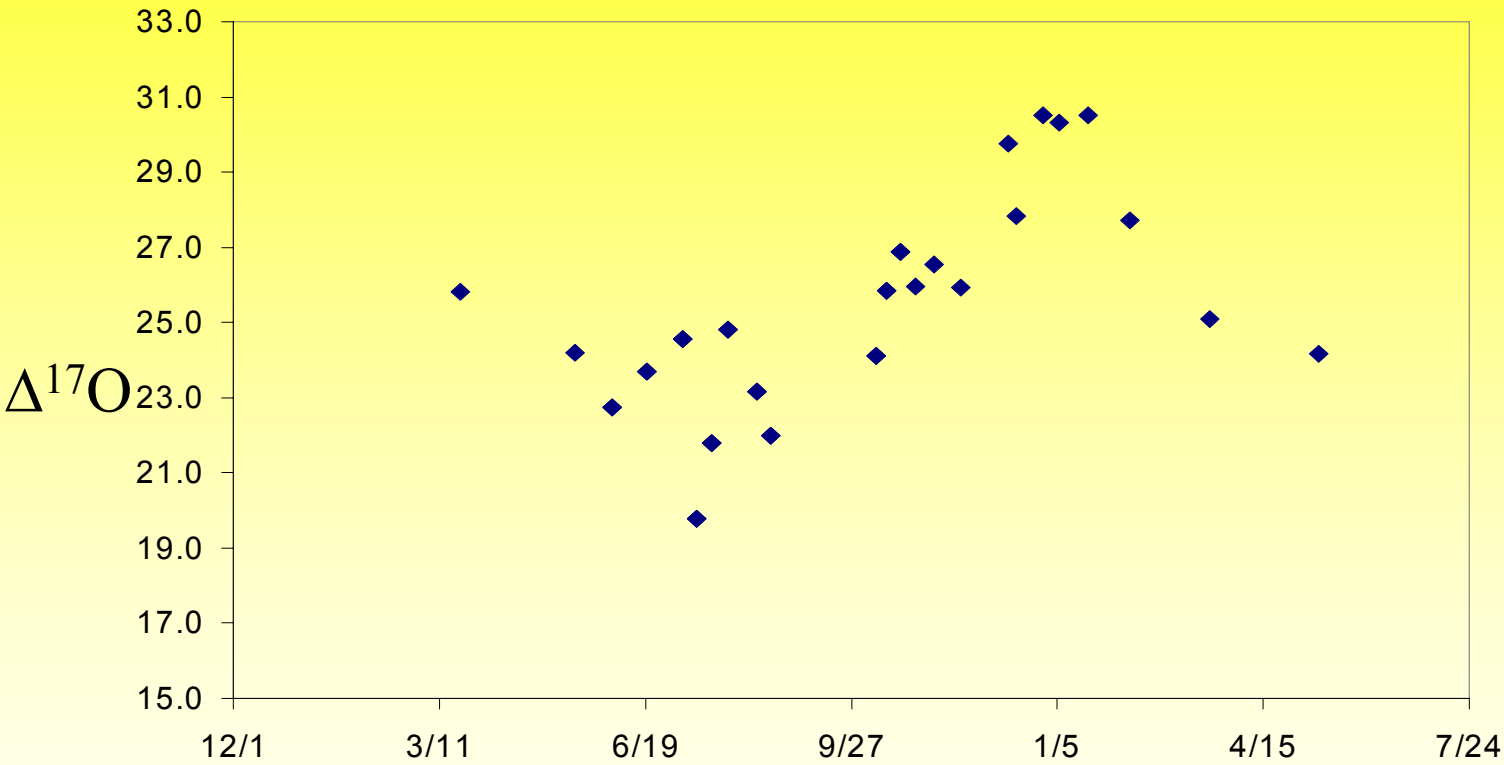
$$HCl + HNO_3 + Ag_2O \rightarrow AgNO_3 + AgCl_{(s)}$$

$$AgNO_3 \xrightarrow{\Delta} Ag_{(s)} + \tfrac{1}{2} O_2 + NO_2$$



(Michalski et al., *Analytical Chemistry*, 2002)

