# Tracing Sources and Biogeochemical Cycling of NH4 and NO3 in the Sacramento River, Delta, and Northern Bay using Stable Isotope Techniques


Carol Kendall, Megan Young, Steve Silva and Tamara Kraus
**(USGS)**

Alex Parker and Dick Dugdale
**(SFSU)**

Marianne Guerin
**(RMA)**

**This file contains an updated version of the presentation made on August 19, 2009 at the CA Waterboards-sponsored NH4 Summit meeting in Rancho Cordova, CA.**

**Animations were removed and some additional slides were added for improved explanation of isotope terminology and fundamentals.**

**This PDF file includes the "speaker notes" that were added to the original Powerpoint file, and then saved during the pdf conversion.**

**Click on the comment boxes in upper left of most slides. This feature can be toggled off and on.**

# Isotope Terminology

Isotope data are reported rather strangely -- in terms of Delta (δ) values, in units of ‰ (parts-per-thousand, or permil):

$$\delta^{15}\text{N} = \left[\left(\frac{\left({}^{15}\text{N}/{}^{14}\text{N}\right)_{\text{sample}}}{\left({}^{15}\text{N}/{}^{14}\text{N}\right)_{\text{AIR}}}\right) - 1\right] \times 1000$$

$$\delta^{18}\text{O} = \left[\left(\frac{\left({}^{18}\text{O}/{}^{16}\text{O}\right)_{\text{sample}}}{\left({}^{18}\text{O}/{}^{16}\text{O}\right)_{\text{VSMOW}}}\right) - 1\right] \times 1000$$

**The δ values of the reference standards (i.e., AIR and VSMOW) are defined as 0. Because of the choices of reference standards, the δ values of some materials have negative values, meaning that their isotope ratios are LOWER than those of the standard.**

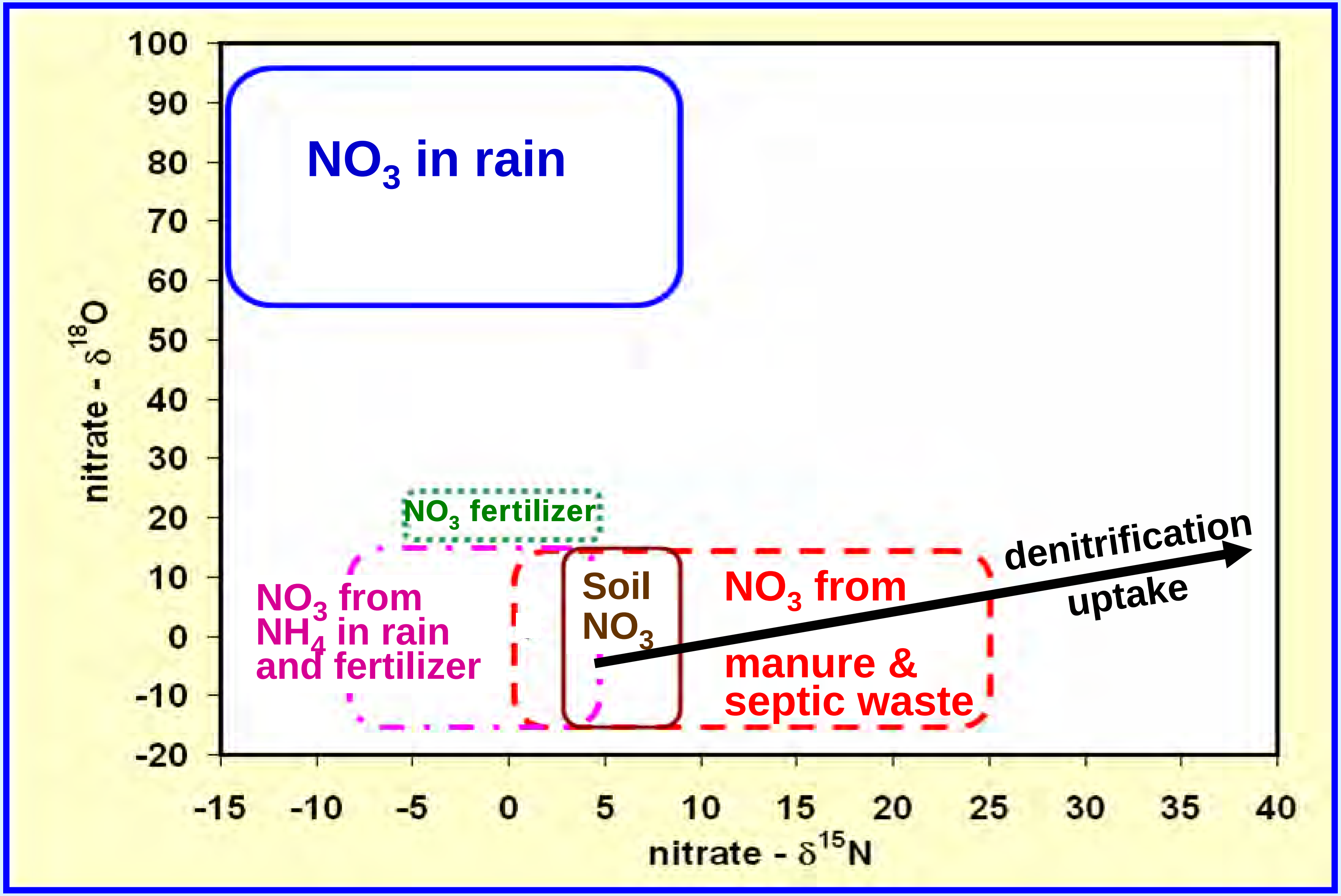
# How do isotopes help trace sources of nutrients and organic matter ?

