

California Groundwater Resources Association
"Isotope Methods for Groundwater Investigations"
Short-course
March 28, 2007
Concord, CA
(<http://www.grac.org/isotope.asp>)
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This file contains the entire set of slides used for the nitrate isotope portion of the short-course – except for a few slides with unpublished data.

ISOTOPE BIOGEOCHEMISTRY:
Tracers of solutes or reactions

This part of the short course will focus on two specific kinds of applications:

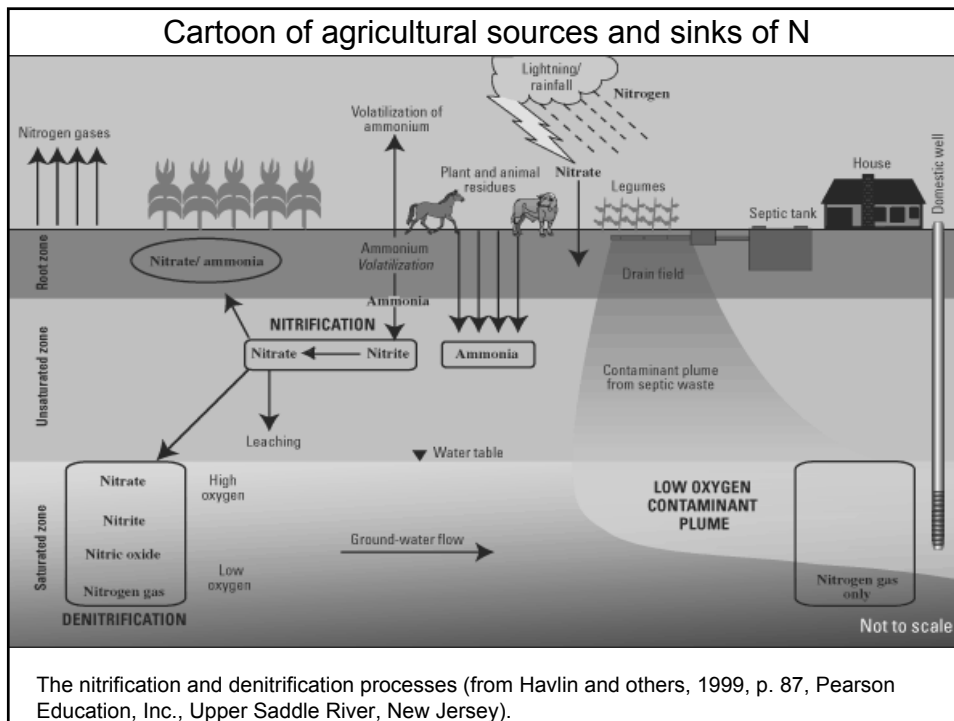
- tracing sources of nitrate, and
- ecological applications.

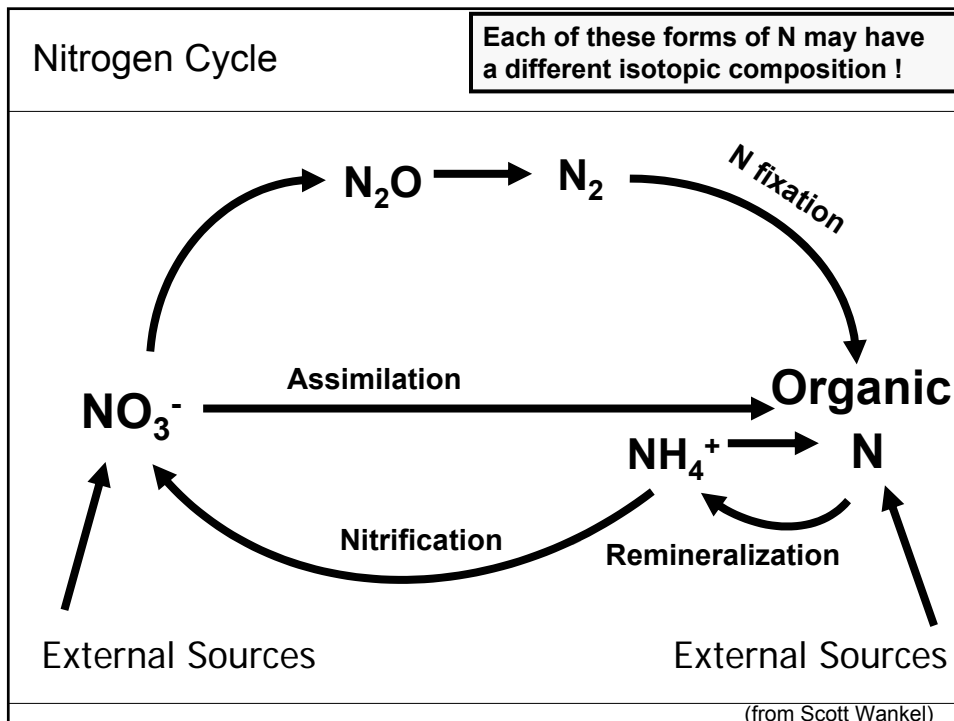
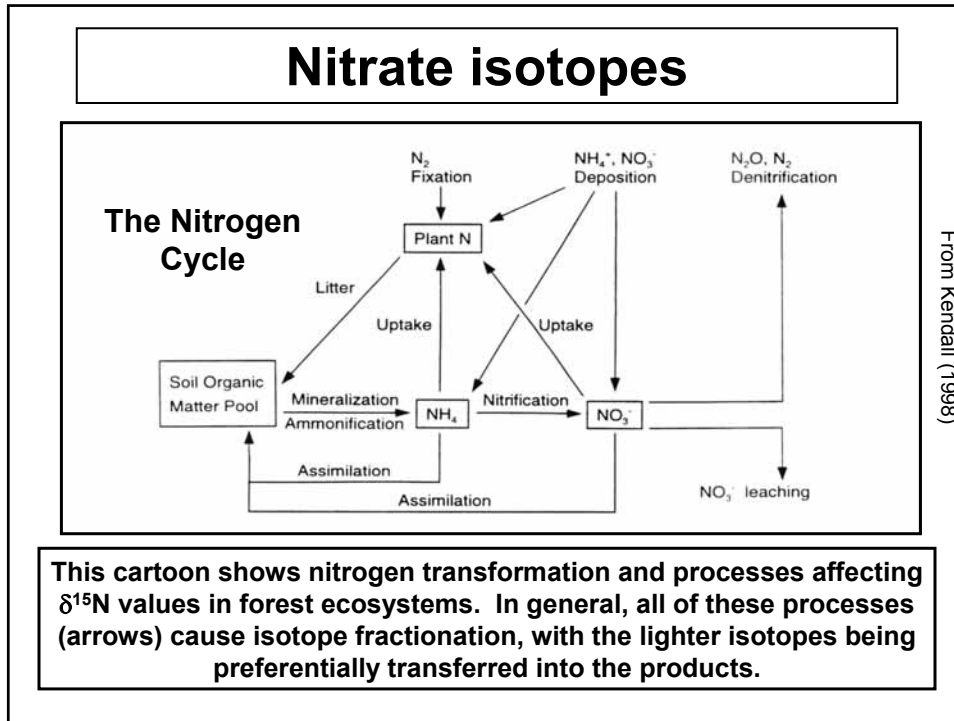
Other major biogeochemical applications are tracing sources of organic contaminants, determining degradation reactions, and geochemical modeling – and there are a LOT of other kinds of applications, with all sorts of isotopes.

On-line presentations

For information about using isotopes to trace sources of nitrate and organic matter, I have several web-based seminars that can be accessed from the following URLs:

- an informal presentation at the SJR DO TMDL technical working group (TWG) meeting in March 2006 about the status of our DO TMDL-related research: <http://www.sjrdotmdl.org/meetings013.html> (click on the Kendall link further down on the page).
- a USGS seminar in May 2005 about tracing causes of hypoxia at: <http://www.rcamnl.wr.usgs.gov/wrdseminar/pastseminars2005.html> (click on the Kendall link further down on the page).
- a CUAHSI seminar in April 2005 about tracing sources of organics and nutrients in watersheds at: <http://www.cuahsi.org/sem-archive.html> (click on the Kendall link further down on the page).
- a seminar about tracing agricultural contaminants with isotopes given at an EPA workshop on Animal Feeding Operations (AFOs) in December 2004 at: <http://www.epa.gov/osp/regions/afo.htm> (click on the Kendall link further down on the page).





How do isotopes help trace sources of nitrate ?

Sources and sinks can often be identified, traced, and semi-quantified because:

- ❖ nitrate derived from different sources and land uses often has distinctively different isotope compositions, and
- ❖ different kinds of sinks can sometimes cause distinctive shifts in isotopic compositions.

In other words, different sources nitrate often have distinctive isotope “fingerprints” that can provide a better understanding of the system than just chemical data.

Isotope Nomenclature

There are 2 stable nitrogen isotopes (^{15}N , ^{14}N).

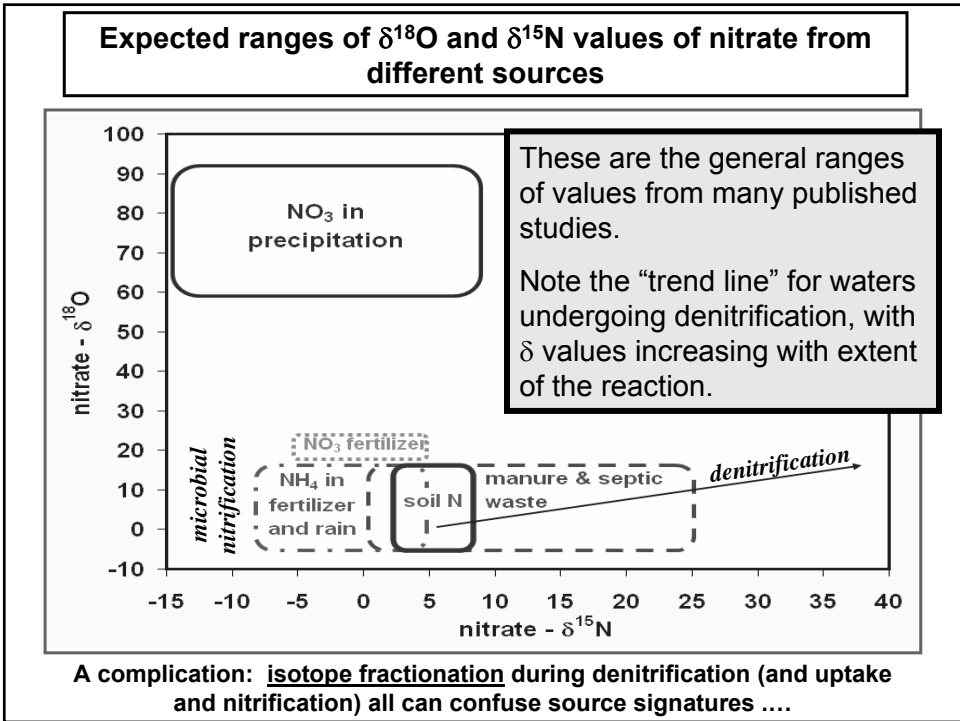
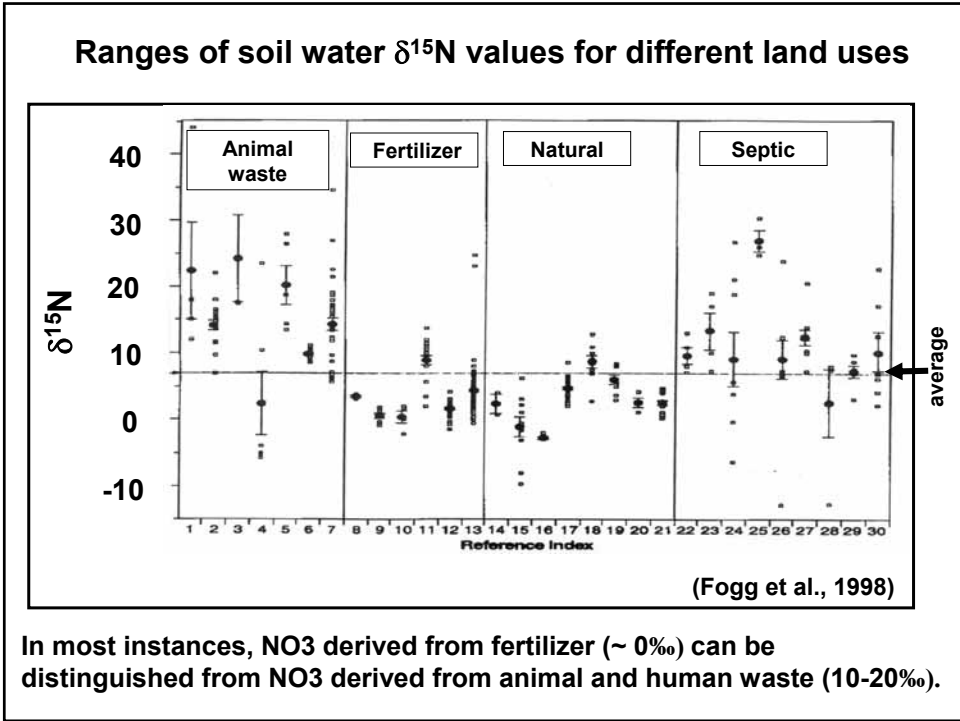
There are 3 stable oxygen isotopes (^{18}O , ^{17}O , ^{16}O).

Ratios of $^{18}\text{O}/^{16}\text{O}$ are reported as $\delta^{18}\text{O}$.

Ratios of $^{17}\text{O}/^{16}\text{O}$ are reported as $\delta^{17}\text{O}$.

The standard for N isotopes is Air – which is defined as 0.

The standard for O isotopes is V-SMOW – which is defined as 0.



Isotopic Fractionation (the changes in the isotopic compositions of materials because of processes) can make different sources more distinctive or hide differences between sources.

How does this work? During biological processes (e.g., assimilation, nitrification, denitrification), the lighter isotope (^{14}N) is concentrated in the products while the heavier isotope (^{15}N) is concentrated in the residual reactants.

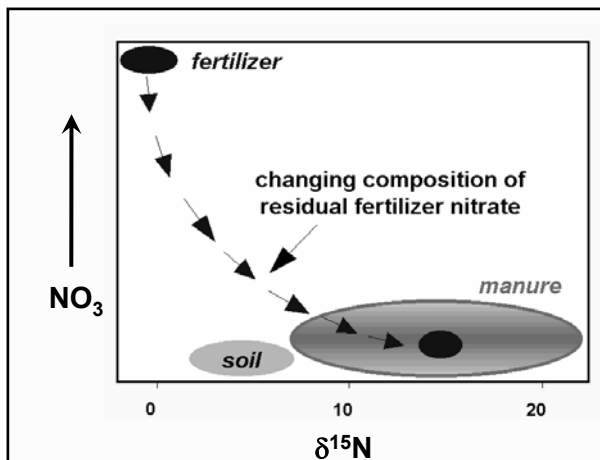
Example: during the reaction $\text{NO}_3 \rightarrow \text{N}_2$, the resulting N_2 has a lower $\delta^{15}\text{N}$ than the residual NO_3 .

- ❖ The magnitude of the fractionation is dependent on a variety of environmental conditions.
- ❖ Biological fractionations can make it very difficult to identify sources and quantify mixing proportions.

The following slide is a cartoon showing how fractionation complicates interpretation...

An example:

Cartoon showing how denitrification can increase the $\delta^{15}\text{N}$ value of residual NO_3 derived from fertilizer, causing problems for interpretations of sources of N



Therefore, we often cannot easily distinguish between:

- (1) a manure source and
- (2) a fertilizer source that has denitrified to have the same $\delta^{15}\text{N}$ as manure.

Solution: use a multi-isotope approach

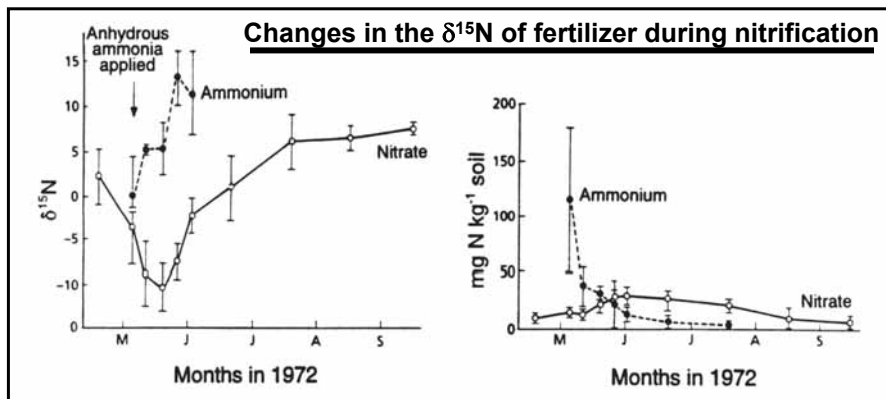
Processes causing fractionation of nitrate isotopes

Common microbial processes that may be expected to fractionate oxygen isotopes in NO_3 , leaving the residual NO_3 enriched in ^{15}N and ^{18}O , include: assimilation (uptake), absorption/desorption, and denitrification. Of these three, there are limited data only on denitrification. Denitrification along a flowpath changes the $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of residual nitrate in a distinctive manner, making the combined analysis of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of nitrate a powerful tool for recognizing denitrification. Nitrification also causes isotope fractionation.

There seems to be little information about possible O isotope exchange between water and nitrate. Many have speculated that NO_3 might behave somewhat like SO_4 , with slow exchange rates with water except at high temperatures and low pH values. Experiments in our lab and elsewhere show that nitrate only exchanges in really low-pH water. This needs further testing; however, the consistency of data from field areas argues against significant rapid exchange.

The next few slides will discuss what is known about processes causing fractionation....