Seasonal Variation of Nitrate $\Delta^{17}O$ in La Jolla, Ca

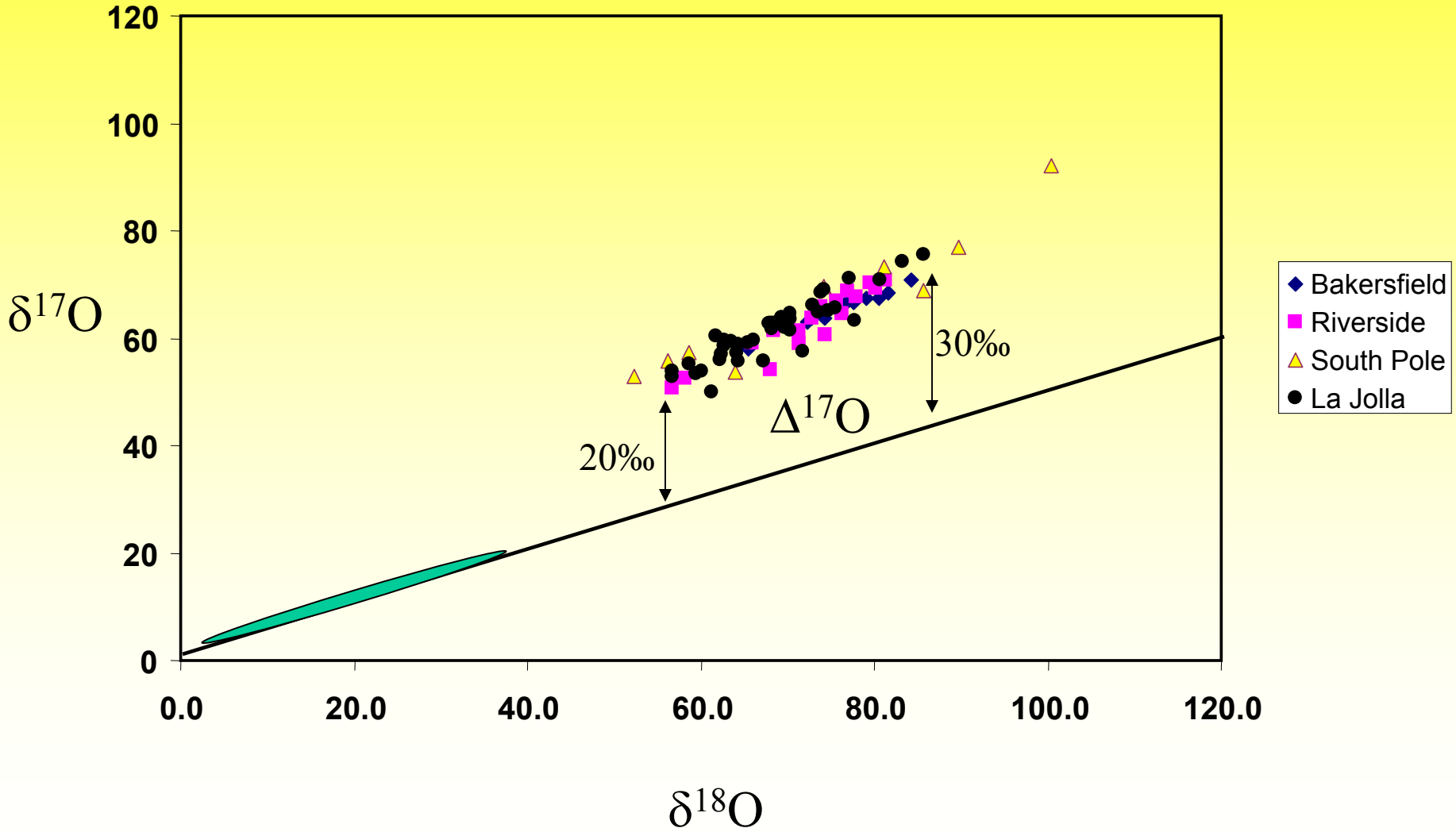


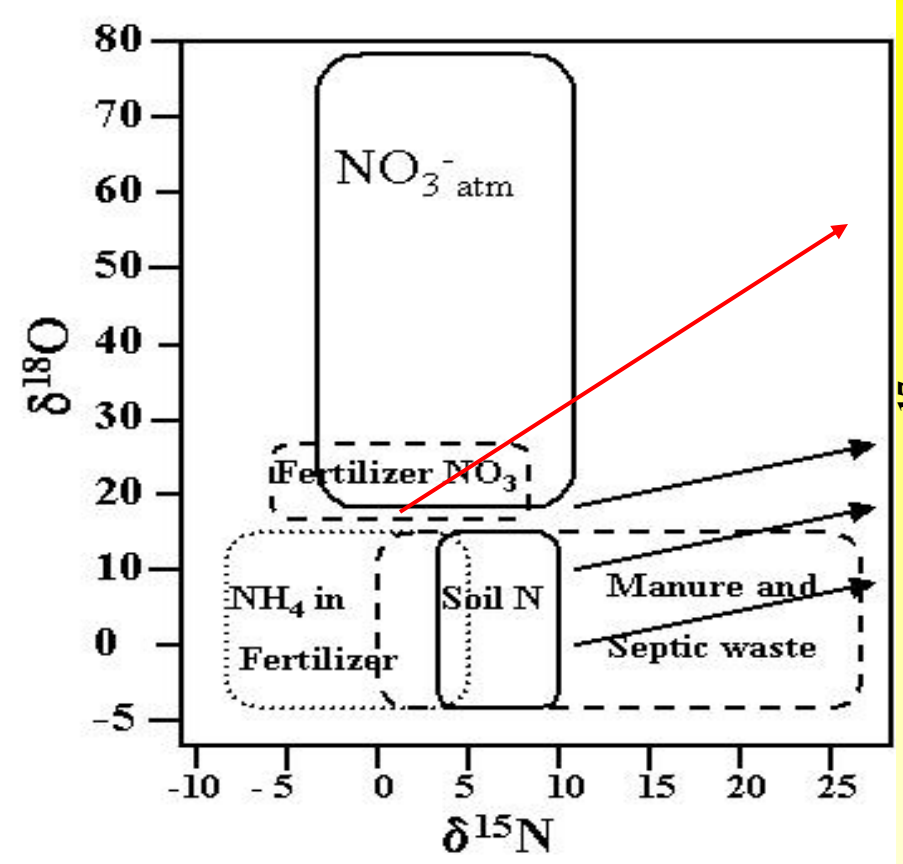
$$NO_2 + OH + M \longrightarrow HNO_3 + M \qquad \Delta^{17}O = 21‰$$

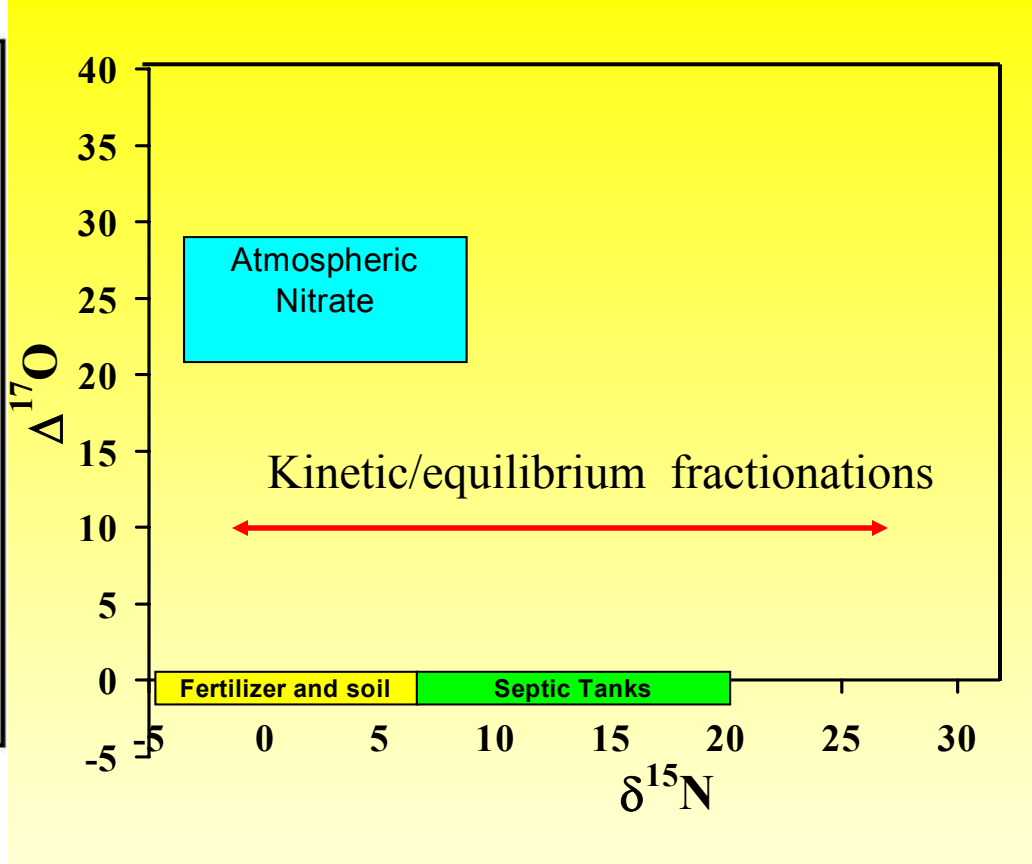
$$N_2O_5 + surf./H_2O \longrightarrow 2HNO_3 \qquad \Delta^{17}O = 28‰$$