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

- nutrients and organic matter derived from different sources and land uses often have distinctively different isotope compositions, and
- different kinds of sinks can sometimes cause distinctive shifts in isotopic compositions.

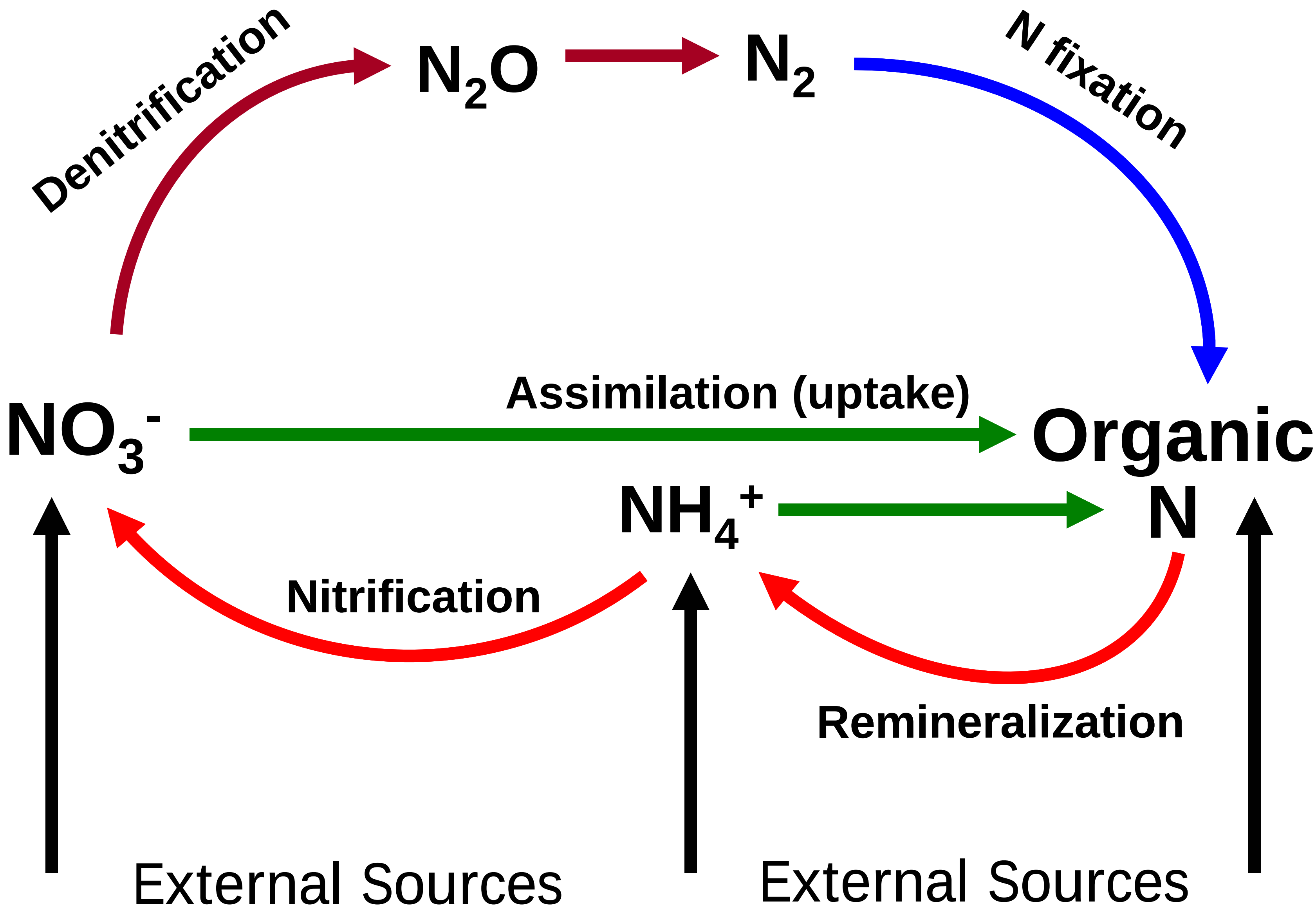
**In other words, different sources of nutrients and organic matter often have distinctive isotope "fingerprints" that can provide a better understanding of the system than just chemical data.**

# Different sources of nitrate (colored boxes) often have different and characteristic $\delta^{15}N$ and $\delta^{18}O$ values