Another example of how fractionation makes source determination more difficult



(Modified from Feigin et al. 1974)

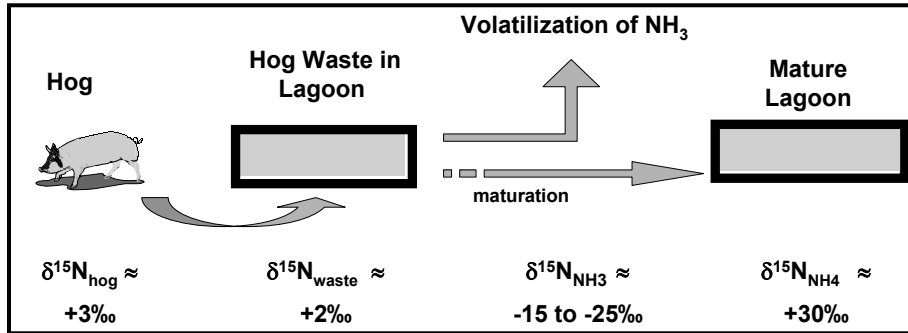
Hence, the $\delta^{15}\text{N}$ of nitrate produced by nitrification of ammonium or urea fertilizers may be different than the original fertilizer, especially immediately after fertilizer application.

After anhydrous ammonia is applied, the $\delta^{15}\text{N}$ of soil nitrate first drops and then rises to higher than original values.

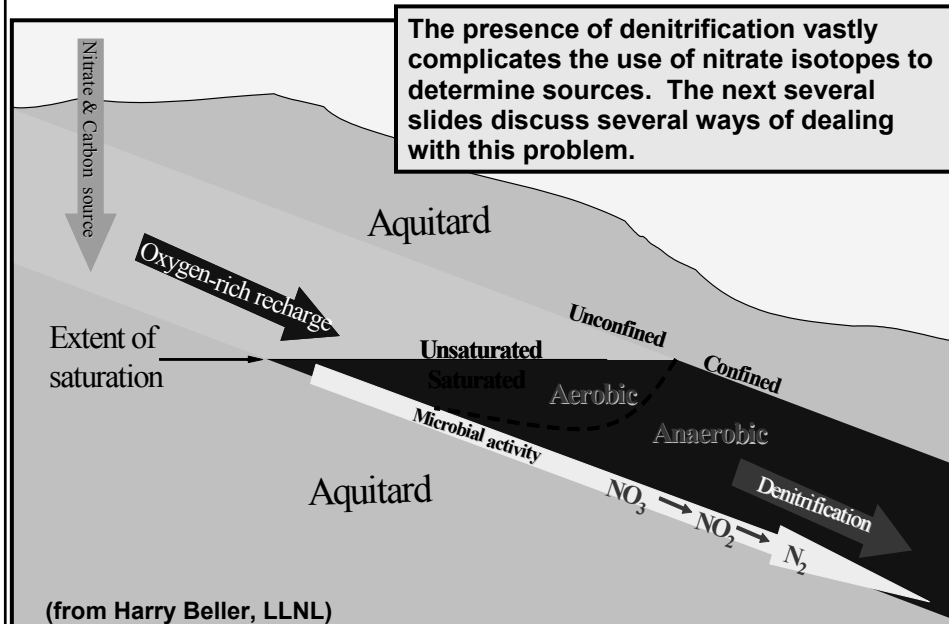
Volatilization of ammonia causes the increasingly high $\delta^{15}\text{N}$ values of soil ammonium and nitrate.

Another example of fractionation – but in this case, it is useful and provides a way of tracing sources of NH_4 :

- The $\delta^{15}\text{N}$ of NH_4 derived from volatilization of NH_3 from animal waste lagoons is very low compared to the $\delta^{15}\text{N}$ of other N sources.
- Nitrification of NH_4 produces NO_3 with a $\delta^{15}\text{N}$ that is only about 0 to 2‰ higher than the $\delta^{15}\text{N}$ of the NH_4 (if most of the NH_4 is nitrified).
- Contributions of atmospheric N from NH_3 emissions, or leakage of lagoon waste into groundwater or streams, can often be readily quantified using $\delta^{15}\text{N}$.



Conceptual model of denitrification in a confined aquifer



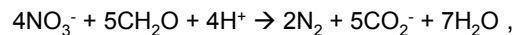
How to distinguish mixing from denitrification?

1. Geochemical evidence of a reducing environment (e.g., low dissolved O_2 , high H_2S , etc).
2. Analysis of the NO_3 for $\delta^{18}O$ as well as $\delta^{15}N$, to see if there is a systematic increase in $\delta^{18}O$ with increase in $\delta^{15}N$ and decrease in NO_3 , consistent with denitrification.
3. Hyperbolic vs exponential relationships between $\delta^{15}N$ and NO_3 (i.e., mixing is a hyperbolic function whereas denitrification is exponential). Hence, if mixing of two sources is responsible for the curvilinear relationship between $\delta^{15}N$ and NO_3 , plotting $\delta^{15}N$ vs $1/NO_3$ will result in a straight line. In contrast, if denitrification (or assimilation) is responsible for the relationship, plotting $\delta^{15}N$ vs $\ln NO_3$ will produce a straight line.
4. Analysis of dissolved N_2 (produced by the denitrification of NO_3) for $\delta^{15}N$, to show that there are systematic increases in the $\delta^{15}N$ of N_2 with decreases in NO_3 and increases in the $\delta^{15}N$ of NO_3 .
5. No change in $\Delta^{17}O$ during a process that has $\delta^{18}O$ and/or $\delta^{15}N$ trends characteristic of denitrification (if material has $\Delta^{17}O > 0$).

Besides just using water chemistry to determine if denitrification is **POSSIBLE**, analysis of some solutes for isotopic composition can help demonstrate (and perhaps even quantify) denitrification.

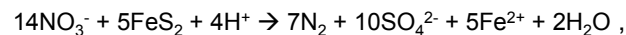
For example:

- Where denitrification proceeds via the oxidation of organic carbon:

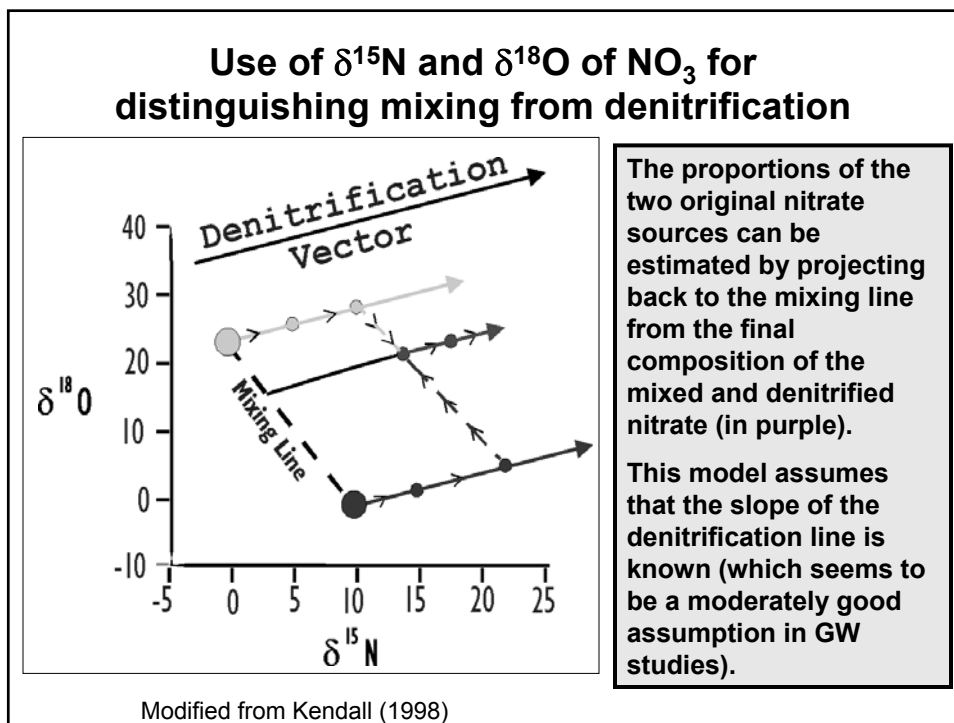
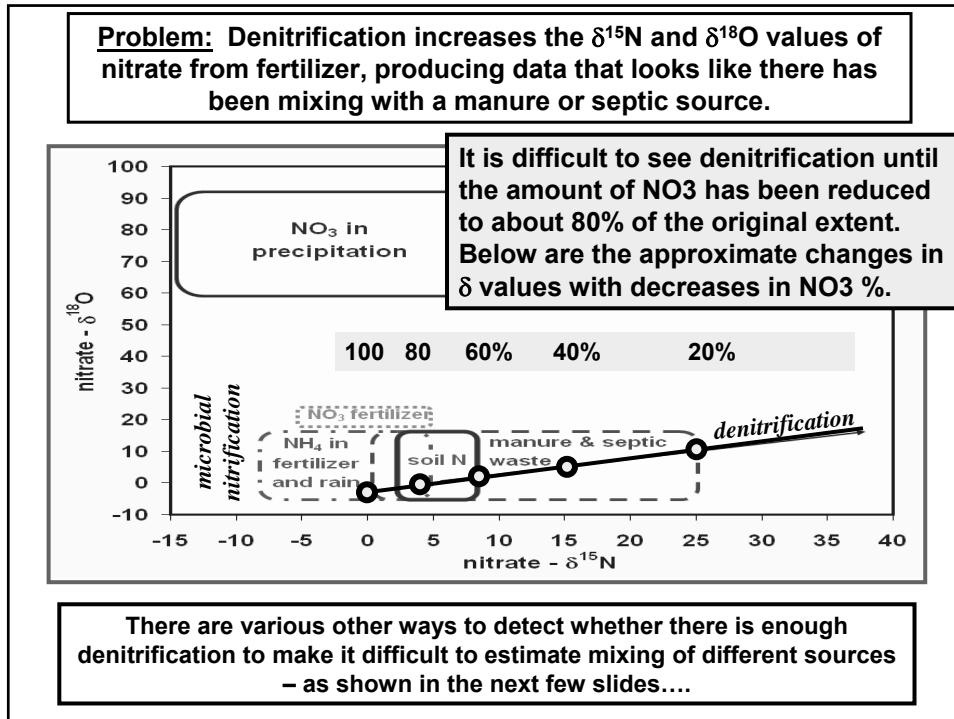


a decrease the increases in $\delta^{15}N$ and $\delta^{18}O$ should be accompanied by a decrease in $\delta^{13}C$ of DIC.

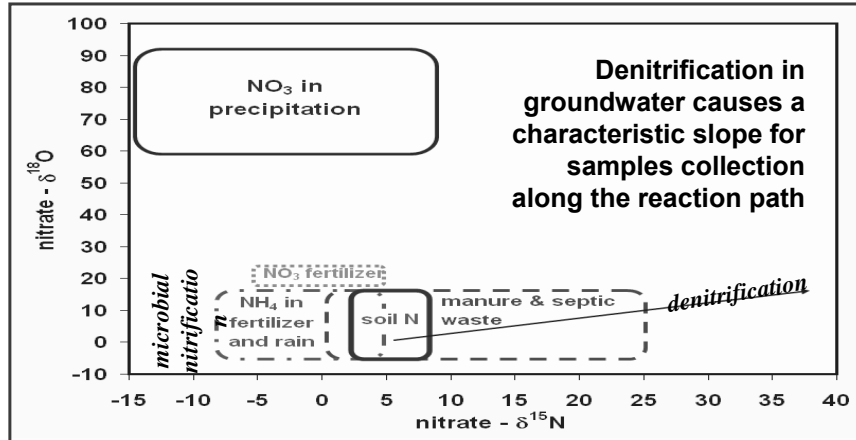
- If the electron donor is H_2S instead of organic carbon:



the $\delta^{34}S$ of sulfate is likely to decrease – and the $\delta^{18}O$ of the sulfate will probably also show a change (depending on the $\delta^{18}O$ of the ambient water and O_2).



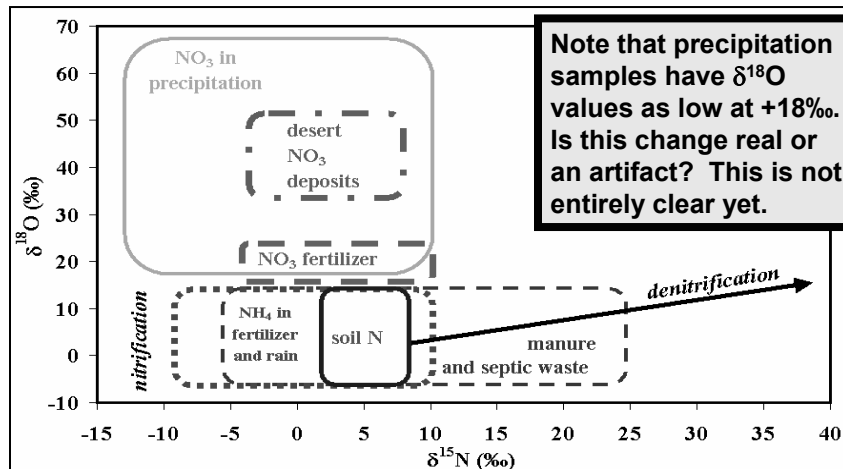
Analysis of nitrate for both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ can help resolve the question of mixing vs denitrification as the source of the high $\delta^{15}\text{N}$ values



Denitrification in groundwater causes a characteristic slope for samples collection along the reaction path

The main reason I put this slide here was that I thought this would be a good time to point out an interesting change in the $\delta^{18}\text{O}$ values of precipitation nitrate on this type of plot in some publications – as shown on the next slide....

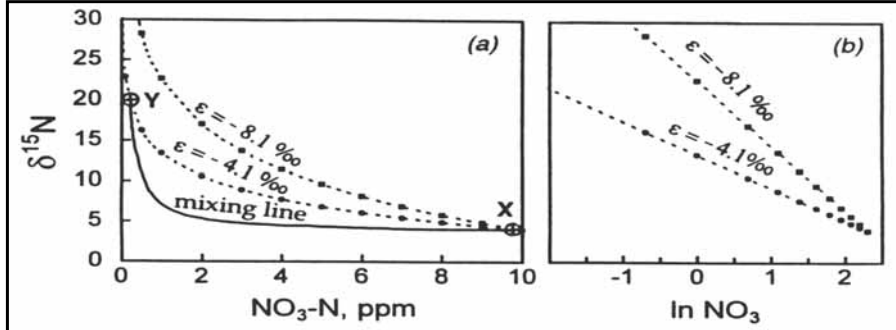
Typical pre-2005 plot of the different ranges of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values for sources



Note that precipitation samples have $\delta^{18}\text{O}$ values as low as +18‰. Is this change real or an artifact? This is not entirely clear yet.

The main difference is the low values for $\delta^{18}\text{O}$ of atmospheric nitrate: some recent studies have suggested that the previous values $< 50\text{‰}$ may be erroneous (contamination by organics, exchange with glass, etc).

How to differentiate the curve (on plots of nitrate concentration vs $\delta^{15}\text{N}$) resulting from mixing of two nitrate sources, from the curve resulting from denitrification



From Kendall (1998)

The basic point is that mixing is a hyperbolic function whereas denitrification is exponential. Hence, if mixing of two sources is responsible for the curvilinear relationship between $\delta^{15}\text{N}$ and NO_3 , plotting $\delta^{15}\text{N}$ vs $1/\text{NO}_3$ will result in a straight line.

In contrast, if denitrification (or assimilation) is responsible for the relationship, plotting $\delta^{15}\text{N}$ vs $\ln \text{NO}_3$ will produce a straight line.

Terminology used to express isotope fractionations

Kinetic fractionation factors can be defined as:

$$\alpha_{p-s} = R_p/R_s$$

where R_p and R_s are the $^{15}\text{N}/^{14}\text{N}$ ratios of the product and substrate (reactant), respectively.

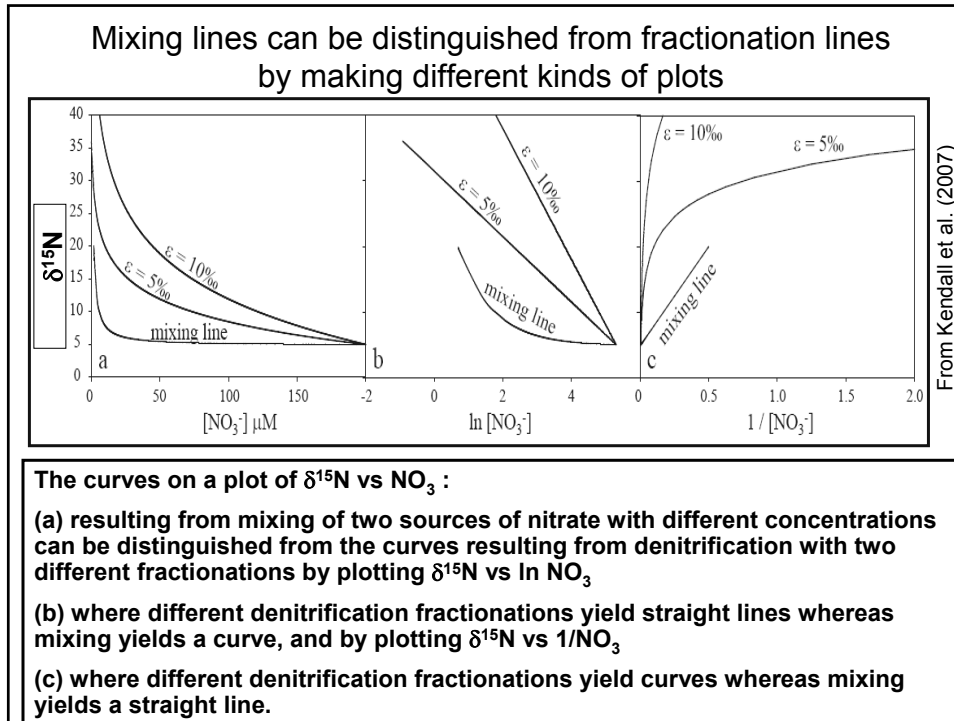
An isotope enrichment factor, ϵ , can be defined as:

$$\epsilon_{p-s} = 1000 * (\alpha - 1).$$

Be aware that both α and ϵ values are defined in various ways by different authors. In the biological literature, these terms are commonly defined "in reverse" of normal usage to avoid using values of $\epsilon < 0$, or α values < 1 .

For example, the enrichment factor is sometimes defined in reverse (i.e., ϵ_{s-p}), fractionation factors are commonly defined in reverse (i.e., $\alpha = R_s/R_p$), many use the relation $\beta = 1/\alpha$ so that $\beta > 1$, and some workers define a "discrimination factor" $D_{s/p} = (\alpha_{s/p} - 1) * 1000$ where s/p denotes substrate relative to products.