Michalski et al. *GRL*, 2002

Atmospheric Nitrate $\Delta^{17}O$ from Multiple Environments







Tracing Nitrate Source Using Stable Isotopes

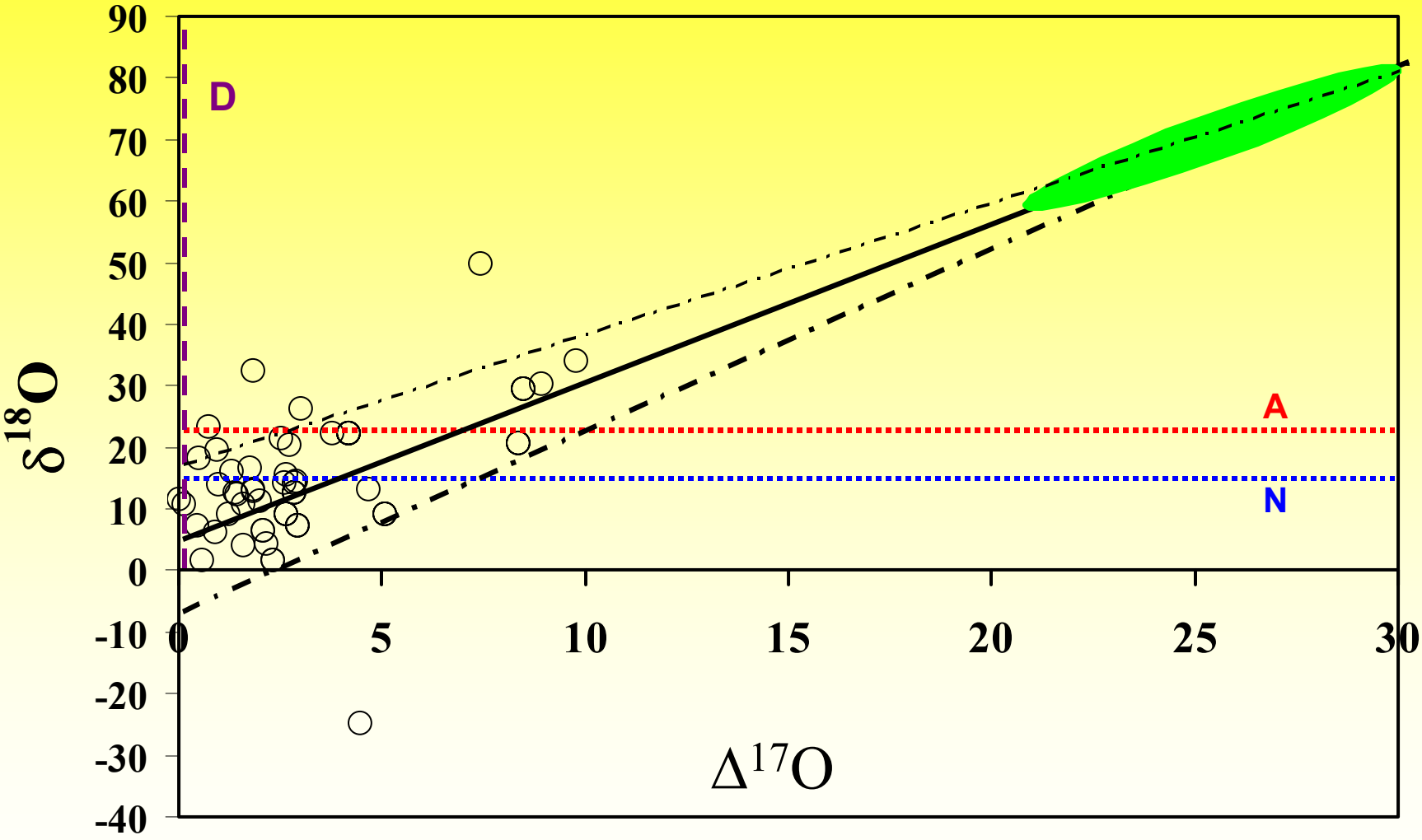
Stable Isotopes in Catchment Hydrology

Carol Kendal , editor

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

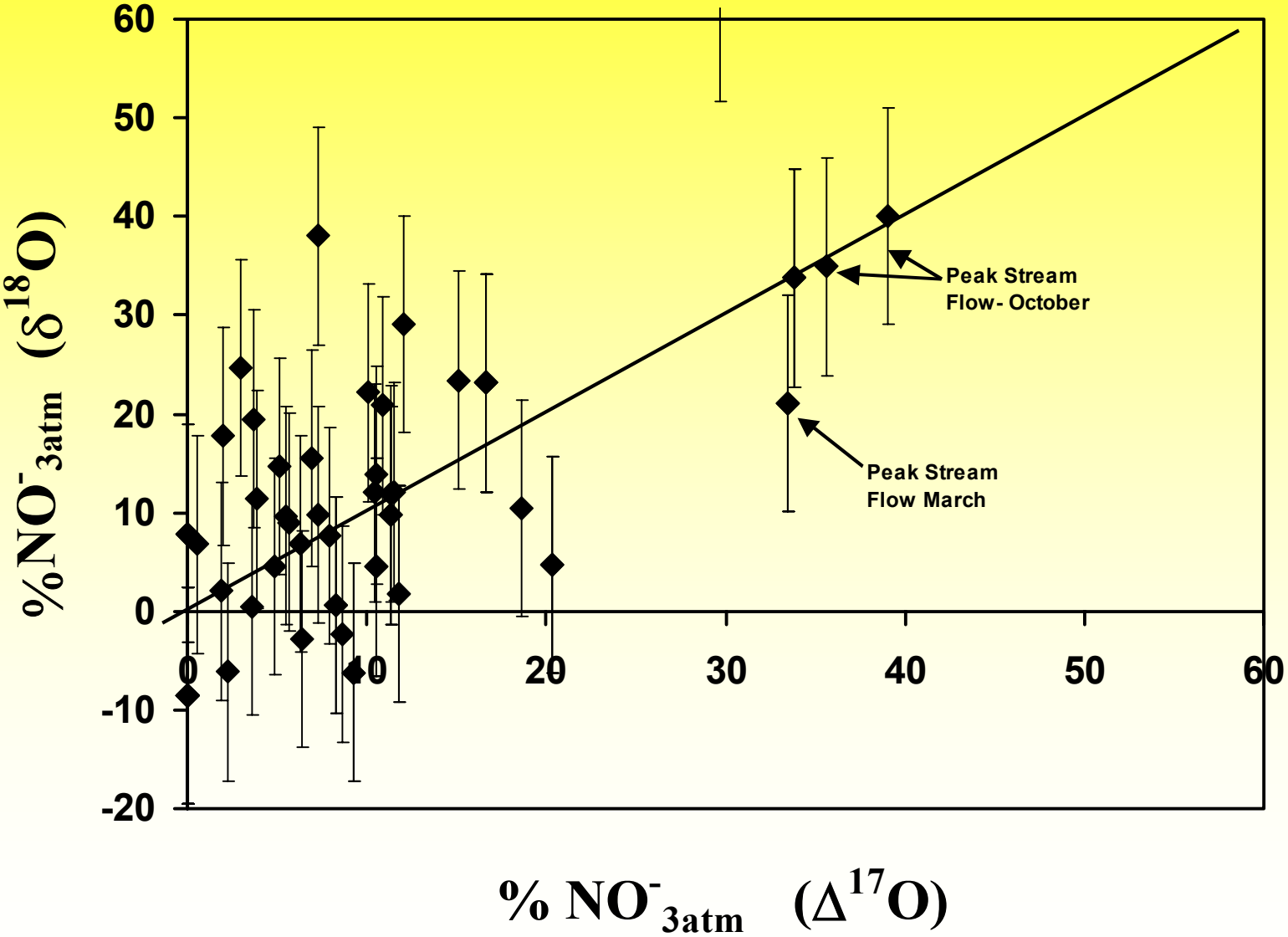
(Michalski et al., *GRL*, 2002)