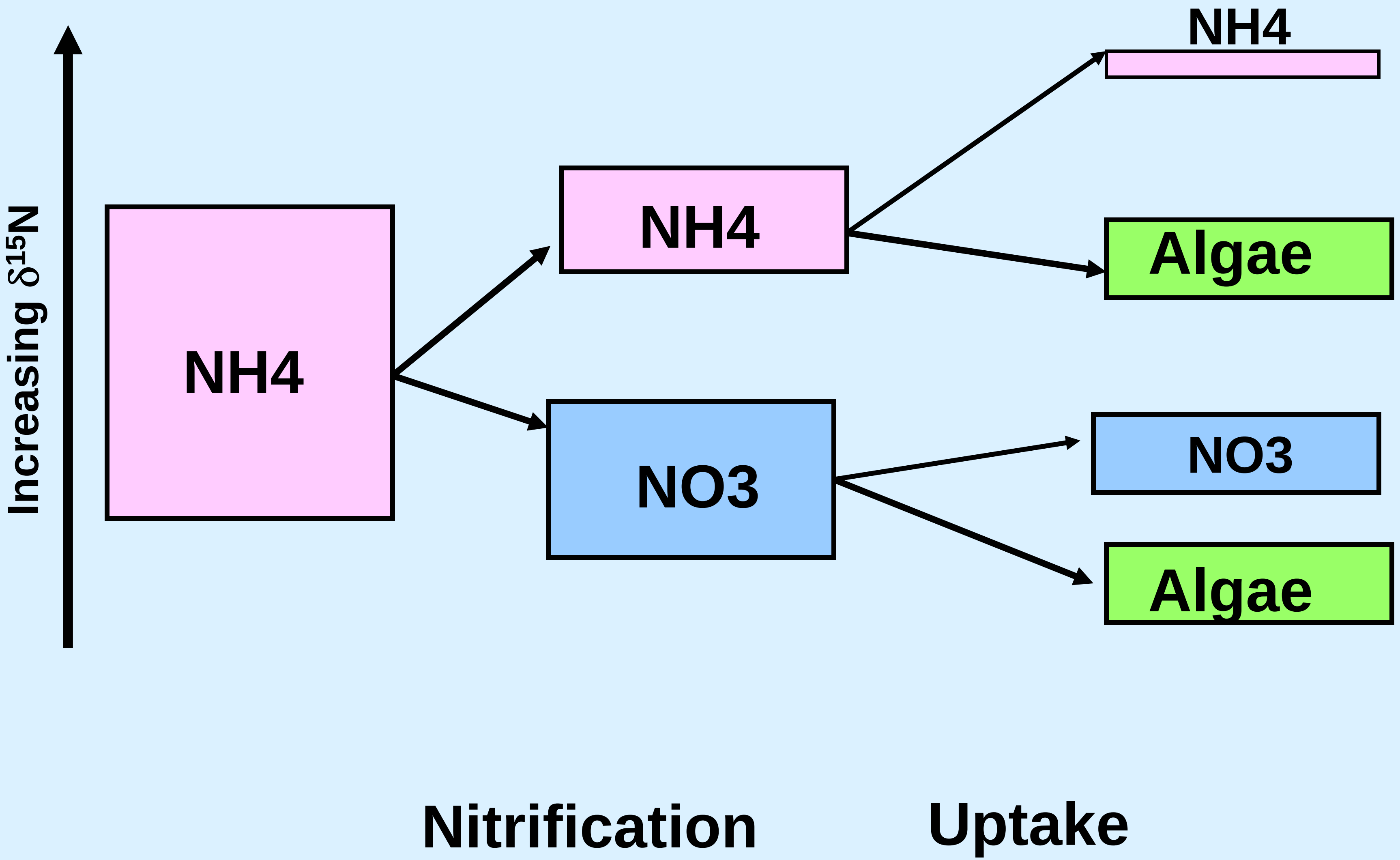


# Nitrogen Cycle

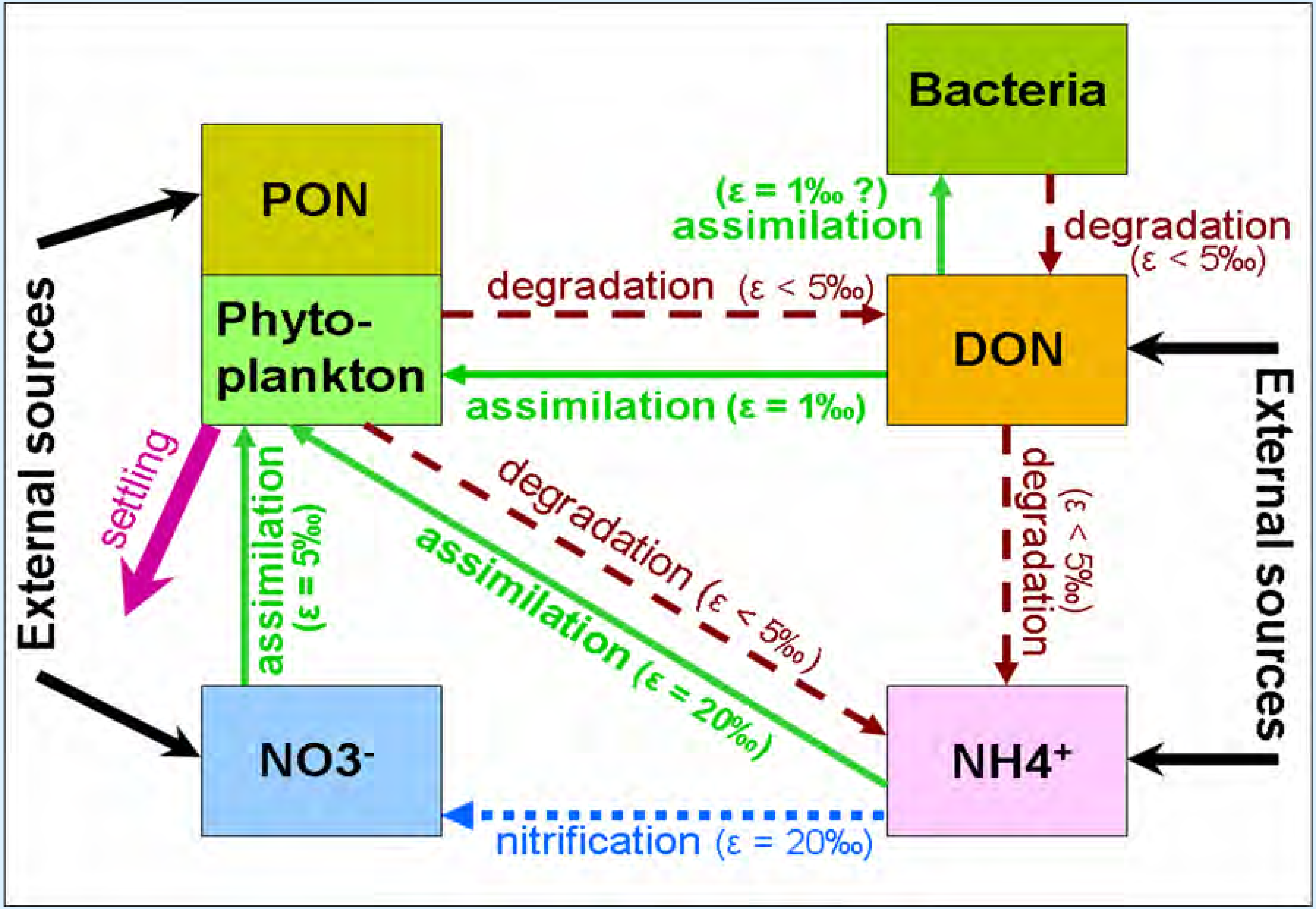
**Each of these forms of N may have a different isotopic composition.**



## Cartoon showing how biological processes result in distinctive changes in isotopic composition.