It is important to remember that environmental conditions strongly affect kinetic (biological) fractionations, especially concentration of nitrate and which step of a reaction is the rate-determining one. If a rate determining step has minimal fractionation, the net reaction has little fractionation.



Fractionation during denitrification

During denitrification, the $\delta^{15}\text{N}$ value of the residual nitrate increases in proportion to the logarithm of the residual nitrate fraction. This can be expressed using the classical Rayleigh equation, that may be approximated in some situations (Mariotti et al., 1982) as:

$$\delta_p = \delta_{R0} + \epsilon \ln C/C_0$$

where δ_R is the $\delta^{15}\text{N}$ value of the reactant nitrate at time t, δ_{R0} is the initial $\delta^{15}\text{N}$ value of the nitrate, C is the NO_3^- content at time t, C_0 is the initial NO_3^- content, and ϵ is the enrichment factor (with $\epsilon < 0$ to make the algebra work).

Since mixing and denitrification curves can be similar, data should also be plotted as $\delta^{15}\text{N}$ vs. $1/\text{NO}_3^-$ (which will yield a straight line for mixtures of two sources), and $\delta^{15}\text{N}$ vs. $\ln \text{NO}_3^-$ (which will yield a straight line for any process, like denitrification, which can be described using the Rayleigh equation -- i.e., any exponential relation).

Under favorable circumstances, plotting data in this way can provide supporting evidence for the determination of whether mixing or denitrification has occurred (Mariotti et al., 1988), and can be used to estimate the enrichment factor and initial conditions.

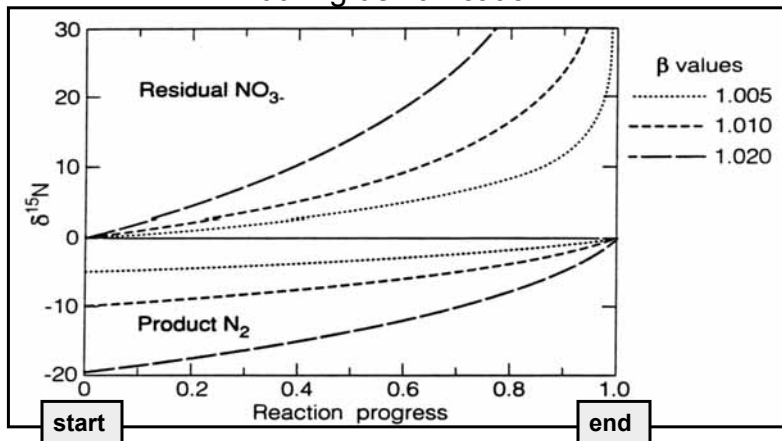
In my opinion, the best way to quantify the extent of denitrification – and perhaps be able to quantify the mixing of sources of nitrate prior to denitrification – is to analyze the $\delta^{15}\text{N}$ of the dissolved N_2 gas in addition to analyzing nitrate and other isotopes in the water.

The idea is to determine how much of the N_2 is derived from denitrification, apply a fractionation factor, and then back-calculate the original $\delta^{15}\text{N}$ of the TOTAL original nitrate.

Gas samples are easy to collect, archive moderately well, and are not hard to analyze for $\delta^{15}\text{N}$. However, you must also have the gas analyzed for gas ratios, like N_2/Ar or N_2/Xe , to calculate how much of the N_2 is “natural” – i.e., enters during recharge.

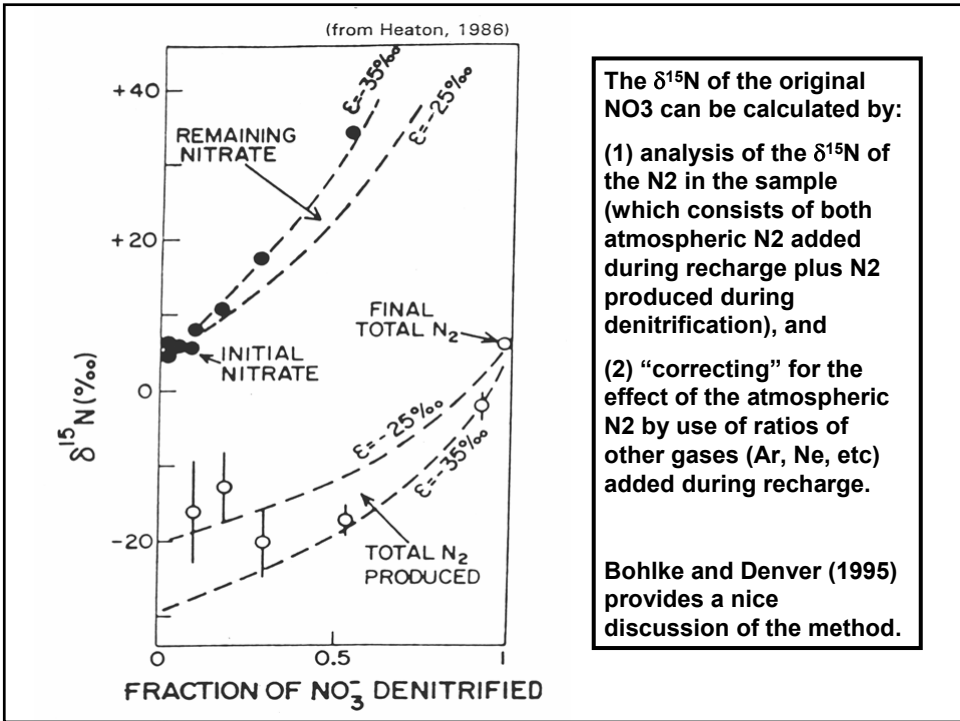
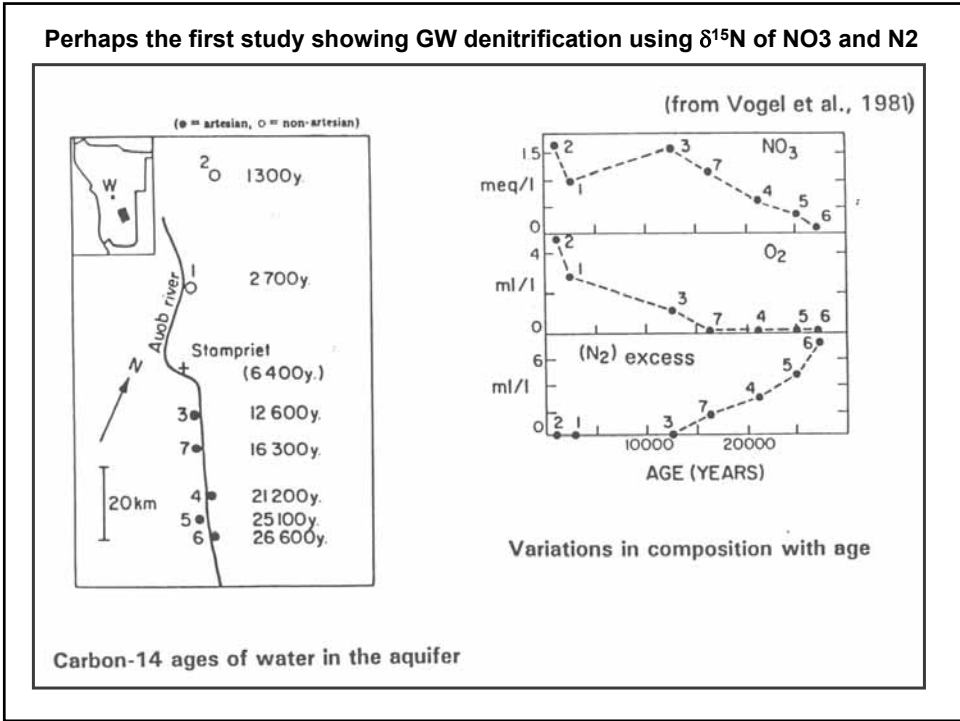
The next slides discuss this method of quantifying denitrification....

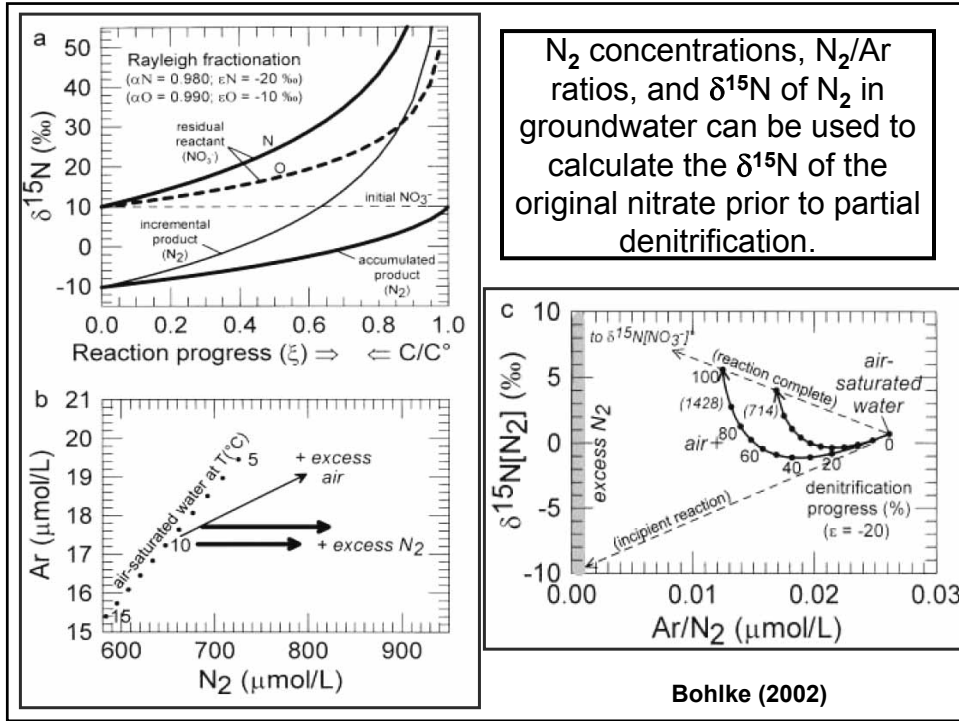
Changes in the $\delta^{15}\text{N}$ of residual nitrate and produced N_2 during denitrification



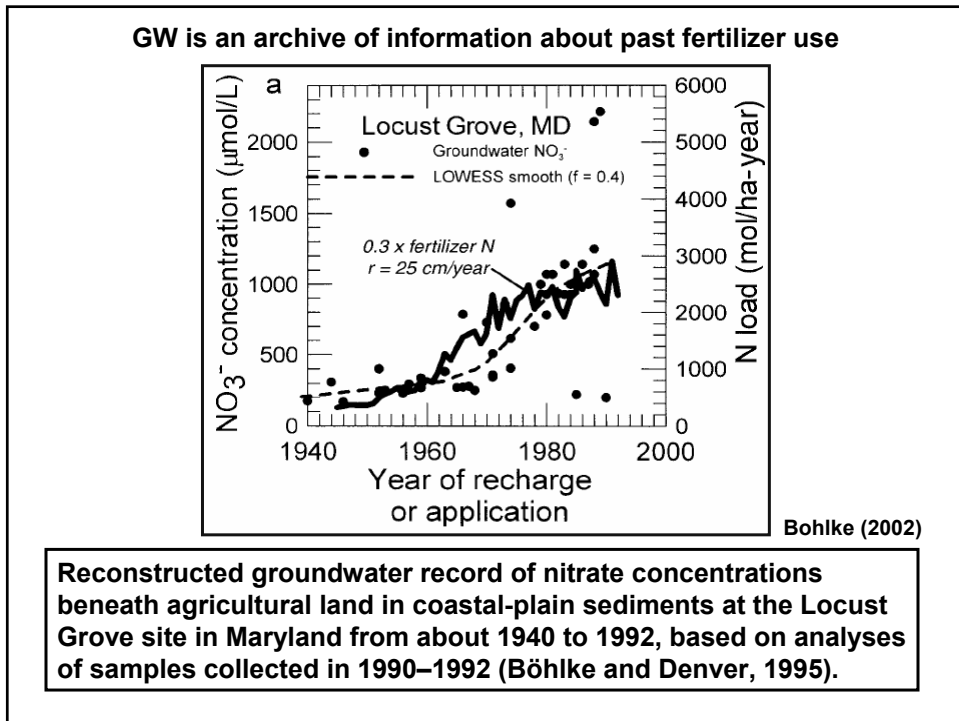
This diagram shows how the $\delta^{15}\text{N}$ of residual NO_3 increases as low- $\delta^{15}\text{N}$ NO_3 is removed by denitrification to N_2 . Hence, the $\delta^{15}\text{N}$ of the N_2 continues to increase as the reaction progresses.

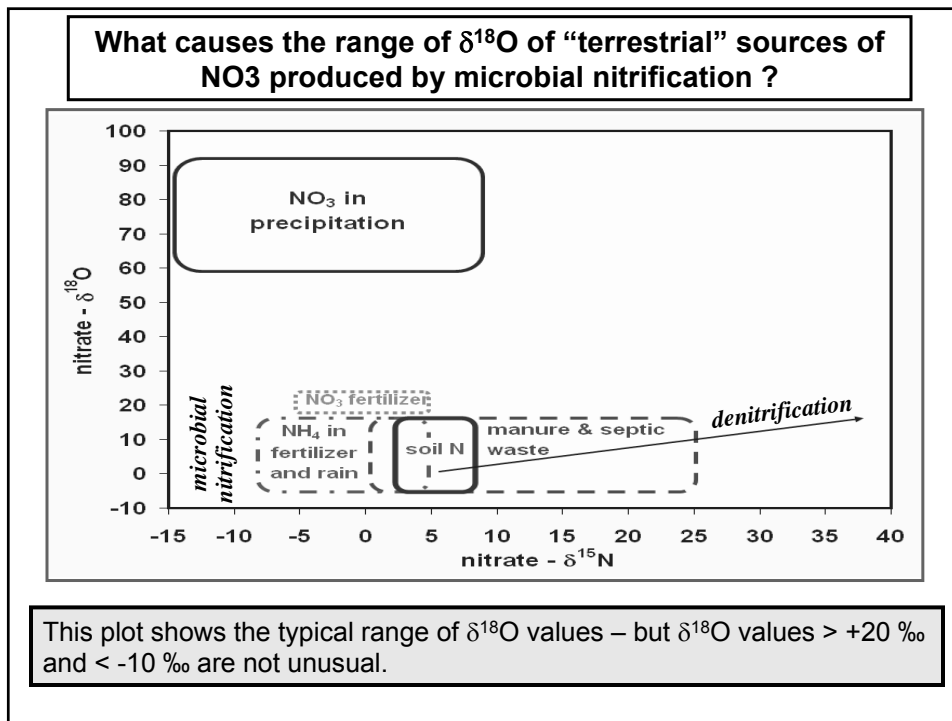
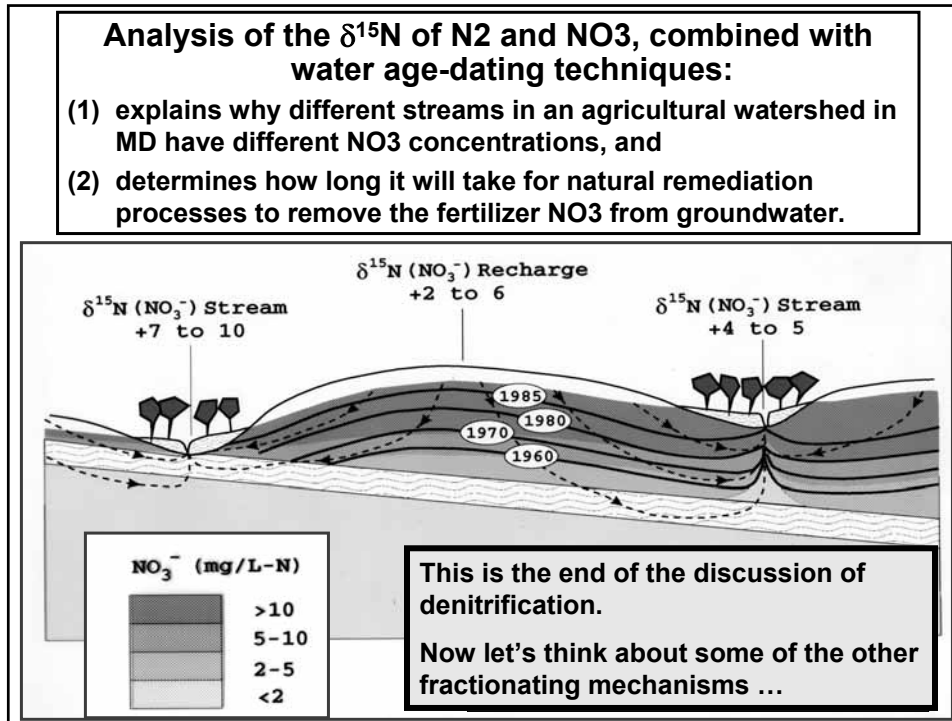
The different curves are for different Rayleigh fractionation factors.





N_2 concentrations, N_2/Ar ratios, and $\delta^{15}\text{N}$ of N_2 in groundwater can be used to calculate the $\delta^{15}\text{N}$ of the original nitrate prior to partial denitrification.





How nitrate produced by nitrification obtains its $\delta^{18}\text{O}$ value

Biochemical and bacteriological literature to date indicates that nitrate produced by microbial nitrification in laboratory cultures derives two oxygens from the oxygen in water molecules and one oxygen from O_2 .