$NO_3^-{}_{atm}$ Detection using $\Delta^{17}O$

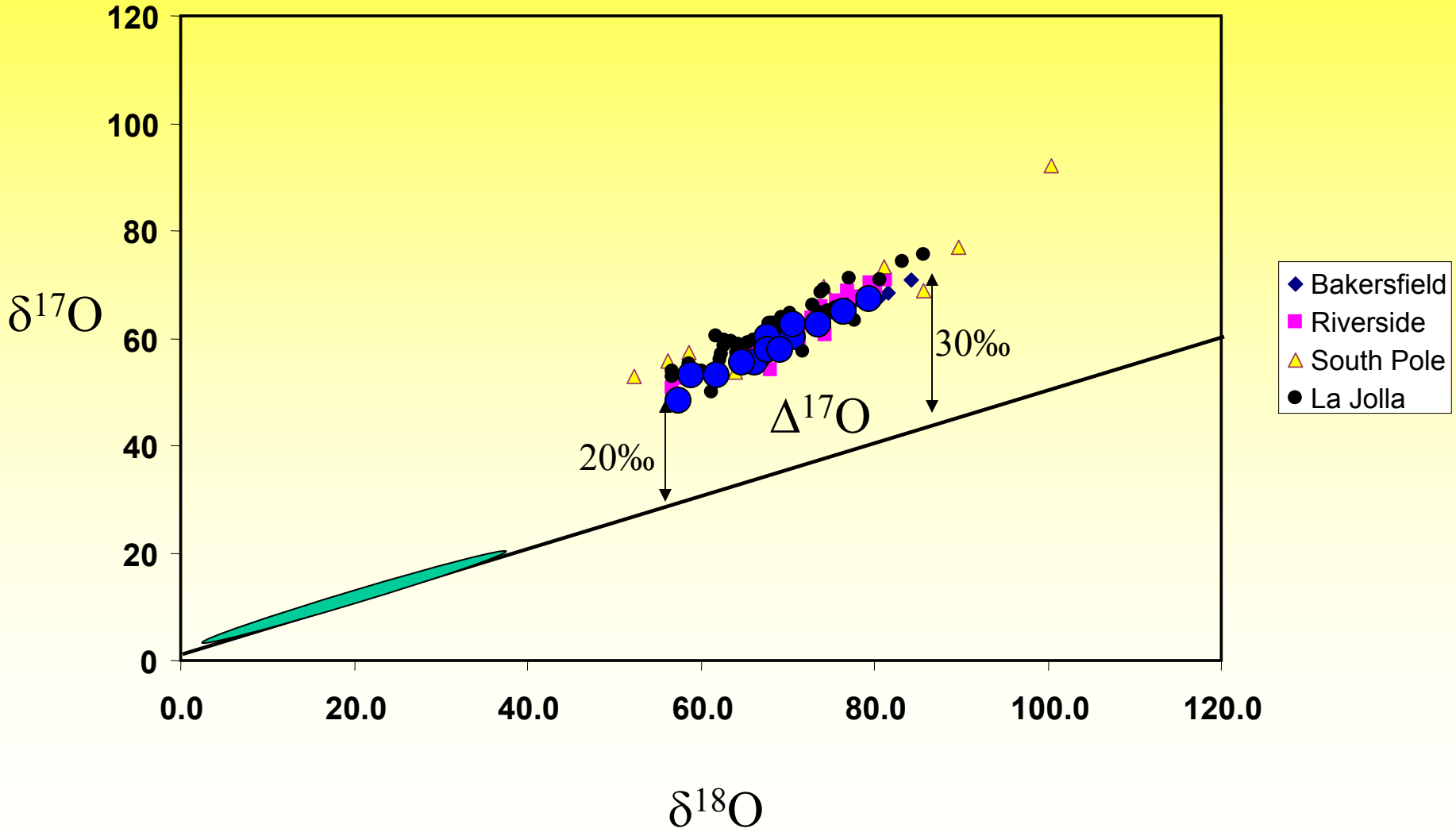


Michalski et al., *Envi. Sci. and Tech*, 2004

Quantifying $NO_3^-{}_{atm}$ using $\Delta^{17}O$