# Nitrogen cycling model for the Bay
## (with approximate isotope fractionations)



# We employ a comprehensive multi-isotope approach for biogeochemical studies

## Standard analyses:

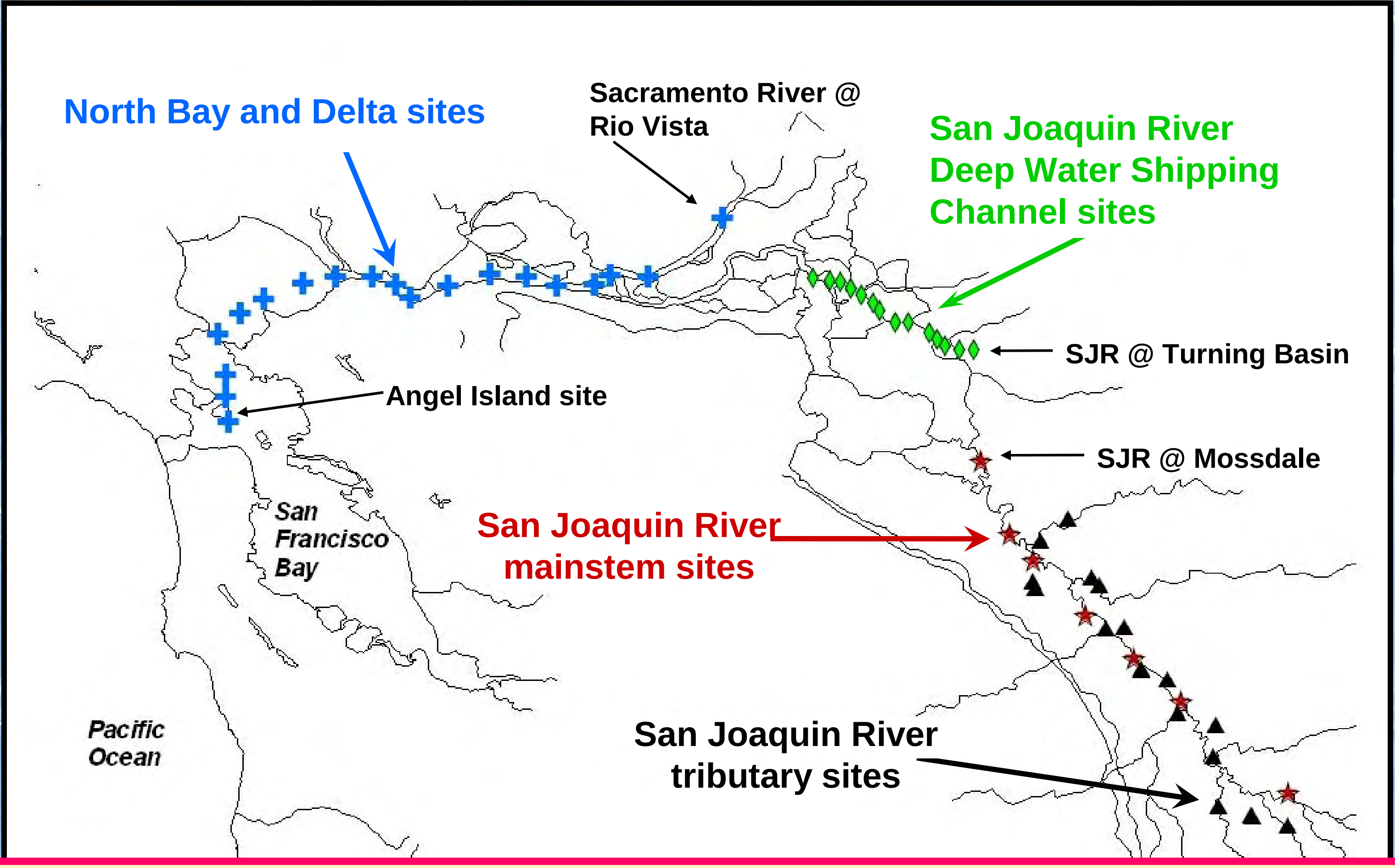
- Water $\delta^{18}O$ and $\delta^{2}H$
- NO3 $\delta^{15}N$ and $\delta^{18}O$
- POM $\delta^{13}C$, $\delta^{15}N$, and C:N
- DOC $\delta^{13}C$