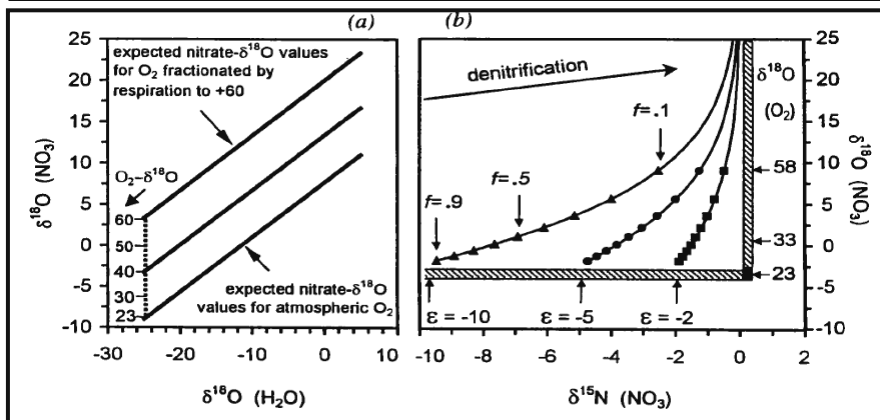
If the oxygens are incorporated without any fractionation, then the $\delta^{18}\text{O}$ of microbial nitrate can be calculated (in theory!) if the $\delta^{18}\text{O}$ of water and O_2 are known, as shown below:

$$\delta^{18}\text{O}_{(\text{NO}_3)} = \frac{2}{3} \delta^{18}\text{O}_{(\text{H}_2\text{O})} + \frac{1}{3} \delta^{18}\text{O}_{(\text{O}_2)}$$

For waters with $\delta^{18}\text{O}$ values in the normal range of -25 to +4‰, the $\delta^{18}\text{O}$ of soil nitrate formed from *in situ* nitrification of ammonium, should be in the range of -10 to +10‰, respectively. For highly evaporated water (+20‰), the $\delta^{18}\text{O}$ of nitrate could be as high as about +21‰ (Böhlke et al., 1997).

The above model makes four critical assumptions: (1) the proportions of oxygen from water and O_2 are the same in soils as observed in laboratory cultures, (2) there are no fractionations resulting from the incorporation of oxygen from water or O_2 , (3) the $\delta^{18}\text{O}$ of water used by the microbes is identical to that of the bulk soil water, and (4) the $\delta^{18}\text{O}$ of the O_2 used by the microbes is identical to that of atmospheric O_2 .

Causes of the wide range of $\delta^{18}\text{O}$ values produced by nitrification



Kendall (1998)

(a) The range of nitrate- $\delta^{18}\text{O}$ values expected for microbial nitrification with ambient H_2O - $\delta^{18}\text{O}$ values ranging from -25 to +4‰ (winter to summer precipitation values), and O_2 - $\delta^{18}\text{O}$ values ranging from that of the atmosphere (+23‰) to +60‰ for soil O_2 fractionated by respiration.

(b) Microbial nitrification can produce a wide range of nitrate- $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values; several scenarios for how these values might evolve over time are shown.

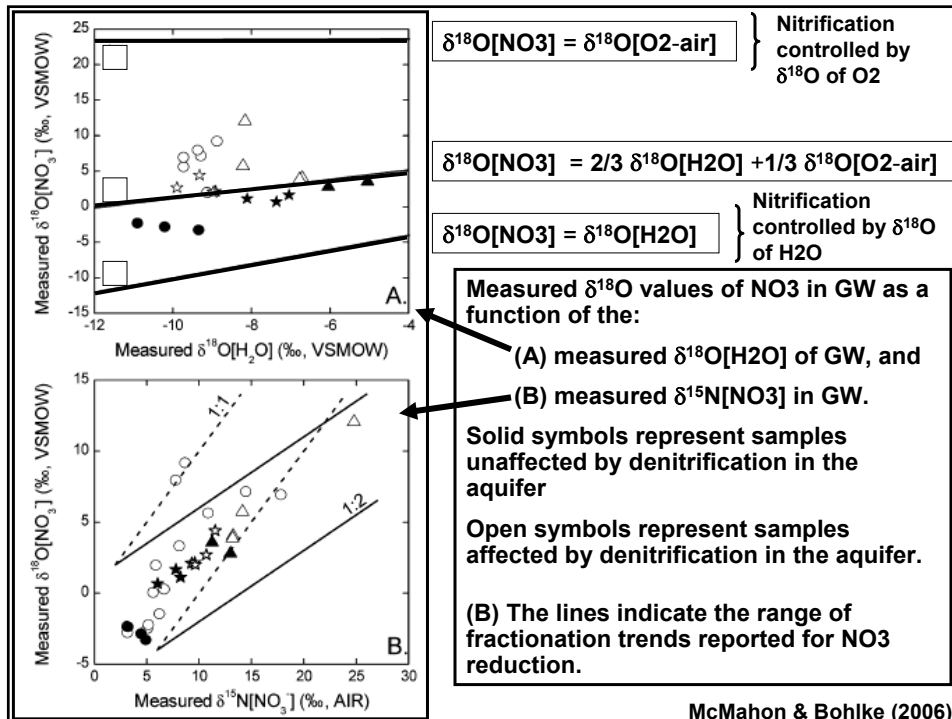
Often it has been found that the $\delta^{18}\text{O}$ of microbial NO_3^- is a few ‰ higher than expected for the equation and assumptions above.

A variety of explanations have been offered for these high $\delta^{18}\text{O}_{\text{NO}_3}$ values including:

- (1) nitrification in soil waters with higher than expected $\delta^{18}\text{O}$ values because of evaporation (Böhlke et al. 1997) or seasonal changes in rain $\delta^{18}\text{O}$ (Wassenaar 1995);
- (2) changes in the proportion of O from H_2O and O_2 sources (i.e., > 1/3 from O_2) (Aravena et al. 1993);
- (3) nitrification using O_2 that has a high $\delta^{18}\text{O}$ due to respiration (Kendall 1998);
- (4) nitrification that occurs simultaneously via both heterotrophic and autotrophic pathways (Mayer et al. 2001).

At this time, it is still unresolved how each of these mechanisms affects $\delta^{18}\text{O}_{\text{NO}_3}$ during nitrification reactions. Another mechanism has been proposed for lower $\delta^{18}\text{O}$ than expected: that during nitrification there is exchange between the O in nitrate and water (Casciotti et al., 2002).

Hence, nitrification of different materials (manure, waste, ammonium fertilizer) can get distinctive $\delta^{18}\text{O}$ values if the $\delta^{18}\text{O}$ of the ambient H_2O and O_2 are different. The $\delta^{18}\text{O}$ of water is affected by its source and subsequent evaporative fractionation. The $\delta^{18}\text{O}$ of O_2 gas is affected by all the O-consuming reactions in the subsurface (nitrification, respiration, etc).



What about fractionation of nitrate during assimilation by bacteria or uptake by plants?

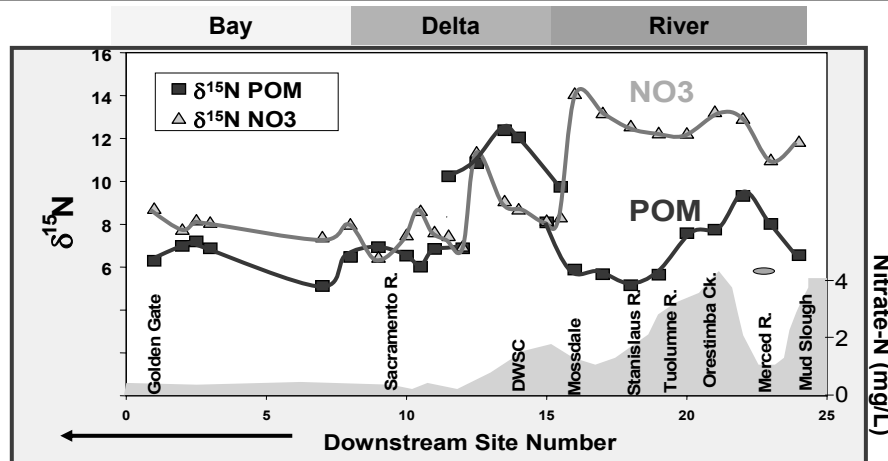
Fogel & Cifuentes (1993) present an elegant model for ammonium assimilation in aquatic algae that predicts total fractionations of -4, -14, or -27 ‰ depending on whether algae cells are nitrogen limited, enzyme limited, or diffusion limited, respectively. However, for the low pH values and low NH_4^+ concentrations common to soils and many aquatic environments, the model predicts that availability of N is the limiting condition and the transport of ammonium across cell walls is probably rapid, resulting in a small (< -4 ‰) overall fractionation.

More recently, Needoba et al. (2004) demonstrated that NO_3^- assimilation by marine phytoplankton imparts a large "apparent fractionation" (-13 to -6 ‰) depending on growth rate and conditions. Fractionations are higher at higher concentrations of nitrate.

While there have been few studies of the effects of O fractionations during assimilation on the $\delta^{18}\text{O}$ of the residual NO_3^- , nitrate assimilation by marine phytoplankton seems to cause ~1:1 changes in the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate, regardless of species or the magnitude of the isotope effect; hence, these fractionations can be viewed as strongly "coupled" (Granger et al. 2004).

Our studies in the Mississippi Basin (Battaglin et al., 2001a&b) and San Joaquin Basin (Kratzer et al., 2004) show $\delta^{15}\text{N}$ fractionations of 4 – 8 ‰, as shown next...

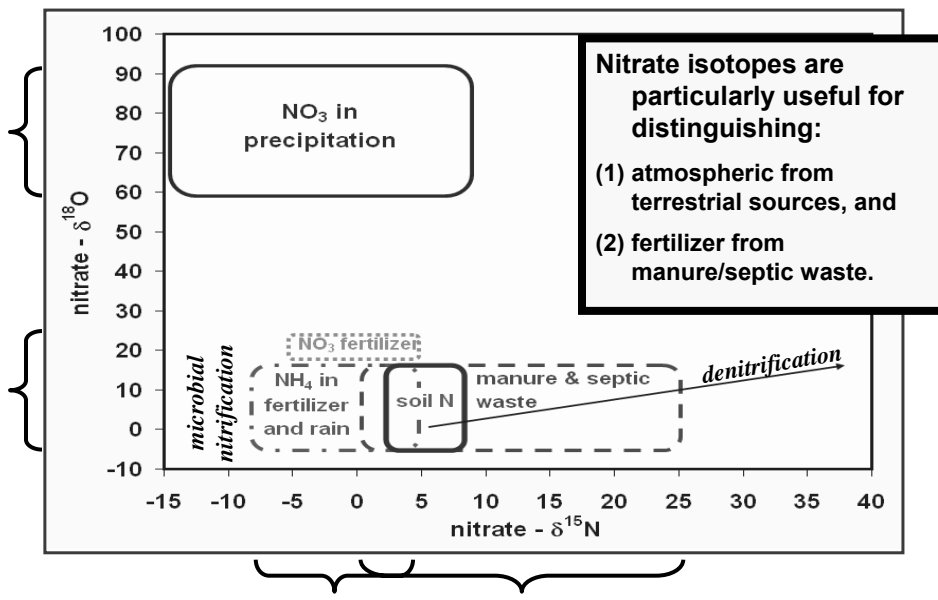
POM in the River section is mostly algae, and its $\delta^{15}\text{N}$ tracks the $\delta^{15}\text{N}$ of nitrate (with fractionations of 2 - 8 ‰). POM and nitrate patterns in the Delta are weird because of the WWTP source inputs. The lower fractionations (1-3 ‰) in the Bay are due to the lower amounts of NO_3^- .



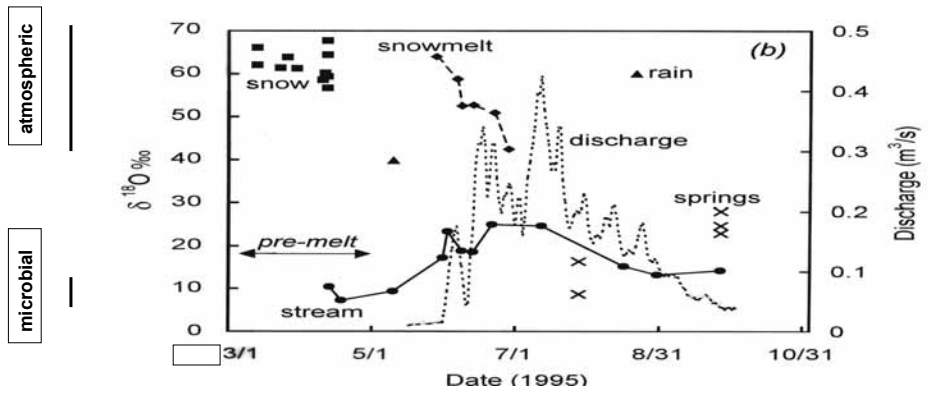
These data suggest that the $\delta^{15}\text{N}$ of algae (and algal POM) can sometimes be a useful proxy for changes in the $\delta^{15}\text{N}$ of nitrate.

Now some examples of successful applications of nitrate isotopes.

How can nitrate isotopes (nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) help determine the dominant source of nitrate?



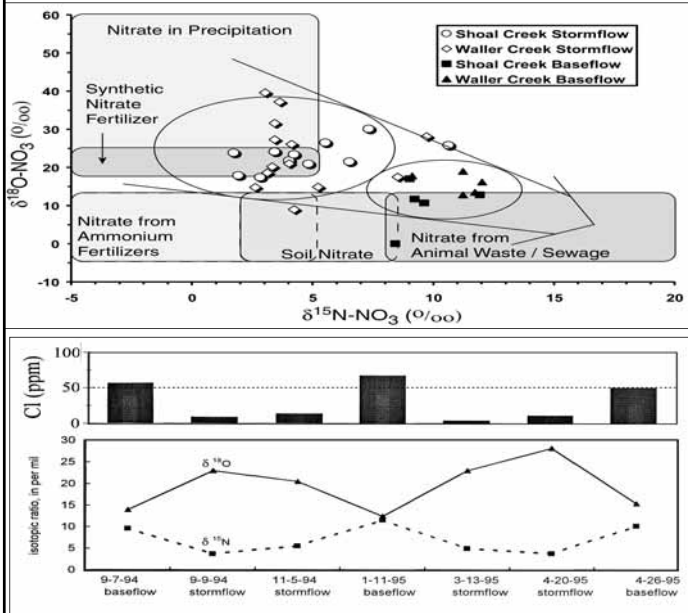
Use of $\delta^{18}\text{O}$ of nitrate to quantify relative proportions of microbial vs atmospheric nitrate during snowmelt in streams in small forested watersheds



These data are from Loch Vale (CO) and show that <50% of the nitrate in streamwater is derived from the melting snowpack in 1995.

(from Kendall 1998; Campbell et al. 2002)

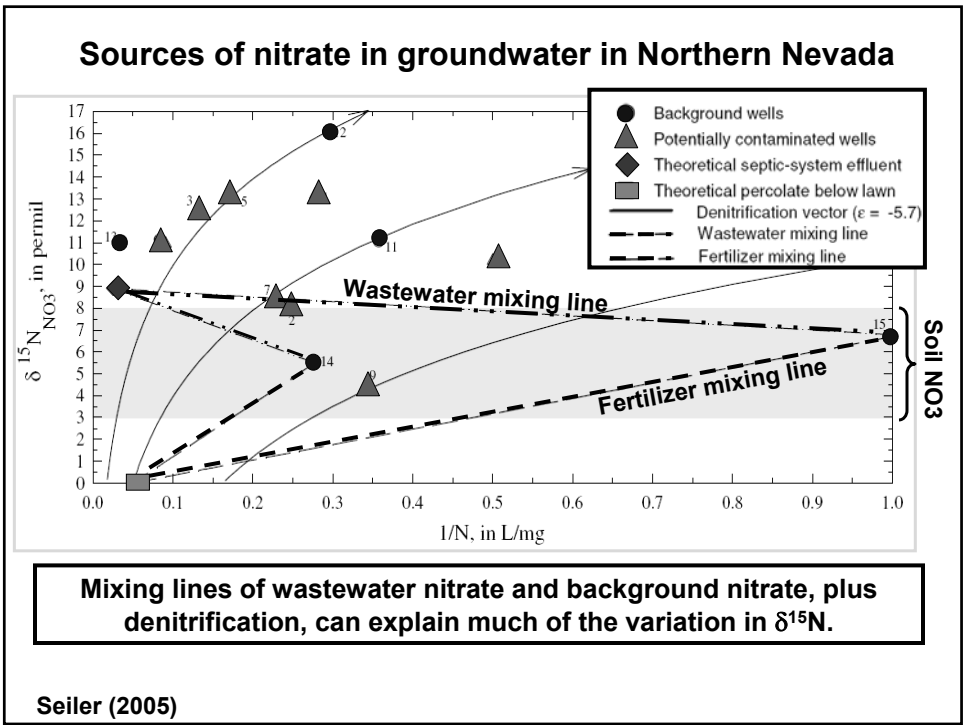
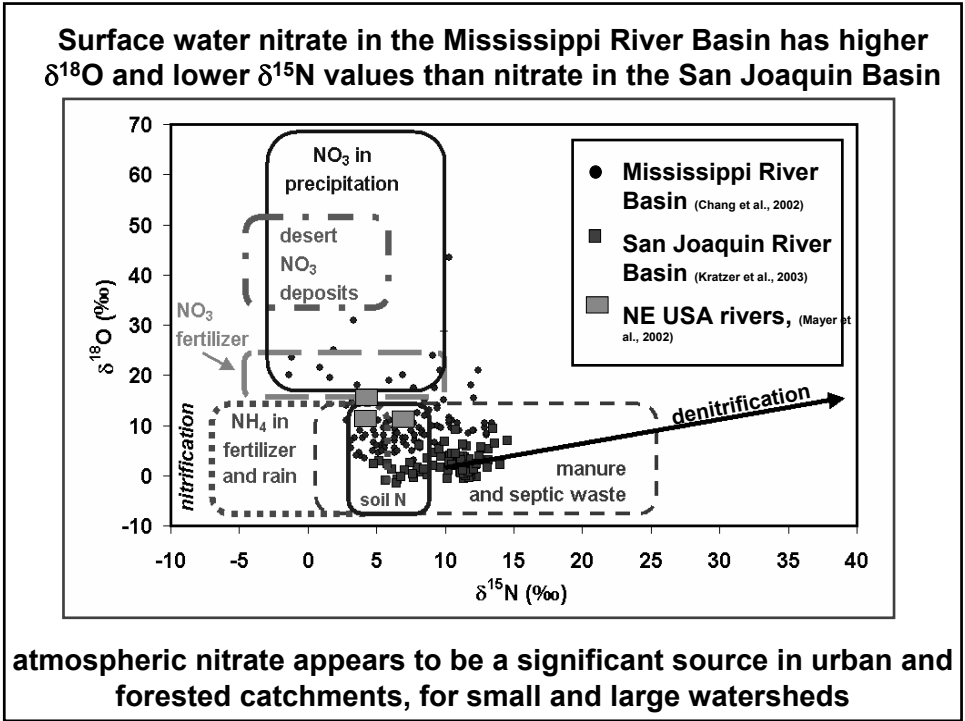
Seasonal contributions of atmospheric NO_3 (from overland flow) and sewage in urban streams in Austin TX

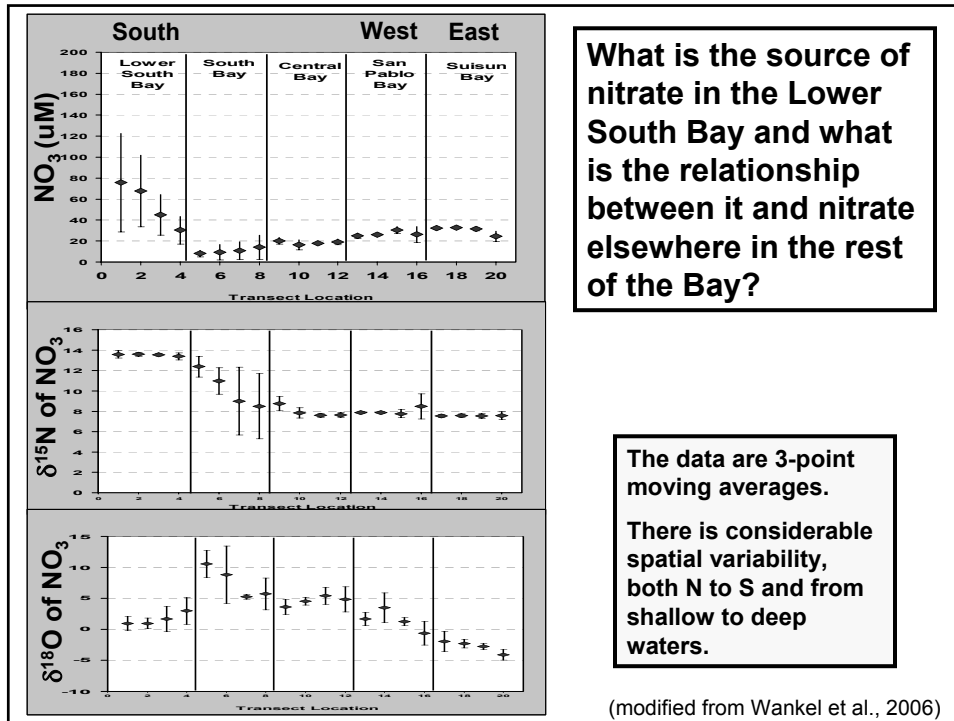


During stormflow conditions, most of the nitrate in these urban streams is derived from atmospheric nitrate.