Atmospheric Nitrate $\Delta^{17}O$ from Multiple Environments



Tahoe Lake and Stream NO_3^- $\Delta^{17}O$

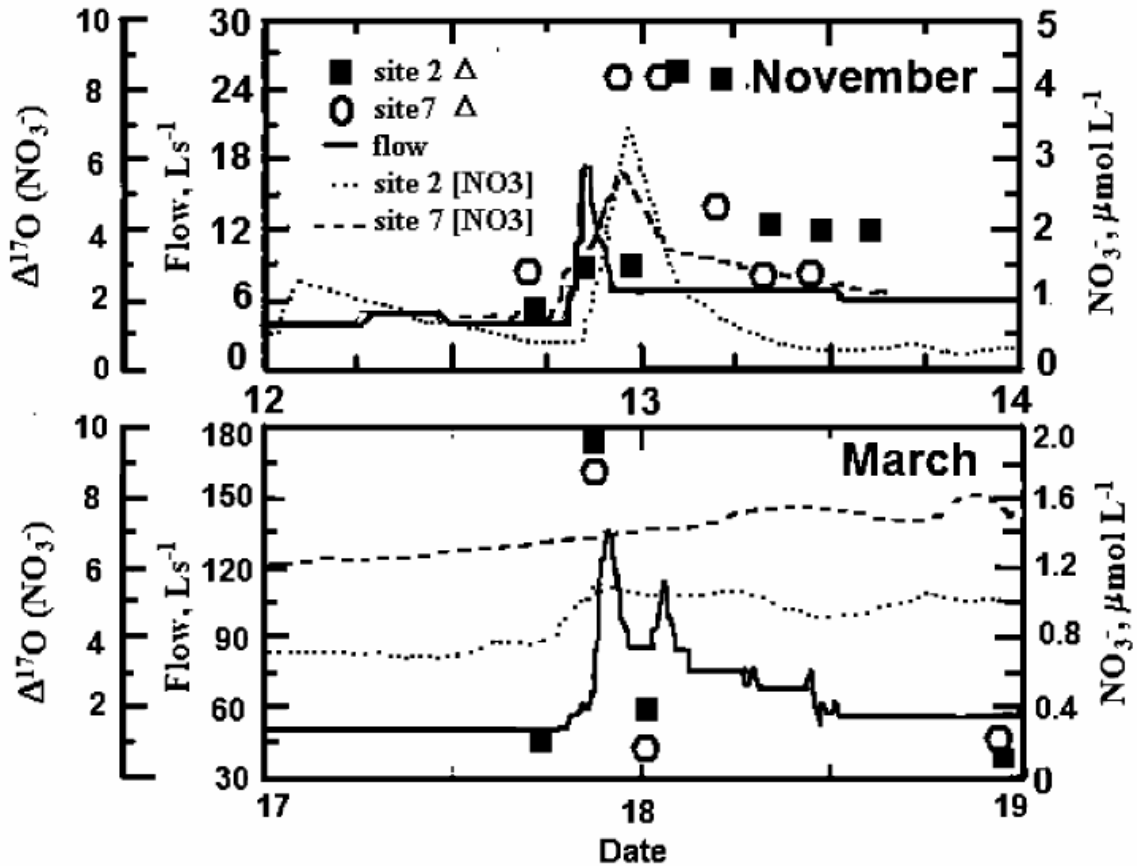
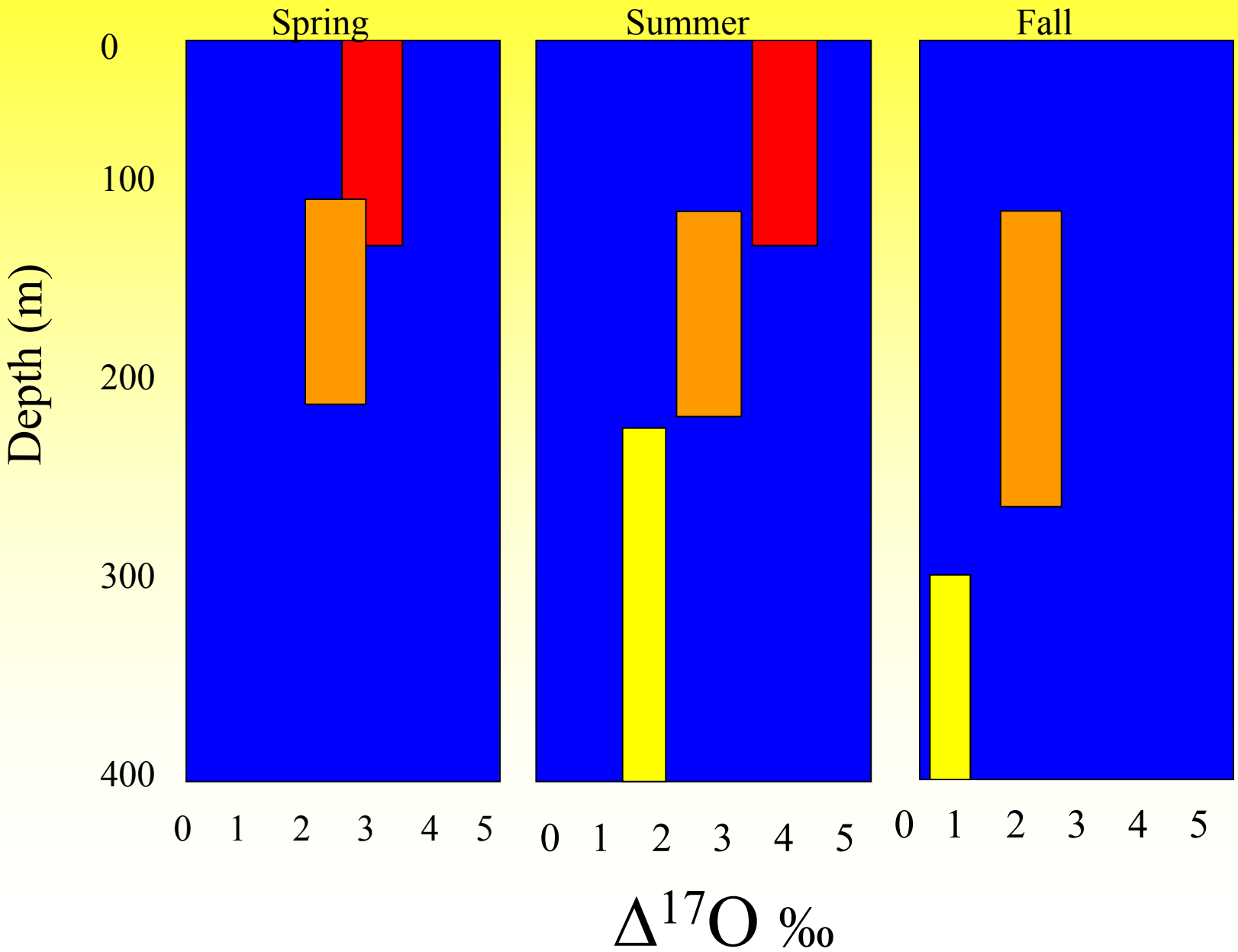
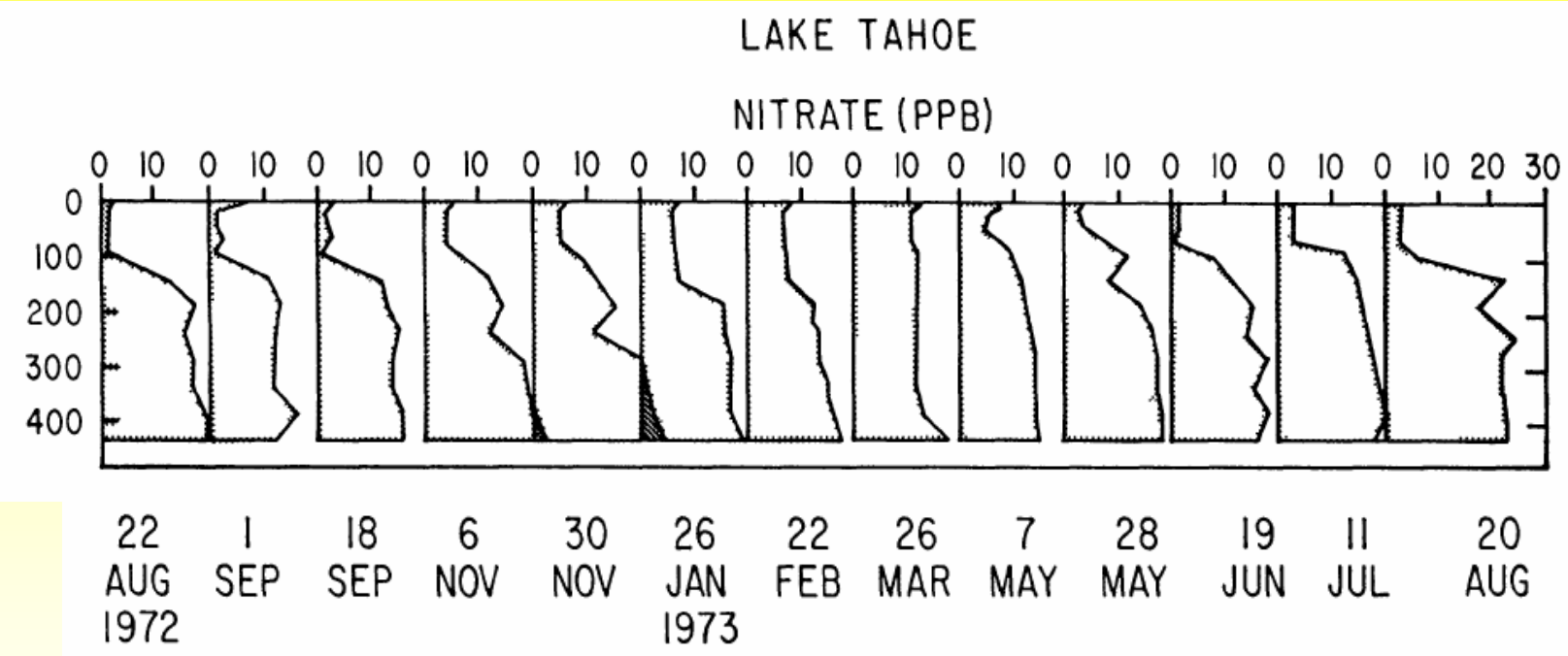