## Other analyses for subsets of samples:

- NH4 $\delta^{15}N$
- PO4 $\delta^{18}O$
- POM $\delta^{34}S$
- NO3 $\Delta^{18}O$
- DO $\delta^{18}O$
- CO2 $\delta^{13}C$
- DIC $\delta^{13}C$
- CH4 $\delta^{13}C$
- N2 $\delta^{15}N$ and N2/Ar
- N2O $\delta^{15}N$ and $\delta^{18}O$
- SO4 $\delta^{34}S$ and $\delta^{18}O$
- DOM $\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$, and C:N
- Biota $\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$, $\delta^{2}H$, and C:N

| Tracer type | Interpretive value |
|---|---|
| **Particulate organic matter (POM) $\delta^{15}N$, $\delta^{13}C$, and $\delta^{34}S$** | information about the source of the C, N, and S -- and the biogeochemical reactions that cycle the elements -- even after incorporation into algal biomass; quantify algal vs terrestrial contributions to biomass. |
| **Nitrate $\delta^{18}O$, $\delta^{15}N$, and $\Delta^{17}O$** | quantify nitrate from different sources (fertilizer, wastewater, wetlands, atmosphere, etc), role in the production of algae, and degree of recycling, evidence for denitrification or assimilation. |
| **Ammonium $\delta^{15}N$** | quantify ammonium from different sources (fertilizer, wastewater, wetlands, etc), role in the production of algae, and degree of recycling, evidence for nitrification or assimilation. |
| **Water $\delta^{18}O$ and $\delta^{2}H$** | ideal conservative tracer of water sources and mixing; useful for quantifying flow contributions from different tributaries and groundwater. |
| **Dissolved organic matter (DOM) $\delta^{15}N$, $\delta^{13}C$, and $\delta^{34}S$** | information about the source of the C, N, and S -- and the biogeochemical reactions that cycle the elements -- even after incorporation into algal biomass; quantify algal vs terrestrial contributions to biomass. |
| **Dissolved inorganic carbon (DIC) $\delta^{13}C$** | information on sources of DIC, evidence for *in situ* algal productivity, evidence for degradation of organic matter, degree of gas exchange with atmosphere, nitrification. |
| **Dissolved Oxygen (DO) gas $\delta^{18}O$** | information about the ratio of productivity to respiration in the water column, source of the $O_2$, degree of gas exchange with atmosphere, biological oxygen demand (BOD) mechanism. |
| **Sulfate $\delta^{34}S$, $\delta^{18}O$, and $\Delta^{17}O$** | quantify sulfate from different sources (soil, wastewater, wetlands, atmosphere, etc), source of algae, and extent recycling. |
| **Phosphate $\delta^{18}O$** | quantify phosphate from different sources; information about the extent of algal production, recycling of material within the river reach, and P limitation. |