During baseflow conditions, the nitrate comes from a mixture of sources dominated by human/animal waste.

(from Silva et al., 2002; Kendall, 1998)

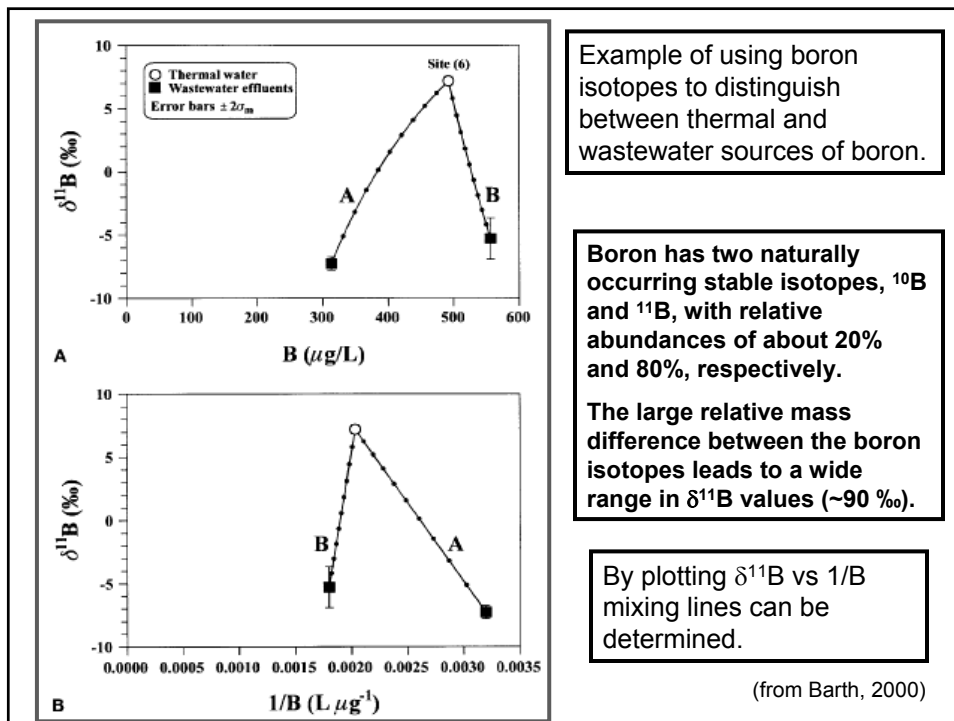




What is the source of nitrate in the Lower South Bay and what is the relationship between it and nitrate elsewhere in the rest of the Bay?

The data are 3-point moving averages.
There is considerable spatial variability, both N to S and from shallow to deep waters.

(modified from Wankel et al., 2006)



Example of using boron isotopes to distinguish between thermal and wastewater sources of boron.

Boron has two naturally occurring stable isotopes, ^{10}B and ^{11}B , with relative abundances of about 20% and 80%, respectively.
The large relative mass difference between the boron isotopes leads to a wide range in $\delta^{11}\text{B}$ values (~ 90 ‰).

By plotting $\delta^{11}\text{B}$ vs $1/B$ mixing lines can be determined.

(from Barth, 2000)

Advantages and disadvantages of Nitrate and Borate isotopes

$\delta^{15}\text{N}$ NO_3 : intrinsic molecule

- Useful for determining mixing processes.
- Isotopic fractionation by natural denitrification.

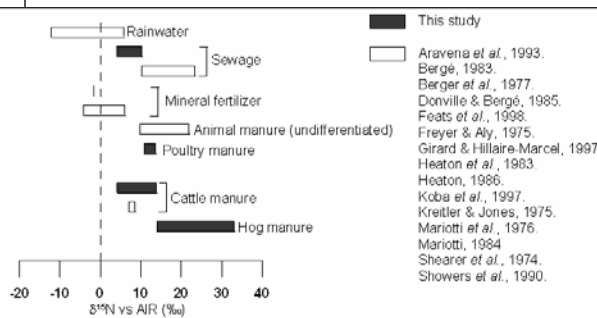
$\delta^{11}\text{B}$ Co-migrant of the NO_3 molecule

- Useful for determining mixing processes.
- Not affected by natural denitrification.
- Isotopic fractionation by adsorption/desorption on clay minerals



From Dave Widory

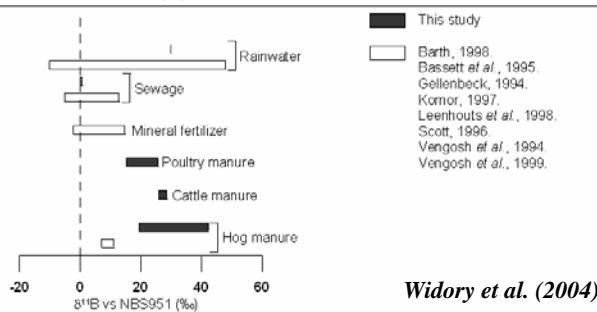
Isotopic characterization of pollution sources



• $\delta^{15}\text{N}$ mainly discriminates fertilizers from sewage and animal manure.

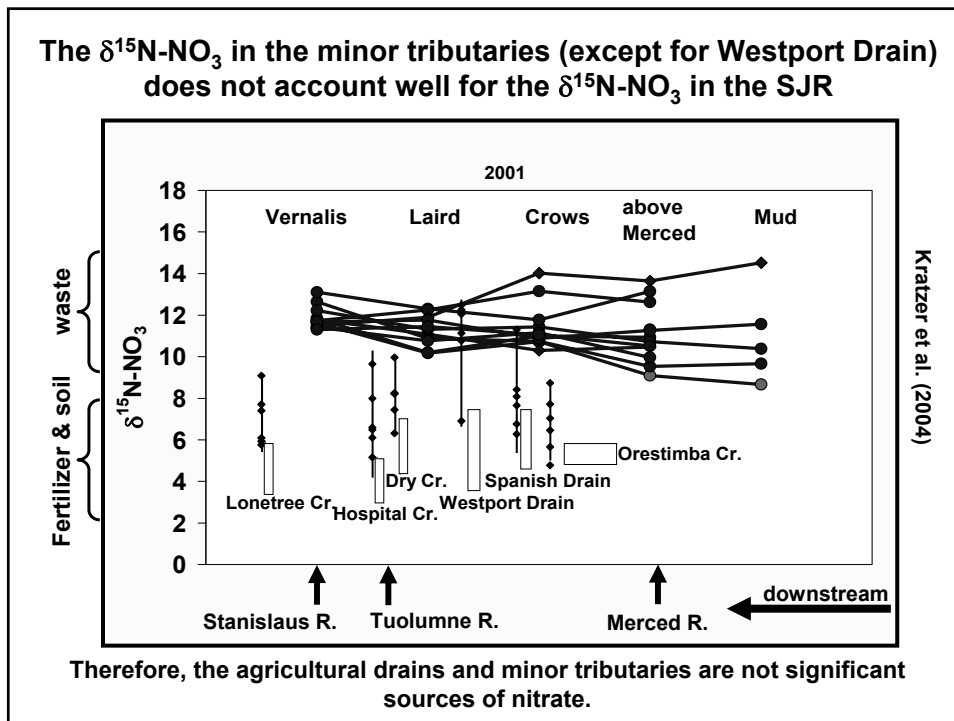
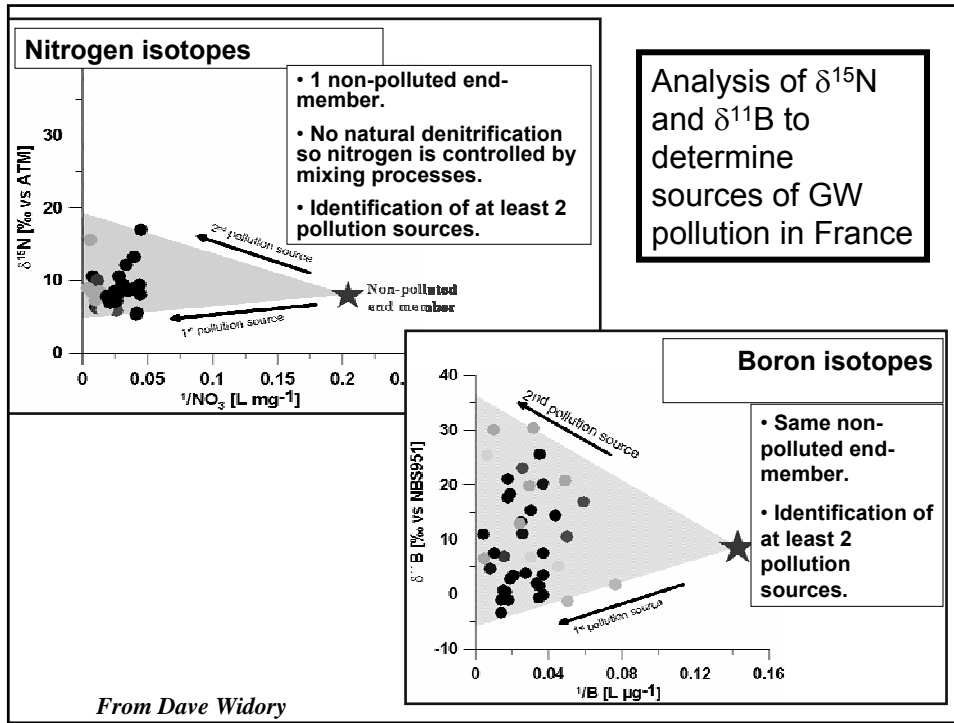
• $\delta^{11}\text{B}$ mainly discriminates animal manure from sewage and fertilizers.

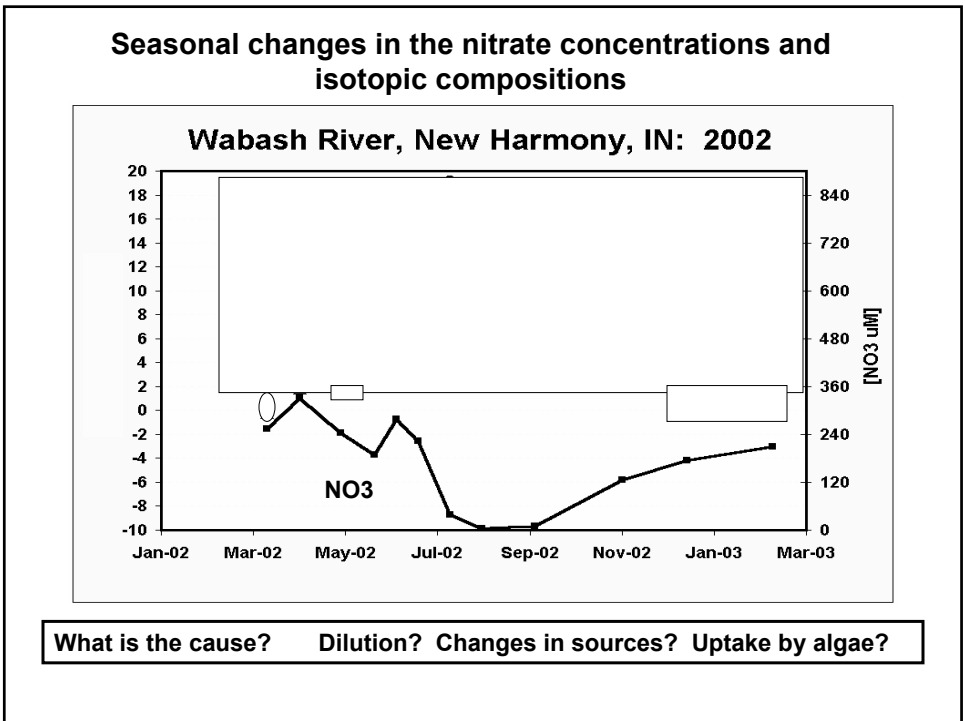
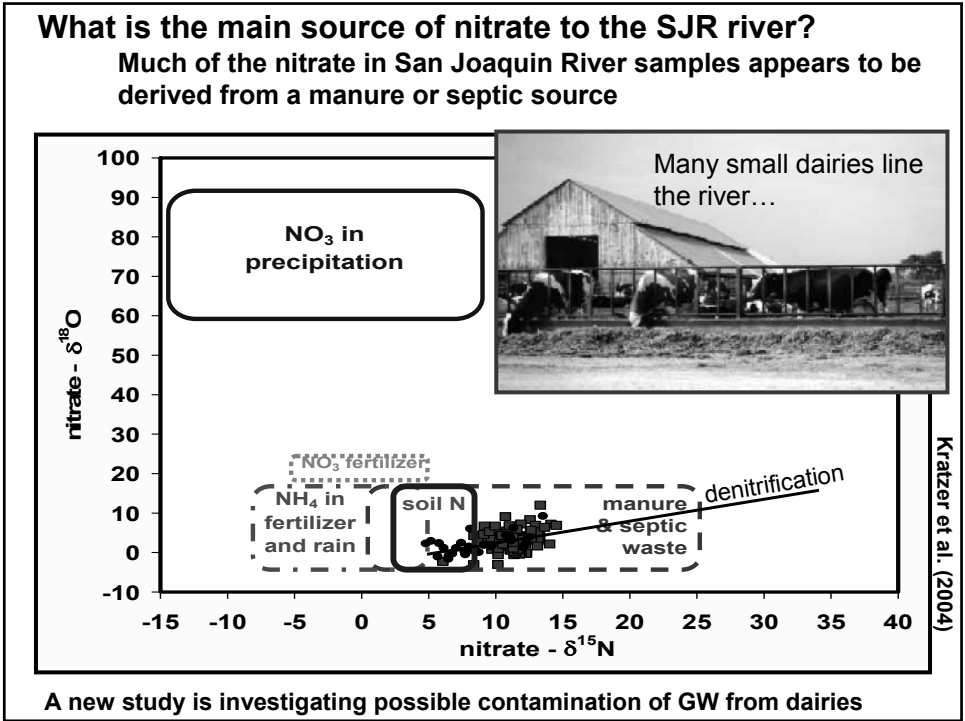
• The combination allows differentiation of sewage vs manure.



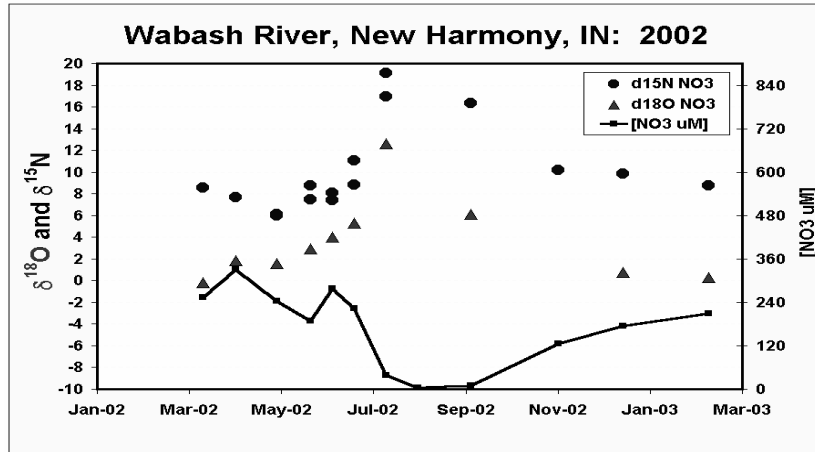
Widory et al. (2004)







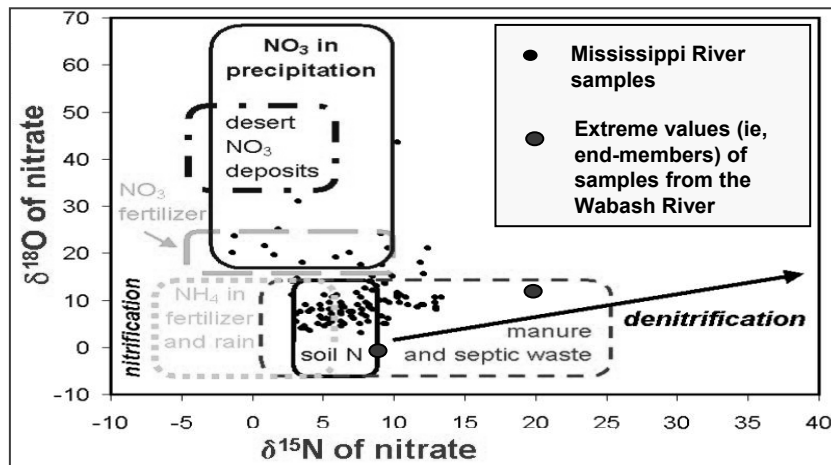
What is causing this seasonal shift in nitrate concentration?
The isotope data suggest that it is caused by a seasonal change in the amounts of 2 different nitrate sources.