FIGURE 5. Streamflow hydrograph for Devil Canyon (solid line), stream NO_3^- concentration for site 2 (dotted line) and site 7 (dashed line), and $\Delta^{17}O$ variations for site 2 (■) and site 7 (○) during November and March rainstorms in the Devil Canyon watershed. The November storm was preceded by an 8 month dry period. The March storm came at the end of the rainy season.

Lake Tahoe Water Column NO_3^- $\Delta^{17}O$

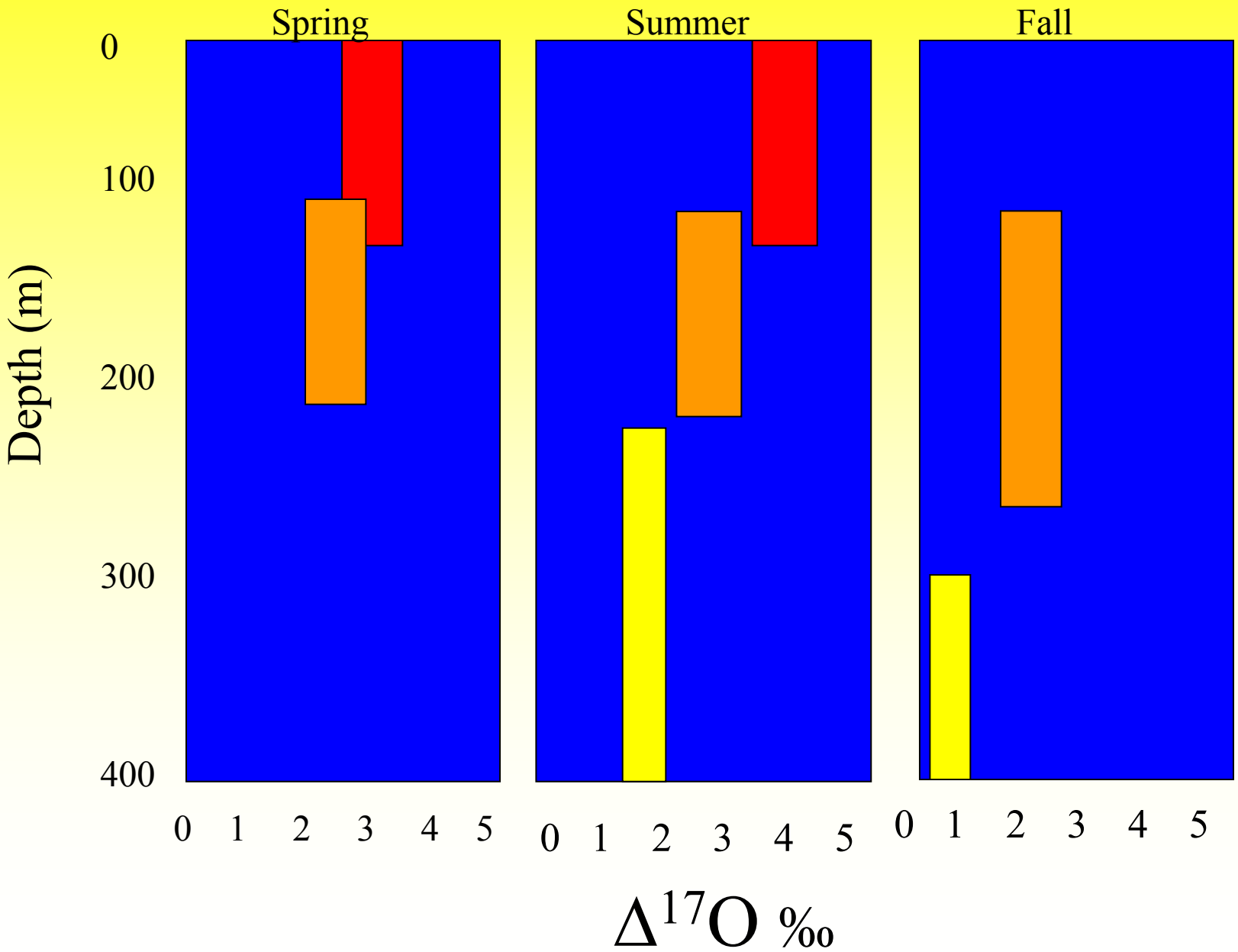


Lake Tahoe Water Column Nitrate Dynamics

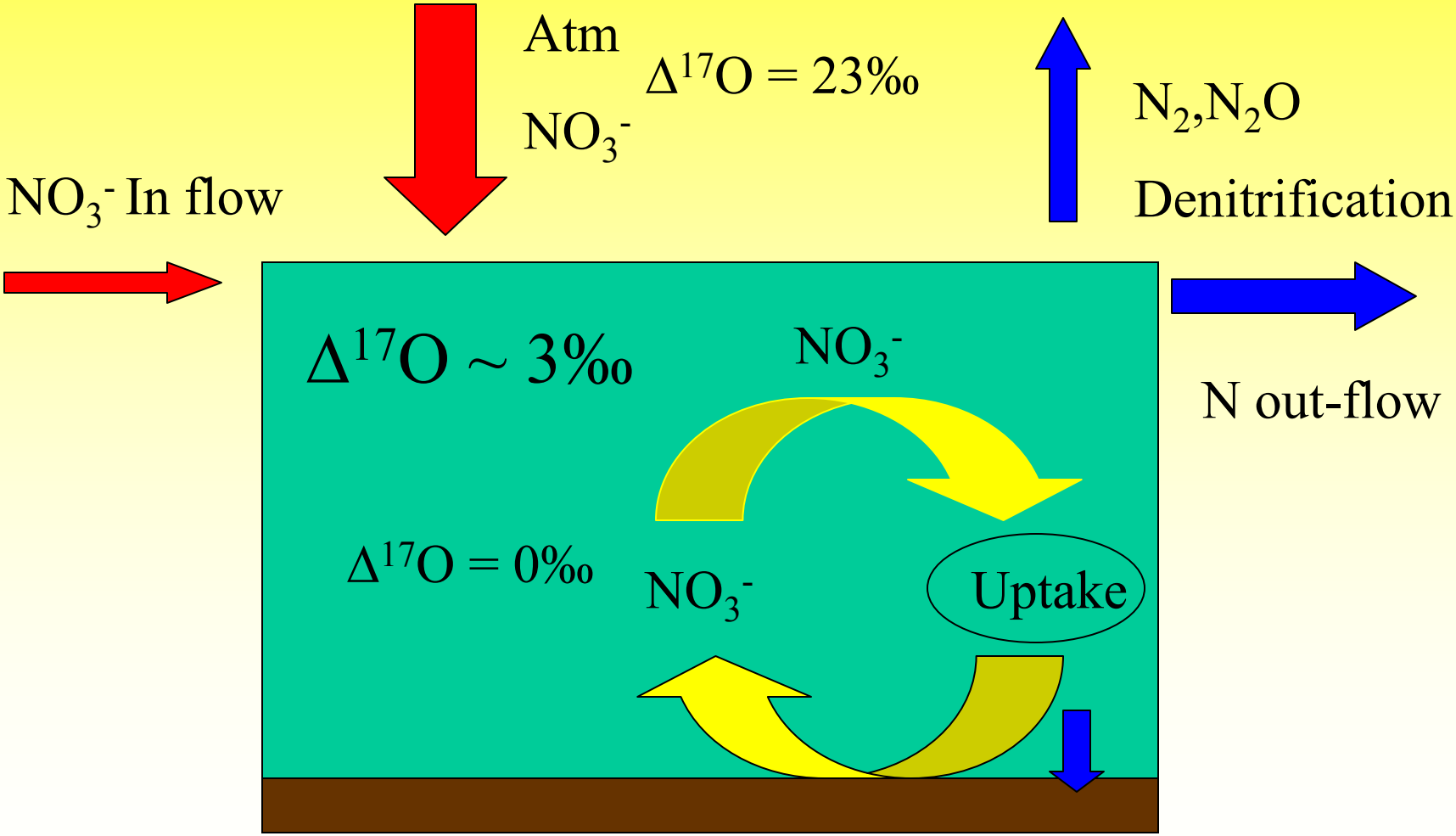


Paerl et al. *Limnology and Oceanography*, 1975

Lake Tahoe Water Column NO_3^- $\Delta^{17}O$



A Simple Nitrate Isotopic Balance Model



Nitrate $\Delta^{17}O$ Mass Balance Calculation

$$\Delta^{17}O_{Lake} = X \bullet \Delta^{17}O_{ATM} + (1-X) \bullet \Delta^{17}O_{nitrif.}$$

$$X = 13\% \qquad (1-X) = 87\%$$

NO_3^- Deposition (wet and dry) = 26 μmol m^2 d^{-1} = 0.13 g N m^2 yr^{-1}

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

Nitrification NO_3^- = 200 μmol m^2 d^{-1} = 1.0g N m^2 yr^{-1}

IF we apply a lake wide NO_3^- steady state approximation

e.g. Input + mineralization = uptake