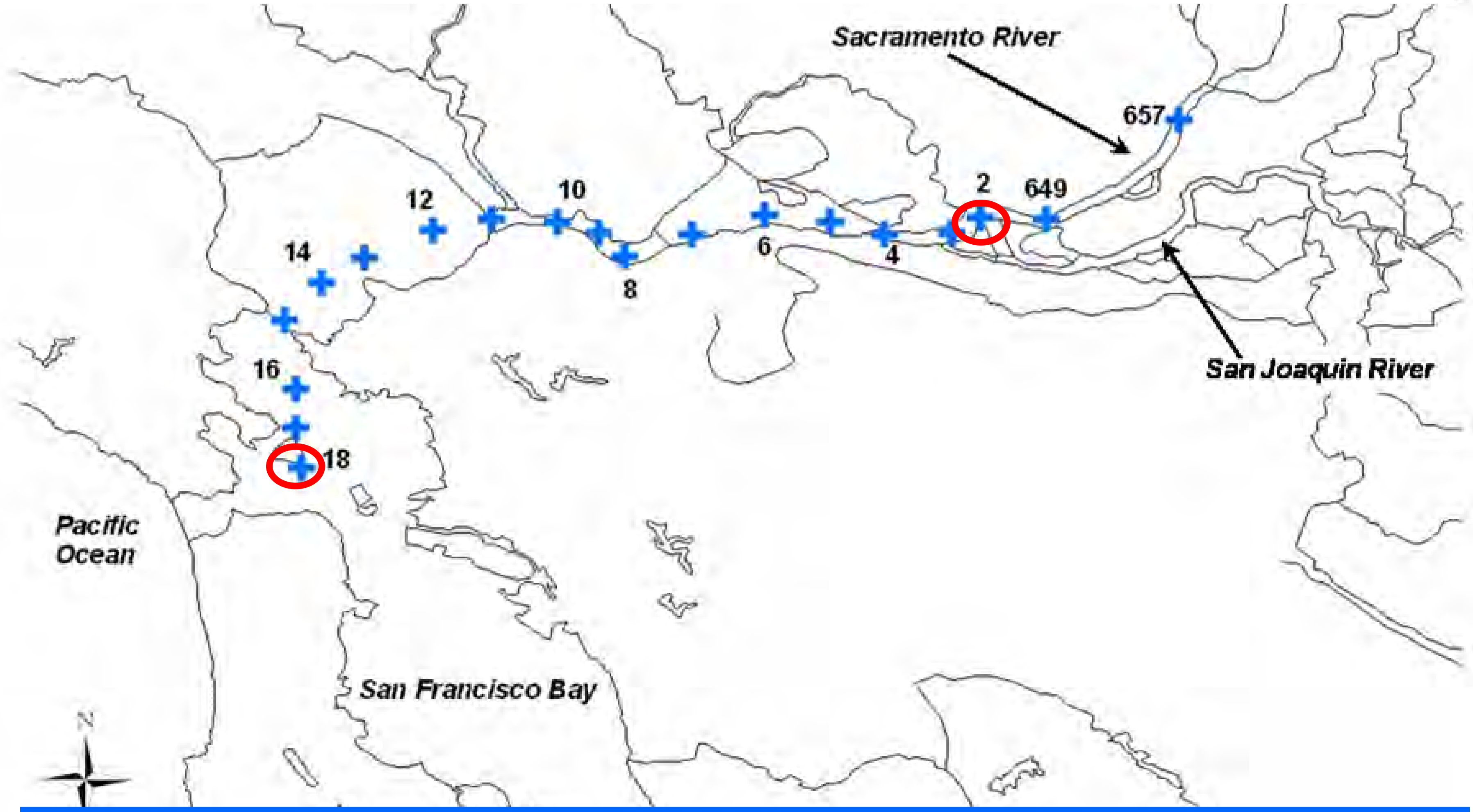
# The data presented are from two studies. The sampling sites for our recent Prop 50 DWP project (PIN700) are shown below.




~21 SJR sites were sampled ~75 times 3/05 to 12/07.

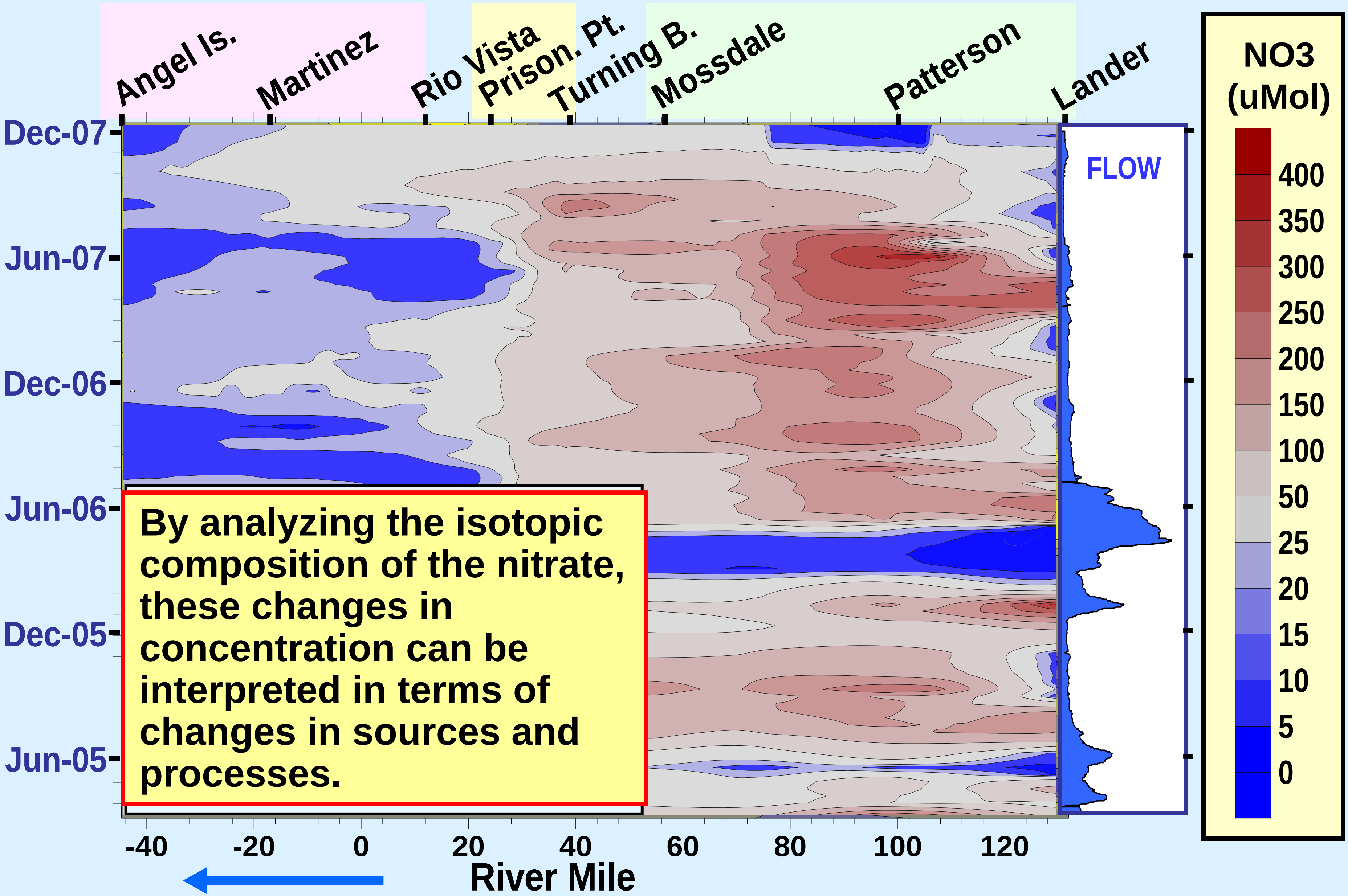
14 DWSC sites were sampled ~ twice monthly during the summer and fall, and 19 northern SFB sites were sampled ~ monthly, 8/06 to 5/08.