Kendall (unpub. data)

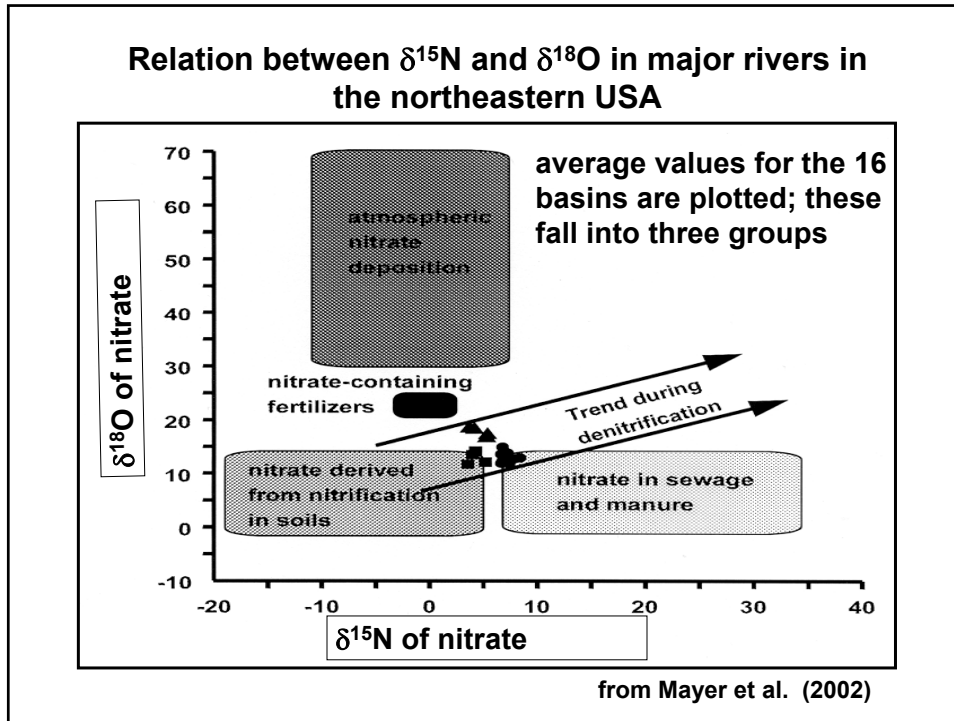
Seasonal shift from a low-NO₃ source with high δ values in the summer, to a high-NO₃ source with low δ values in the winter.

What is causing this seasonal shift in nitrate concentration?
Probably a seasonal mixing of nitrate derived from manure and nitrate from nitrification of soil organic matter



Note this is a pre-2005 plot with ppt with low d18O values

Could these data indicate denitrification? Probably not (because of the slope and because other ways of modeling the data do not support this explanation).



There is another reason to be skeptical about interpreting the data as denitrification when river nitrate data plot along what appears to be a denitrification line: the fact that “benthic denitrification” appears to have little or no N or O fractionation.

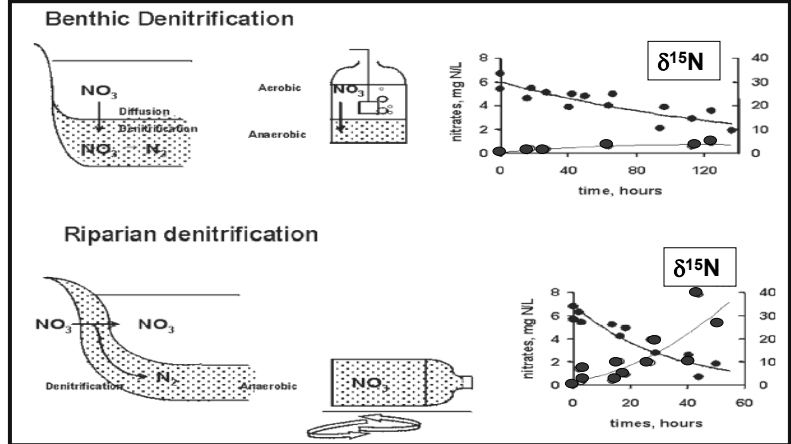
The extent of fractionation during denitrification is highly dependent on environmental conditions. Authors have distinguished between “benthic” denitrification in which NO_3^- diffuses into the anaerobic groundwater from a surficial aerobic environment before denitrification can occur, and “riparian” denitrification where there is partial conversion of the nitrate in the anaerobic groundwater (Sebilo et al. 2003).

The apparent fractionation associated with benthic denitrification is small (ranging from -1.5 to -3.6 ‰), because NO_3^- diffusion through the water-sediment interface, which causes minimal fractionation, is the rate determining step. In contrast, riparian denitrification causes a much larger fractionation (about -18 ‰; Sebilo et al. 2003).

IMPORTANT POINT: If the rate determining step of a reaction has minimal fractionation, the net reaction has minimal fractionation.

Next slide is a cartoon that shows benthic vs riparian denitrification....

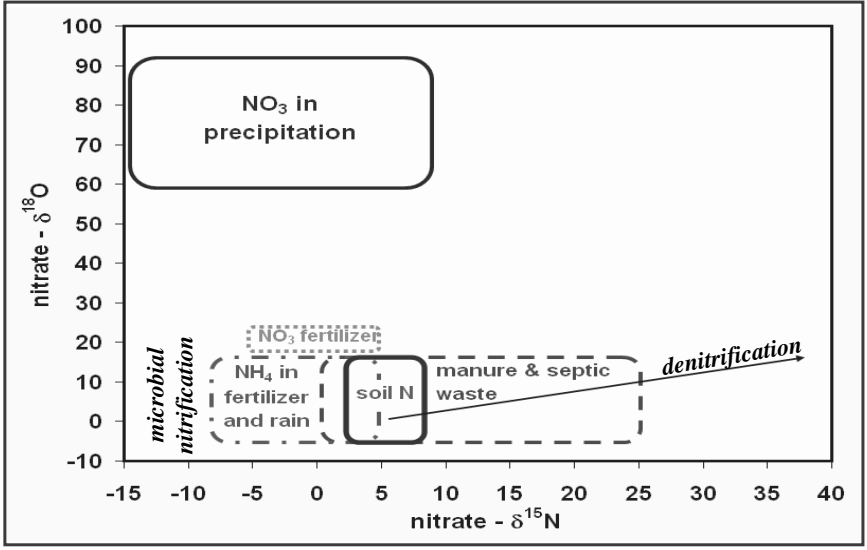
Cartoons showing how benthic denitrification (occurring in anoxic sediments of rivers) would cause little or no enrichment in ^{15}N whereas riparian (GW) denitrification would cause large enrichment.



(modified from Sebito et al., 2003)

The reason why benthic denitrification causes minimal fractionation is because diffusion of nitrate into the anoxic sediments is the rate determining step and it has minimal fractionation.

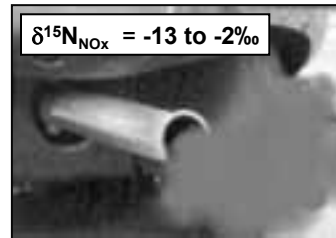
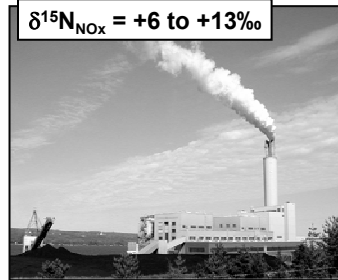
Do different anthropogenic sources of atmospheric nitrate (from NO_x and NH_y) have distinctive $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and/or $\delta^{17}\text{O}$ values?



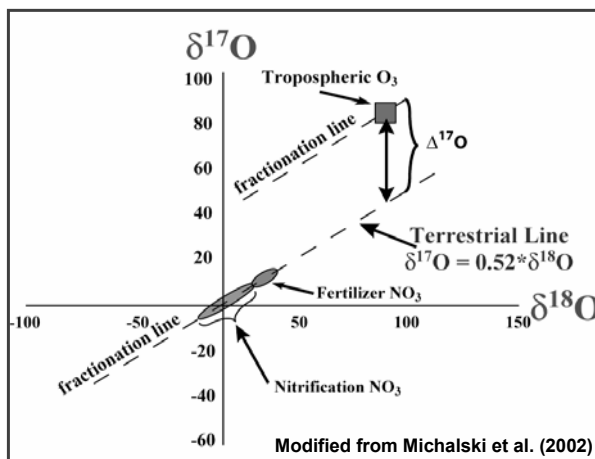
Where does atmospheric nitrate come from?

- Natural processes (fire, lightning, soil emissions)
- Agricultural emissions
- Power plant exhaust
- Vehicle emissions

Two major NO_x sources can have different isotopic signatures (Heaton, 1990).



Example of how mass dependent and non-mass dependent fractionations affect nitrate $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$



All terrestrial-derived samples plot along the terrestrial line, showing the normal mass dependent relation between $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$.

In contrast, atmospheric-derived samples plot above the terrestrial line because of the non-mass dependent relation between $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ in O_3 in the troposphere.

Atmospheric NO_3 is labeled by its $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values

Relations between $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values:

In all terrestrial materials, there is a constant relation between the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of any given substance because isotope fractionations are mass dependent.

The mass dependent fractionation results in:

$$\delta^{17}\text{O} = 0.52 (\delta^{18}\text{O})$$

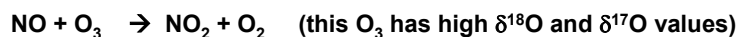
In many oxides derived from high atmospheric processes there "excess ^{17}O " (beyond the ^{17}O expected from the ^{18}O value) derived from a mass independent fractionation (MIF) such that:

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 (\delta^{18}\text{O})$$

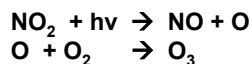
Hence, $\Delta^{17}\text{O}$ values $> 0\text{‰}$ are a useful tracer of O derived from atmospheric processes.

Origin of the high $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of atmospherically derived NO_3

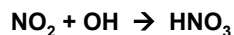
NO generated by combustion, biomass burning, or biological emissions is eventually oxidized to NO_2 by several reactions. One such reaction is:



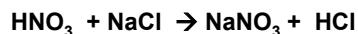
The NO_2 is then photolyzed back to NO , and is the primary source of troposphere O_3 :



The NO is then re-oxidized to NO_2 etc etc. Eventually NO_2 is removed by several "sink" reactions. For example:



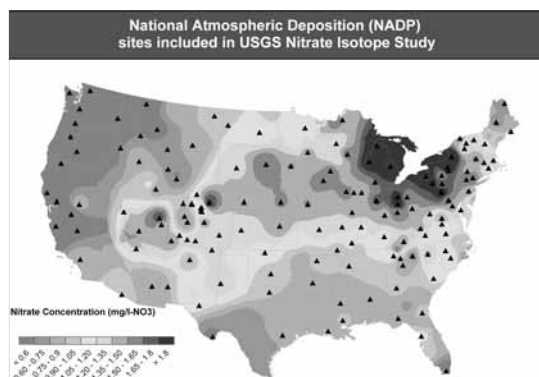
Nitric acid can then react to form nitrate:



So why is $\Delta^{17}\text{O}$ so exciting to isotopists?

1. $\Delta^{17}\text{O}$ values provide a very persuasive indicator of an atmospheric source for the compound (i.e., nitrate, sulfate, etc) with the O.
2. $\delta^{17}\text{O}$ provides an additional tracer for nitrate, meaning that we can solve for an additional source or process term.
3. $\Delta^{17}\text{O}$ is **NOT** affected by any terrestrial fractionating process (e.g., denitrification).

How do nitrate isotopes vary on a national scale?



We have just finished a study that piggybacked on the NADP network, where we analyzed samples for nitrate $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and to a lesser extent $\delta^{17}\text{O}$. Papers are in review.

- 156 NADP sites
- Archived samples (2000)
- Bimonthly, volume-weighted samples
- Tested for changes in $[\text{NO}_3^-]$ during storage. No changes found during 3 year storage period.

NEXT:

A brief review of several potential applications of isotopes to tracing agricultural pollution (and solving agricultural problems) – with my opinions about whether the applications are:

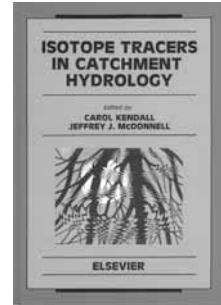
- easily usable tools (i.e., “ready for prime time”), or that they still need more research;
 - under what conditions do the tools work best,
 - what additional isotope and chemical tracers appear to be beneficial for the application, and
 - selected examples.
- **For more information, see the list of references.**

**Tracing sources of agricultural N
using isotopic techniques:
the state of the science**

**(from materials prepared for an EPA-sponsored
workshop on AFOs, December 2004, College Park MD.**

<http://www.epa.gov/osp/regions/afo.htm>

While stable isotopes have become common tools for tracing sources of waters and solutes in small watersheds, they are currently under-utilized in larger basins, especially in agricultural and urban rivers.



Why is this?

Perhaps because one of the first attempts to use natural abundance ^{15}N to understand the causes of the increases in nitrate concentrations in surface waters in many agricultural areas (Kohl et al., 1971, Science) elicited a hyper-critical response by 10 prominent soil scientists and agronomists (Hauck et al., 1972, Science), which concluded that use of ^{15}N was a “questionable approach.”

Current Isotopic Tools for Agricultural Pollution Studies

- Nitrate: analyzed for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ (and sometimes for $\delta^{17}\text{O}$).
- POM (particulate organic matter): filtered, acidified, and analyzed for $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ (and sometimes for $\delta^{34}\text{S}$).
- Water: analyzed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$.
- DIC (dissolved inorganic carbon): analyzed for $\delta^{13}\text{C}$.
- DOC (dissolved organic carbon): analyzed for $\delta^{13}\text{C}$.
- DON (dissolved organic nitrogen): analyzed for $\delta^{15}\text{N}$.
- Ammonium: analyzed for $\delta^{15}\text{N}$.
- Phosphate: analyzed for $\delta^{18}\text{O}$.
- Sulfate: analyzed for $\delta^{34}\text{S}$ (and sometimes for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$).
- O_2 (DO = dissolved oxygen): analyzed for $\delta^{18}\text{O}$.

Some even newer tools: B, Li, Sr, U isotopes

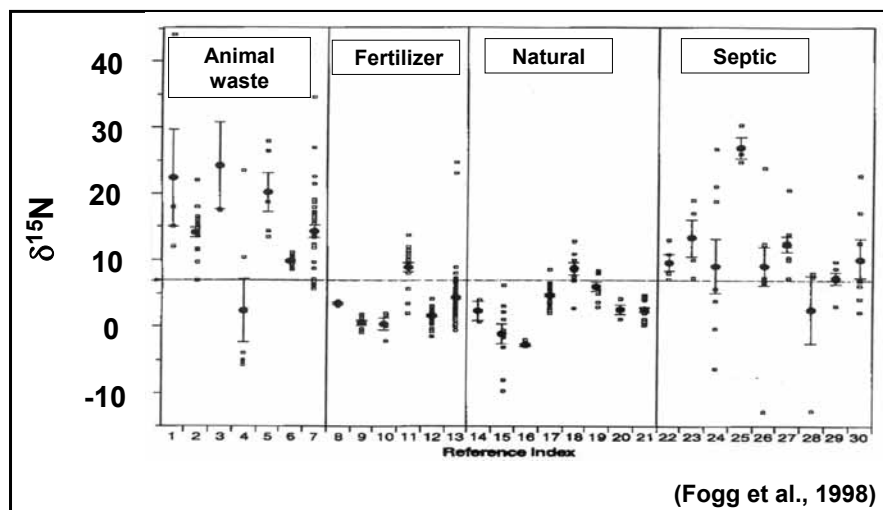
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A brief review of several potential applications of isotopes to tracing agricultural pollution (and solving agricultural problems) – with my opinions about whether the applications are:

- easily usable tools (i.e., “ready for prime time”), or that they still need more research;
 - under what conditions do the tools work best,
 - what additional isotope and chemical tracers appear to be beneficial for the application, and
 - selected examples.
- **For more information, see the list of references.**

Fertilizer vs animal waste source of nitrate: nitrate- $\delta^{15}\text{N}$

Tool usually works.



Fertilizer vs animal waste source of nitrate: nitrate- $\delta^{15}\text{N}$

Tool often works.

But it is more costly if the soils are clayey or the groundwater is not well-oxygenated, so that significant denitrification is suspected.

In this case, quantification can be successful if ...

the effects of denitrification can be estimated using:

- analysis of dissolved N_2 for $\delta^{15}\text{N}$ (to correct for the N_2 produced by denitrification),
- nitrate- $\delta^{18}\text{O}$ (this tracer usually is not as useful for this purpose as N_2 - $\delta^{15}\text{N}$); and
- geochemical modeling using chemical data and perhaps $\text{DIC-}\delta^{13}\text{C}$, SO_4 - $\delta^{34}\text{S}$, $^{87}\text{Sr}/^{86}\text{Sr}$, etc.
- use of all 3 methods, along with age-dating of the water using CFCs or $^3\text{He}/\text{T}$, will improve quantification of source contributions.

What about use in rivers, streams, and wetlands?