Then algal uptake ~ 1.13g N m^2 yr^{-1}

10 μg N-NO_3^- L^{-1} = (1000 L m^{-3}•100 m) = 1.0g N m^2 yr^{-1}

Paerl et al. *Limnology and Oceanography*, 1975

Difficulties with the Study:

Analytical Interference by Organic Material !

$$AgNO_3 + C\ (\text{organic}) \xrightarrow{\Delta} CO_2 + CO + Ag^{(s)}$$

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

		44	45	46
NO_3^- →	N_2O	$^{14}N^{14}N^{16}O$	$^{14}N^{15}N^{16}O$	$^{14}N^{14}N^{18}O$
			$^{14}N^{17}N^{16}O$	

Sample size 20-100 nmol, No anion or DOC removal required

Isobaric interference inhibits accurate $\Delta^{17}O$ measurements

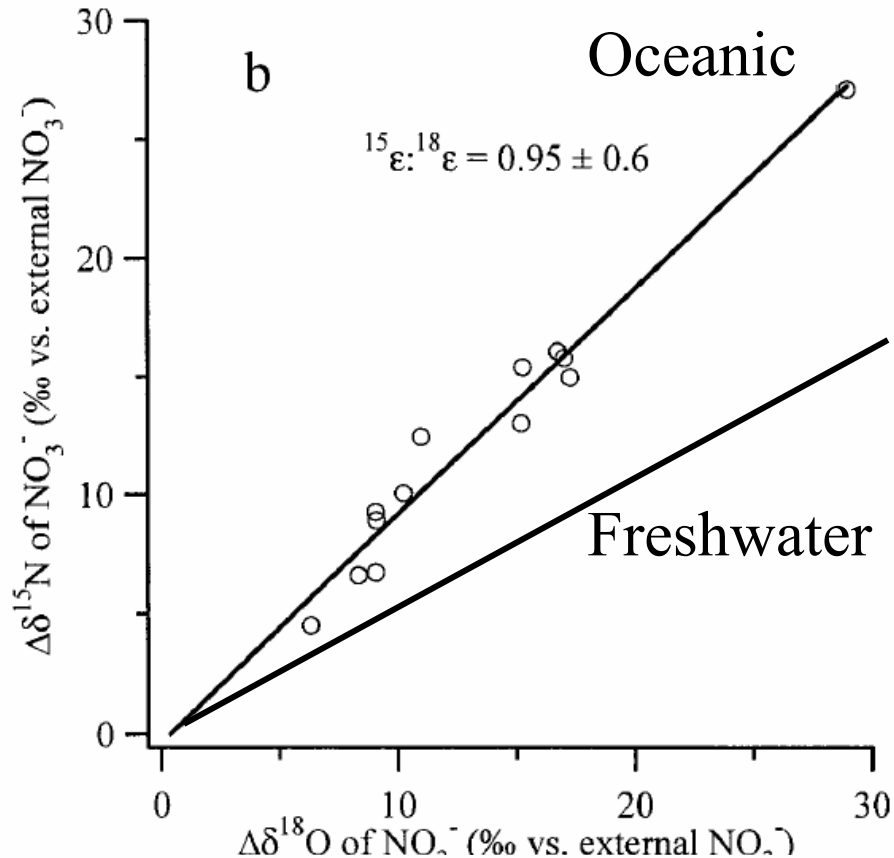
High-Precision Isotopic Determination of the $^{18}O/^{16}O$ and $^{17}O/^{16}O$ Ratios in Nitrous Oxide

Steven S. Cliff and Mark H. Thiemens'

***Anal. Chem.* 1994,66,** 2791-2793

N_2O → (Gold Reduction) → $N_2 + O_2$ $^{16}O^{16}O$ $^{16}O^{17}O$ $^{16}O^{18}O$

Mass Dependent Fractionations in Nitrate Systems



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

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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 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.