## To show the spatial relations among sites, many plots show the data arranged in order of River Mile (RM).



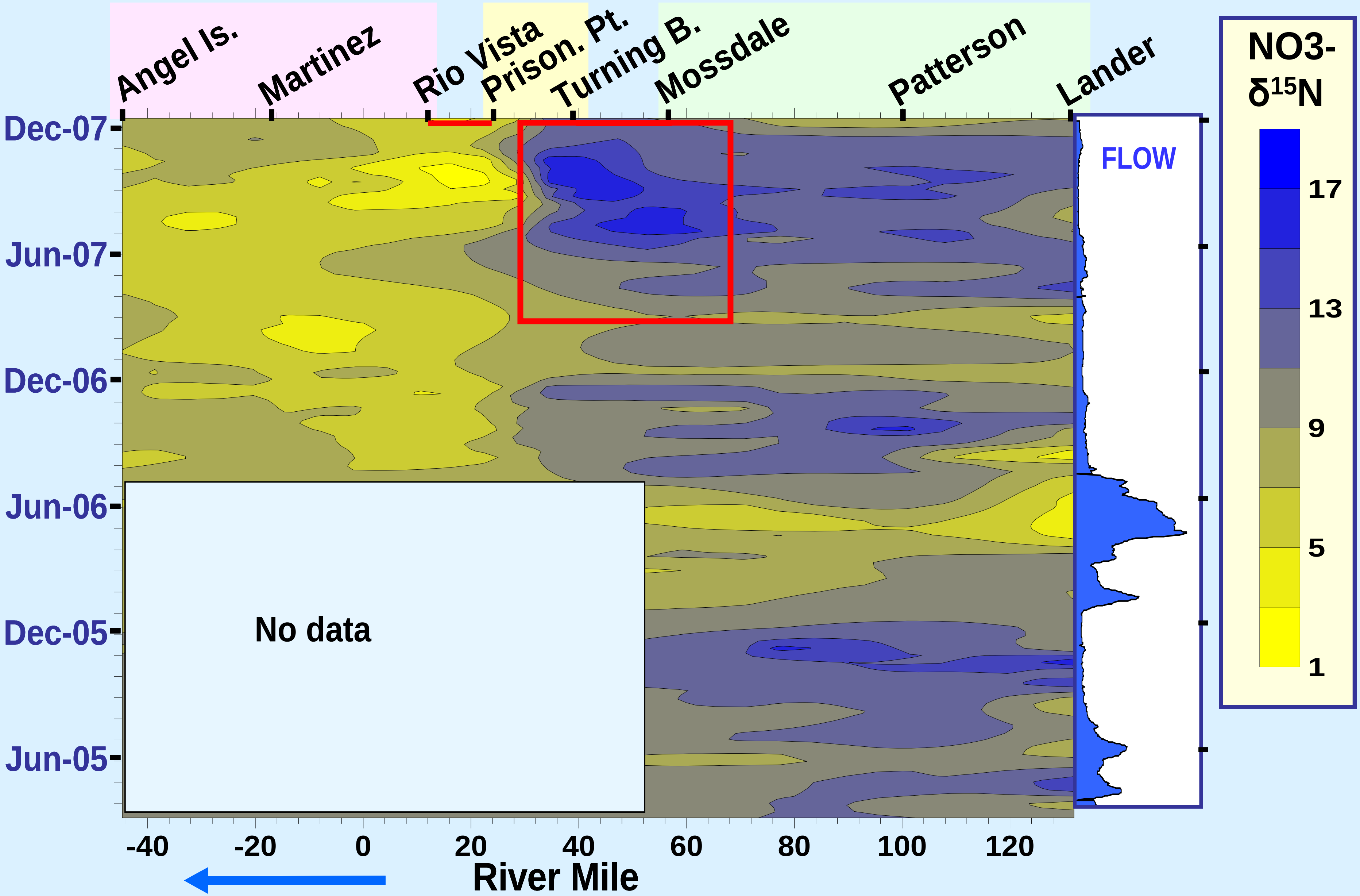

**We have used the RM values from USGS topo maps, where RM = 0 where the SJR converges with the Sacramento River at St. 2 (Chain Island), and RM = -45 at St. 18 southeast of Angel Island.**