Fertilizer vs animal waste source of nitrate: nitrate- $\delta^{15}\text{N}$

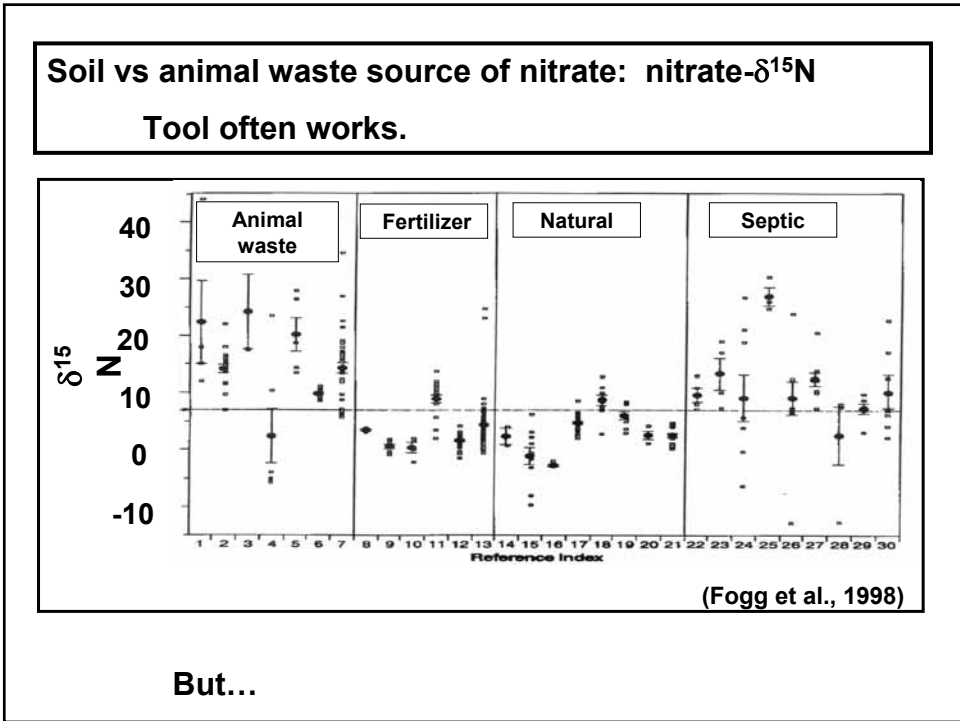
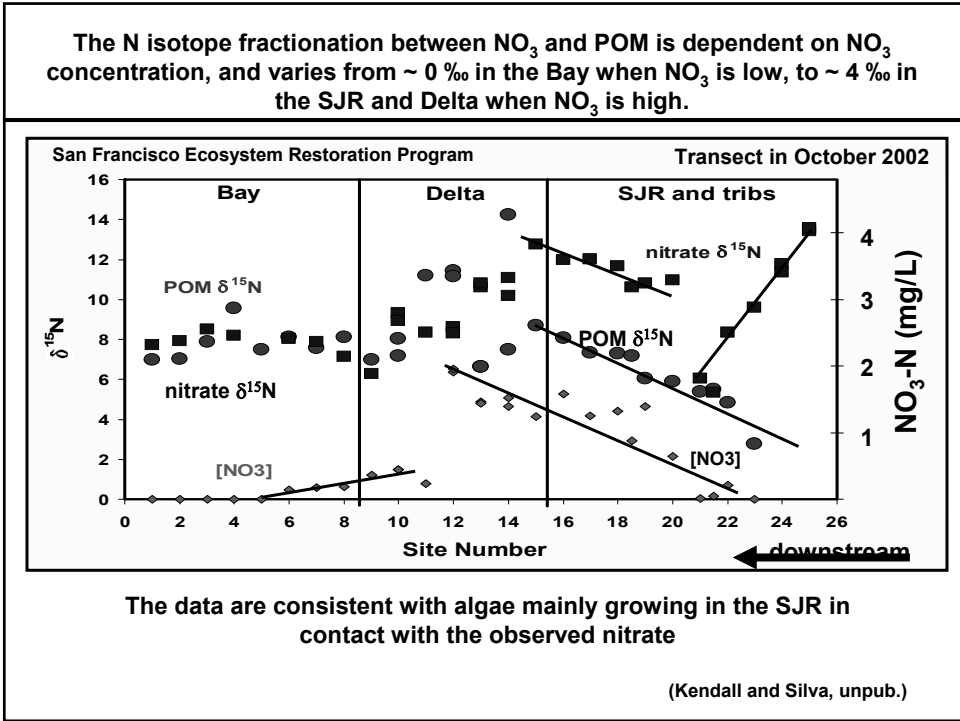
Tool often works.

But may require a fair amount of biogeochemical and hydrologic data.

This can provide semi-quantitative to quantitative estimates of contributions in streams and rivers if:

- denitrification in the riparian zone and/or hyporheic zone can be ruled out or quantified,
- nitrate from soil organic matter is insignificant (or its $\delta^{15}\text{N}$ is similar to fertilizer),
- uptake of nitrate by phytoplankton is minimal (or data are adjusted for this fractionation),
- nitrification in the stream is minimal (or data are adjusted for this fractionation).

or ... use other chemical and/or isotopic tracers (e.g., nitrate- $\delta^{18}\text{O}$ or $\text{POM-}\delta^{15}\text{N}/\delta^{13}\text{C}/\delta^{34}\text{S}$) in addition to nitrate- $\delta^{15}\text{N}$.



Soil vs animal waste source of nitrate: nitrate- $\delta^{15}\text{N}$

Tool often works...

But sometimes does not work because soil nitrates can be quite variable in $\delta^{15}\text{N}$ and sometimes overlap the $\delta^{15}\text{N}$ values of animal manure. More likely to work with pigs than other animals because pig waste from lagoons usually has a much higher nitrate- $\delta^{15}\text{N}$.

Quantification using only nitrate- $\delta^{15}\text{N}$ can be successful if:

- the groundwater is well-oxygenated, the soils are sandy instead of clayey, so denitrification can be ruled out,
- nitrate from soil organic matter is insignificant (or its $\delta^{15}\text{N}$ is similar to fertilizer), and
- nitrates from representative source areas (under the fields, feedlots, manure lagoons, septic fields, etc) are analyzed to insure that the nitrate- $\delta^{15}\text{N}$ values of possible sources are a few ‰ different.

Soil vs animal waste source of nitrate: nitrate- $\delta^{15}\text{N}$

Tool often works.

Do you need nitrate- $\delta^{18}\text{O}$?

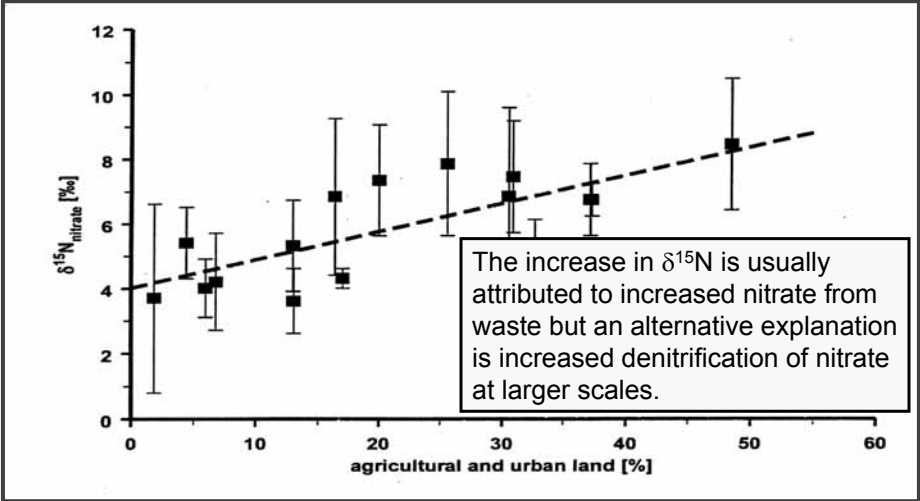
No ...

but it probably would help improve the quantification if there is some difference in

- the water- $\delta^{18}\text{O}$ of soil water vs groundwater or lagoon water, or
- in the O_2 - $\delta^{18}\text{O}$ in the soil zone or groundwater;
- these instances are not uncommon).

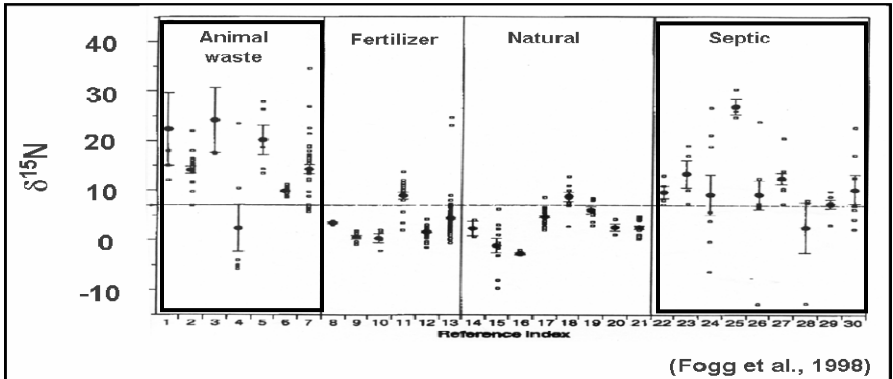
Therefore, obtaining nitrate- $\delta^{18}\text{O}$ is recommended.

Positive correlation of $\delta^{15}\text{N}$ and land use in major river basins in NE USA



from Mayer et al. (2002)

Septic waste vs animal manure: nitrate- $\delta^{15}\text{N}$
Tool usually does NOT work using only nitrate- $\delta^{15}\text{N}$.
(because the nitrate- $\delta^{15}\text{N}$ values are usually overlapping).



But...

Septic waste vs animal manure: nitrate- $\delta^{15}\text{N}$

Tool usually does NOT work using only nitrate- $\delta^{15}\text{N}$.

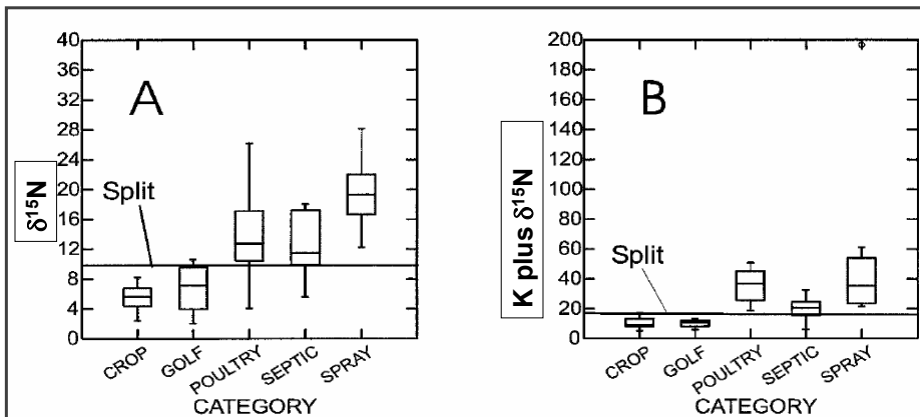
(because the nitrate- $\delta^{15}\text{N}$ values are usually overlapping).

However, these types of waste can sometimes be distinguished if:

- the average diets of the humans and animals are at different trophic levels,
- nitrate- $\delta^{18}\text{O}$ values of the wastes are different,
- other isotope tracers that are specific for the different sources are used (B, Sr, S, C, Li, U),
- other chemical tracers that are specific for the different sources are used (caffeine, pharmaceuticals, K, REEs, heavy metals, etc).

See example of usefulness of K for distinguishing septic vs poultry waste ...

The use of 2 tracers (K plus $\delta^{15}\text{N}$ of NO_3) did a better job of distinguishing sources of nitrate from five source categories than the use of $\delta^{15}\text{N}$ alone



Spruill et al 2002 (JEQ)

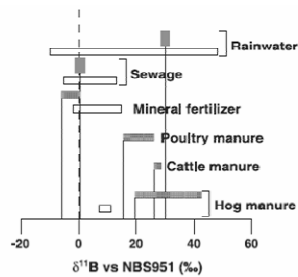
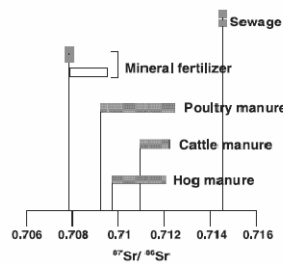
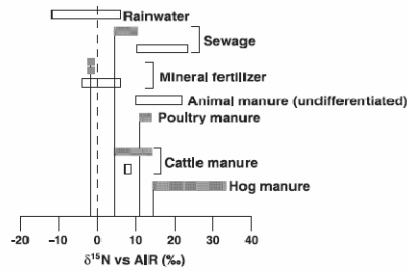
Nitrate from waste from different kinds of farm animals:

Tool maybe will work.

There have been several very recent, very promising studies in Europe. We are investigating this in the US as parts of collaborations with Harter (UCD) and Hutchins (EPA).

Therefore, semi-quantification of contributions of nitrate derived from different kinds of farm animals might be possible if:

- nitrate- $\delta^{15}\text{N}$ and nitrate- $\delta^{18}\text{O}$ are not expected to provide clear separations without the combined use of other tracers,
- other isotope tracers that are specific for the different sources are used (B, Sr, S, C, Li), and/or
- other chemical tracers that are specific for the different sources are used (caffeine, pharmaceuticals, REEs, heavy metals, etc).



$\delta^{15}\text{N}$, $\delta^{11}\text{B}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ characterization of the NO_3 sources present in the watersheds in France show that different kinds of animals have different isotope "signatures"

Widory et al. (2004)

**Why do different kinds of animal waste-derived nitrate
have different B-Li-S-Sr-U isotopic signatures?**

**Mostly because of different sources of washing
materials (for B, S, and maybe Sr) used for people
vs AFOs (that result in differences in septic
waste/WWTPs vs waste lagoons/spraying.**

**Perhaps also because of different food additives. Li
might be useful because pharmaceutical-grade Li
has very high (or sometimes very low ^7Li) because
of the nuclear processing industry.**

**Phosphate from fertilizer vs animal waste/septic waste
vs soil organic matter: phosphate- $\delta^{18}\text{O}$:**

Tool maybe ready for use (needs further study).

**There have been a few recent and very promising studies of
phosphate sources using various isotope tracers.**

U isotopes: Uranium is a trace constituent of geologic sources of
phosphate. Hence, analysis of ^{234}U and ^{238}U can distinguish
between "natural" and "geologic" sources.

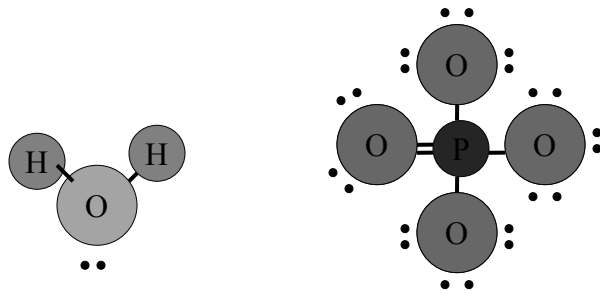
Sr isotopes: Strontium is a trace constituent of geologic sources of
phosphate. Different sources of geologic phosphate (phosphorites vs
carbonatites) appear to have different concentrations of trace metals
and REEs; hence, these can be used as tracers of phosphate and/or
fertilizer source.

All of these isotope tracers will provide more quantitative information if
they are combined with other isotope and chemical tracers.

New isotope tool: the $\delta^{18}\text{O}$ of phosphate (PO_4)

P has only 1 stable isotope so it cannot be used as a natural isotopic tracer. However, the O atoms bound to the P are potentially useful tracers of P sources and sinks.

Since the P-O bond in phosphate is resistant to inorganic hydrolysis, $\delta^{18}\text{O}$ of phosphate may be used as a tracer of phosphate sources and cycling under certain conditions.



New isotope tool: the $\delta^{18}\text{O}$ of phosphate (PO_4)

However, if phosphate is limiting and is actively cycled, $\delta^{18}\text{O}$ of phosphate rapidly equilibrates with water- $\delta^{18}\text{O}$ during ATP-ADP cycling within the cells.

Therefore, PO_4 - $\delta^{18}\text{O}$ is usually only a usable tracer in systems with excess PO_4 where the waters associated with the two sources (e.g., waste vs natural) have $\delta^{18}\text{O}$ values that are **different by several ‰**.

After equilibration, the $\delta^{18}\text{O}$ of PO_4 is 20‰ higher than the water. So if the water in a WWTP or manure lagoon is highly evaporated and has a $\delta^{18}\text{O}$ that is 5‰ higher than the local drinking water, then the $\delta^{18}\text{O}$ of the PO_4 from the evaporated WWTP or lagoon is also (in theory) 5‰ higher than the PO_4 that equilibrated with the local water.

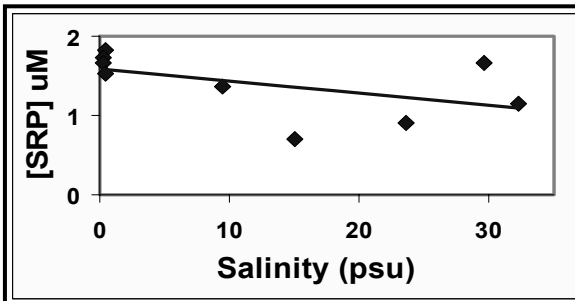
New isotope tool: the $\delta^{18}\text{O}$ of phosphate (PO_4)

Main water management applications:

PO_4 - $\delta^{18}\text{O}$ should be very useful for near-shore investigations of sources of PO_4 to the marine ecosystems where the suspected sources are WWTPs, AFOs, upwelling marine waters, and other sources.

PO_4 - $\delta^{18}\text{O}$ is also likely to be useful in any location where there is evaporative enrichment of water- $\delta^{18}\text{O}$ in a lagoon, or locations where the public supply water is from a much different geographic location or elevation than the local soil water or groundwater.

North Bay Transect, October 2002

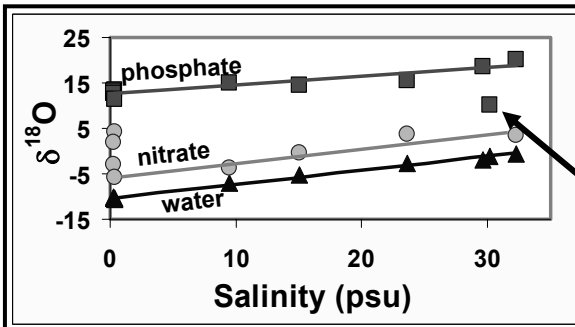


Example of a high-P source

Question: what is the cause of the variability in P concentrations along the salinity gradient?

Poor mixing of stratified waters?