Acknowledgements

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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

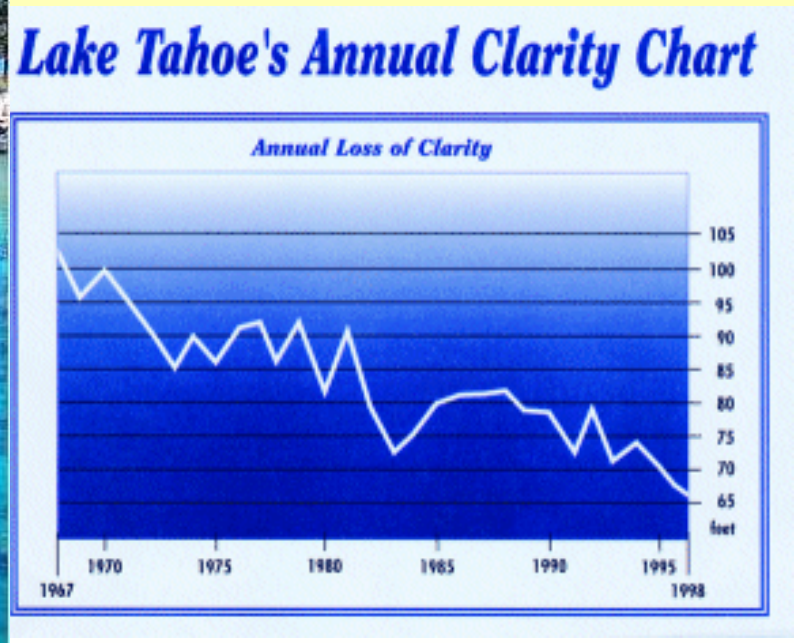
Atmospheric Component

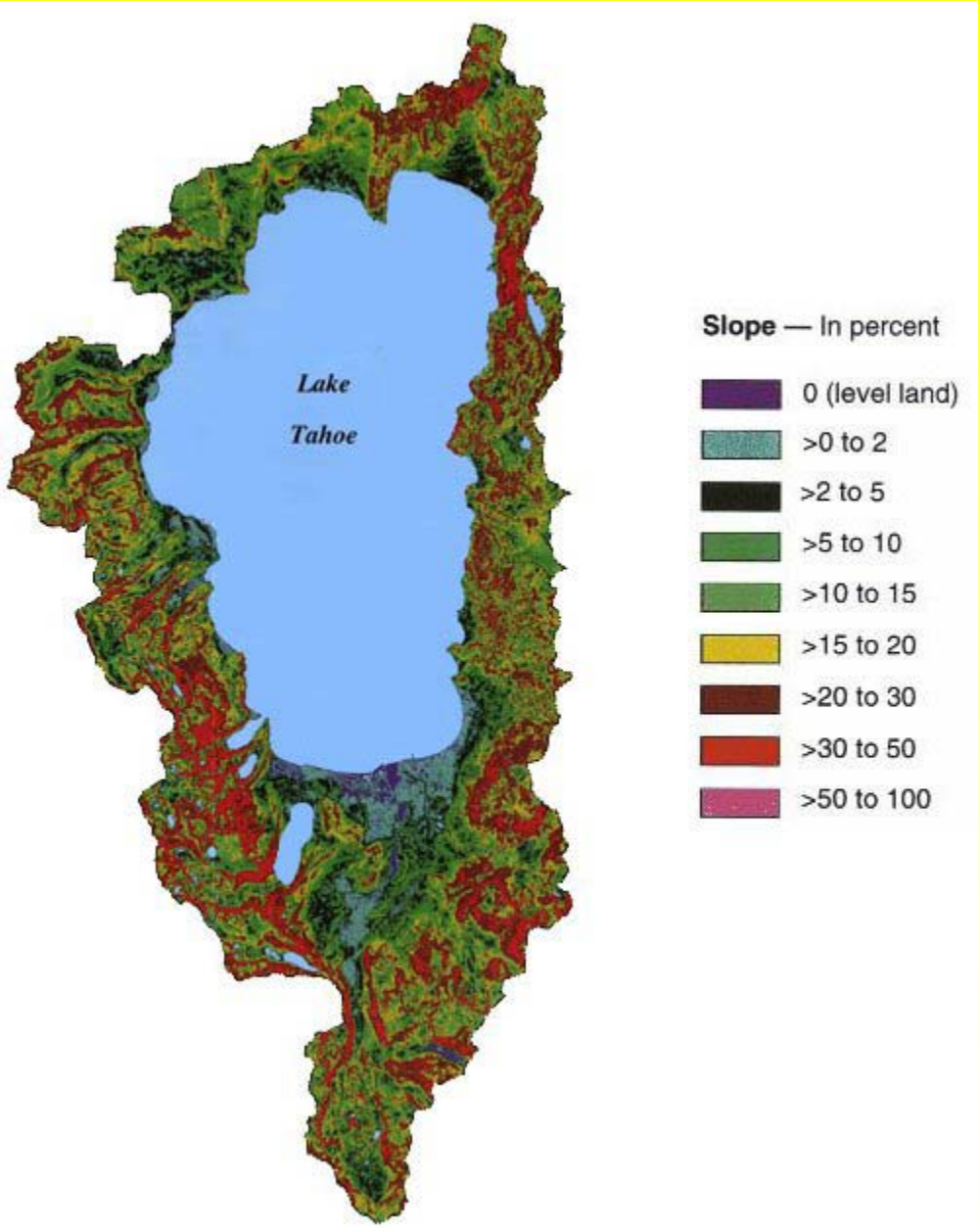
- Characterize $NO_3^-{}_{atm}$ $\Delta^{17}O$ signature within the basin
- Characterize $NO_3^-{}_{atm}$ $\Delta^{17}O$ signature along transport gradient
- Measure $NO_3^-{}_{atm}$ $\Delta^{17}O$ during transport event

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, USA



Lake Tahoe Facts

Surface area	500 km^2
Volume	156 km^3
Watershed area	800 km^2
Oligotrophic	
Annual Visitors	> 23,000,000
Hybrid Cars	6