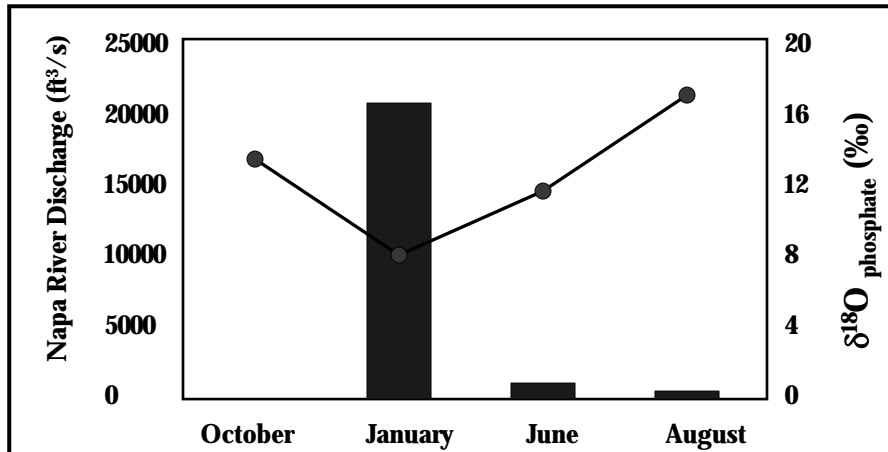
Local point sources?



Anomalous site near mouth of Napa River

McLaughlin et al. (2005)

The anomalous site deviates from the simple mixing relation when Napa River discharge is greatest



Modified from McLaughlin et al., 2005

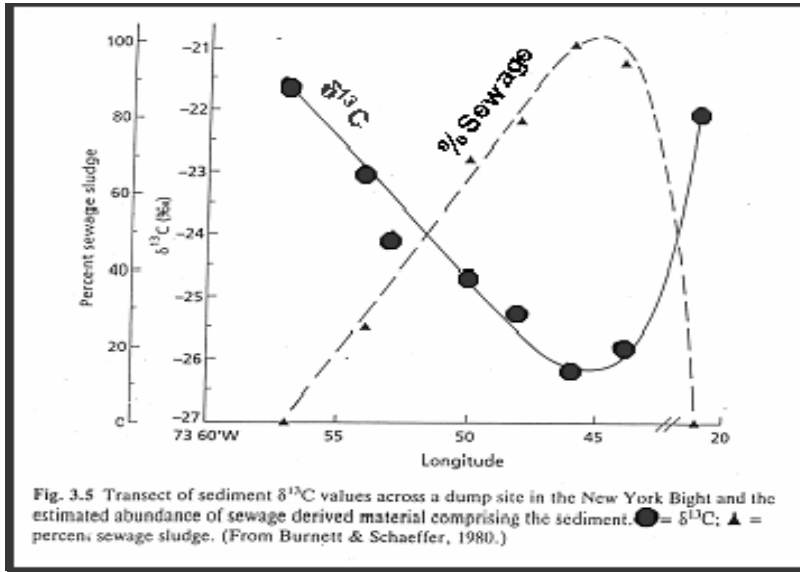
Organic matter from animal waste vs human waste:

Tool often works.

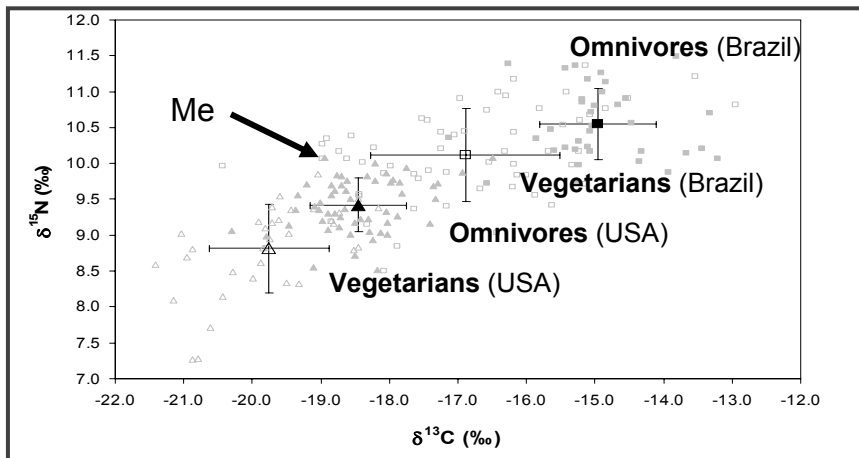
Quantification of waste from human vs animals can be successful if:

- analyzed for $\delta^{15}\text{N}$ and/or $\delta^{13}\text{C}$ of the organic matter (using both is best, and adding $\delta^{34}\text{S}$ can help),
- the average diets of the humans and animals are at different trophic levels (i.e., one group is herbivorous), and/or
- one group eats a diet based on C3 plants, and the other eats a diet primarily based on C4 plants (corn and sugar cane are the main C4 crops);
- other isotope tracers that are specific for the different sources are used (B, Sr, S, C, Li, U),
- other chemical tracers that are specific for the different sources are used (caffeine, pharmaceuticals, K, REEs, heavy metals, etc).

Quantification of sewage contributions to coastal sediments



Isotopic compositions of fingernails as a proxy for diet



Therefore, the isotopic composition of DOM and POM in water is likely to be a useful tracer of source of the organics (human vs different animal types). I will discuss this in more detail in the "Ecological applications" section....

Other useful tools for agricultural studies:

Water isotopes: Analysis of the water for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (these are almost perfect tracers of the water itself) can provide extremely useful information about the sources of the nitrate and other solutes in the water.

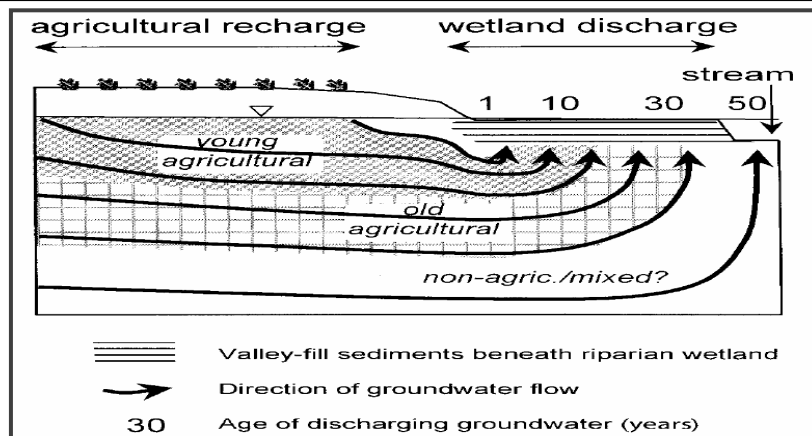
Sulfur isotopes: Analysis of sulfate for $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$, or organic matter for $\delta^{34}\text{S}$, can provide information about fertilizer and waste sources.

Age-dating nitrate contamination of groundwater: One powerful potential application of technological advances in the age-dating of young groundwater is to evaluate the impact of changes in agricultural management practices on water quality. Tracers include tritium (^3H), $^3\text{H}/^3\text{He}$, and CFCs.

Examples of environmental changes that can be assessed by this method include: changes in the amount and types of fertilizers used, different fertilizer application times, relocation of potential pollutant sources, different remediation strategies, determination of timescales for remediation, and the installation of drainage systems.

Simplified representation of GW flow from an upland agricultural recharge area to a riparian wetland.

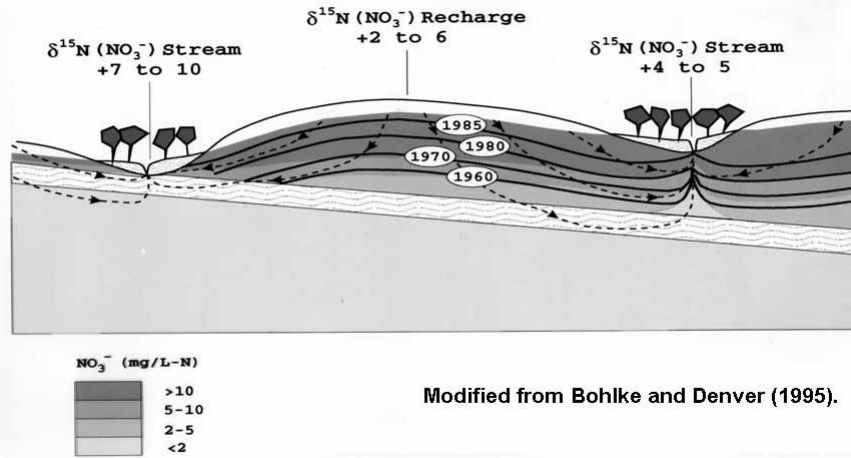
Arrows indicate directions of flow as determined from gradients in hydraulic heads and GW ages (ranging from about 0–50 years).



Bohlke (2002)

Analysis of the $\delta^{15}\text{N}$ of N_2 and NO_3 , combined with water age-dating techniques, explains why:

- (1) different streams in an agricultural watershed in MD have different NO_3 concentrations, and
- (2) determines how long it will take for natural remediation processes to remove the fertilizer NO_3 from groundwater.



Other useful tools for agricultural studies:

Isotope biomonitors: analysis of the $\delta^{15}\text{N}$ of algae, terrestrial plants, and animals as “proxies” for the isotopic compositions of nitrate and/or ammonium – and hence sources and land uses.

Statistical, geochemical, and hydrologic modeling: We are past the time when simple bivariate plots and linear regressions are sufficient for interpreting data. Other approaches: EMMA (End Member Mixing Analysis), geochemical reaction path modeling, principal components analysis, and classification trees.

Other chemical constituents: pharmaceuticals specific to different animal types, trace elements and REE for tracing fertilizers, and basic chemistry. You can do a lot with just simple Cl concentrations for identifying animal waste contamination of rivers and groundwaters.

Some good advice: ALWAYS ARCHIVE SAMPLES

Many of these stable isotope tools archive very well -- filtered, preserved, or frozen (depending on type). DIC and DO are the exceptions; they are good for months not years (unless you make special precautions).

So collect many more samples that you can afford to analyze, and archive them. Then used an "adaptive management practice" to decide what to analyze first.

You might also want to archive samples for possible analysis for metal and semi-metal isotopes. In general, these are filtered thru 0.2 micron and then acidified -- using very pure reagents that don't contain K or anything that might contribute radiogenic materials.

Proposed sampling scheme for all future river nutrient studies

Each time chemistry samples are collected at each site, collect and archive the following samples:

- 1) Nitrate isotope samples: Collect and archive ~60 ml, filtered (0.2 um), frozen, water samples.
- 2) POM isotope samples: Filter ~1L of water through a flat, pre-combusted, glass fiber filter (0.7 um), freeze the filters, and archive them.
- 3) Water isotope samples: Collect and archive 10-20 ml of water (unfrozen).
- 4) DOC/DON and SO₄ isotope samples: If you have sufficient freezer space, save the eluent from filtering the POM samples and save this for future isotope analyses.
- 5) Biota isotope samples: Archive ~1 cc frozen aliquots of biological samples (algae, riparian terrestrial plants, aquatic invertebrates, fish), especially ones collected along river reaches.

After chemical data are examined and modeled, these archived samples can be used to test hypotheses with new isotope data.

Analytical methods commonly in use for nitrate isotope samples

For samples just being analyzed for $\delta^{15}\text{N}$, most labs are using an ammonium diffusion method (Holmes et al., 1998)

For samples being analyzed for both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, the most common method before the last few years was the Silva et al (2000) method of concentrating the sample on resin columns, eluting the nitrate with NaCl, precipitating the N as silver nitrate, followed by pyrolysis. The main drawbacks of the method are the need for large water samples and inability to use the method for saline samples.

Since the publication of Sigman et al. (2001) and Casciotti et al. (2002) many labs have started using the microbial denitrifier method; it converts nitrate to N_2O . It permits analysis of samples almost 3 orders of magnitude smaller samples than the Silva method, is suitable for marine samples, and supposedly is not affected by DOM in the sample.

A new method (McIlvin and Altabet, 2005) that uses sodium azide to reduce nitrate to N_2O is gaining popularity because it appears to be less complicated than the microbial method.

Lab costs?

Nitrate isotopes are not very expensive compared with the expense of collecting the sample and interpreting the data – and they are a LOT cheaper than being wrong!

How much do such isotope analyses cost? \$50-\$200, depending on method, one or both isotopes, lab, single vs duplicate analysis, and market forces.

Prices are dropping rapidly (or will!) due to increased automation and new, more automated, methods.

The best bargain is to interest someone who has an isotope lab – who might add in lots of extra analyses if he/she becomes intrigued or has spare mass spec and/or tech time.

Quality assurance of nitrate isotope samples

Questions to ask:

- Does the laboratory participate in inter-laboratory calibration exercises (round-robins)? Ask to see the documentation of a recent calibration.
- What international standards are analyzed with commercial samples, how frequently are they analyzed, and what are the δ values of these standards?
- Does the laboratory make corrections for sample size, and if so, how is this done?

Quality assurance of nitrate isotope samples

Many laboratories routinely analyze each sample only once (except for QA/QC samples). If high precision data are required, either request duplicate analysis of each sample (and triplicates if the duplicates do not agree within some predetermined range) or send in "blind" duplicates to verify the "real" precision.

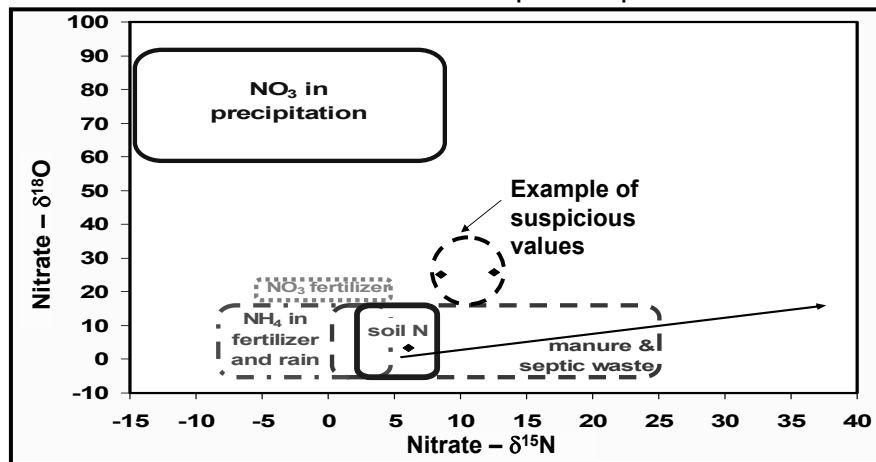
Sending in 10-15% blind duplicates is advisable in any case. If any result seems questionable, immediately request a repeat. Most laboratories keep analyzed samples for a couple months before discarding them and will reanalyze modest numbers of samples at no additional cost.

Quality assurance of nitrate isotope samples

Immediately plot the data on a $\delta^{18}\text{O}$ vs. $\delta^{15}\text{N}$ diagram. Data that plot appreciably outside the compositions expected for "terrestrial" sources of nitrate (e.g., nitrification of soil N, ammonium fertilizers, waste N) and do not plot along a "denitrification" slope should be viewed with skepticism and possibly reanalyzed. Few natural processes produce waters that plot significantly outside these ranges.

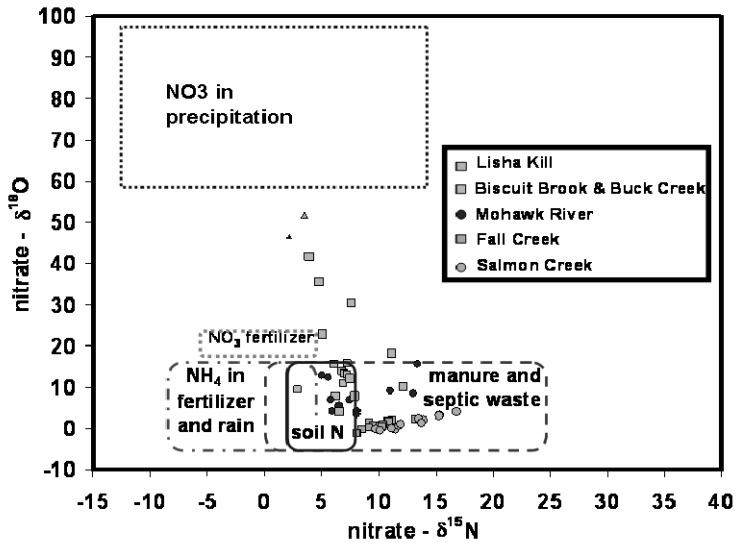
Exceptions include places where much of the nitrate is derived from atmospheric sources or from the application of nitrate-rich (e.g., Chilean nitrate) fertilizers, producing waters with high $\delta^{18}\text{O}$ but normal $\delta^{15}\text{N}$ values.

QA/QC of nitrate isotope samples



What are suspicious values? Basically anything not on the denitrification line or data that plot outside these boxes UNLESS there is reason to suspect that the sample contains a fair amount of atmospheric nitrate. If the suspected nitrate source is wastewater, these "suspicious" samples are definitely suspect and should be reanalyzed!!

Although many samples from these small watershed sites in NY plot outside the boxes, large contributions from atmospheric nitrate are expected so these sample $\delta^{18}\text{O}$ values are probably OK



Summary:

- 1) There has been a lot of progress with isotope characterization and tracing of agricultural contaminant sources in the last few years, particularly with regard to distinguishing between different kinds of animals (including humans) with "uncommonly" used isotopes.
- 2) You should not rely on a single isotope ($\delta^{15}\text{N}$) but instead use a multi-isotope, multi-tracer, approach if you want to answer questions about sources in complicated systems.
- 3) Use a multiple lines of evidence (and multiple testable hypotheses).
- 4) And don't forget that you need to consider the hydrology and basic chemistry of the system – not just isotopes or organics.

Biggest problems for isotope studies:

- **Different sources can have partially overlapping isotopic compositions.**
- **Sources can have considerable spatial and temporal variation in isotopic composition.**
- **Isotope fractionations can blur initially distinctive compositions.**

Solution:

use a multi-isotope, multi-tracer, approach – with a lot of hydrologic and chemical data.

Final words ...

Value of isotopes for water resources management:

- 1) To tell us things about water resources that we didn't know before.**
- 2) To tell us things about water resources that CONTRADICT what we thought we knew before.**
- 3) And therefore, to increase the likelihood that any proposed remediation plans will be effective – because the correct source was identified and quantified.**

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* papers not mentioned in current handouts (but should have been!)