# There are large spatial differences in NO3 concentrations across the SJR-Delta-SFB.

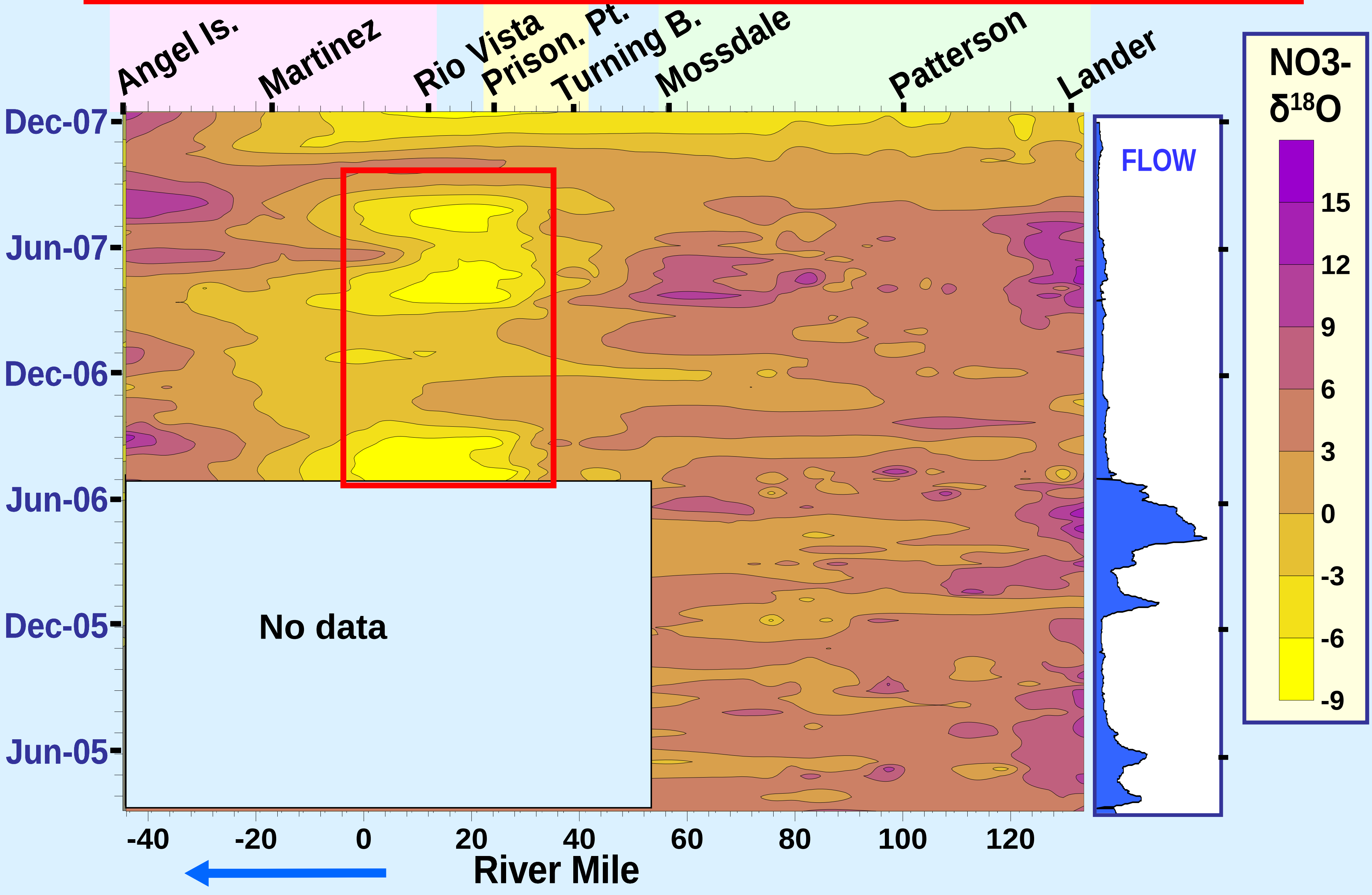



**By analyzing the isotopic composition of the nitrate, these changes in concentration can be interpreted in terms of changes in sources and processes.**

**High δ15N-NO3 values are associated by large algal blooms and/or waste sources. Low values are associated with nitrification.**



## Low $\delta^{18}O$-NO3 values are associated with different sources of NO3, perhaps due to nitrification of NH4 in the Sacramento River or wetlands.



## MAIN QUESTIONS

**Can isotope techniques:**

1) **identify sources of NH4 and NO3 at key locations?**
2) **determine relative biogeochemical reactions rates of different nutrients at different locations?**
3) **identify the sources of dissolved and particulate organic matter?**

**These are similar to our goals in the SJR study except that we are (1) adding analysis of NH4 for $\delta^{15}$N and POM for $\delta^{34}$S, including archived samples, (2) working closely with plankton ecologists, and (3) working closely with a DSM2 modeler.**

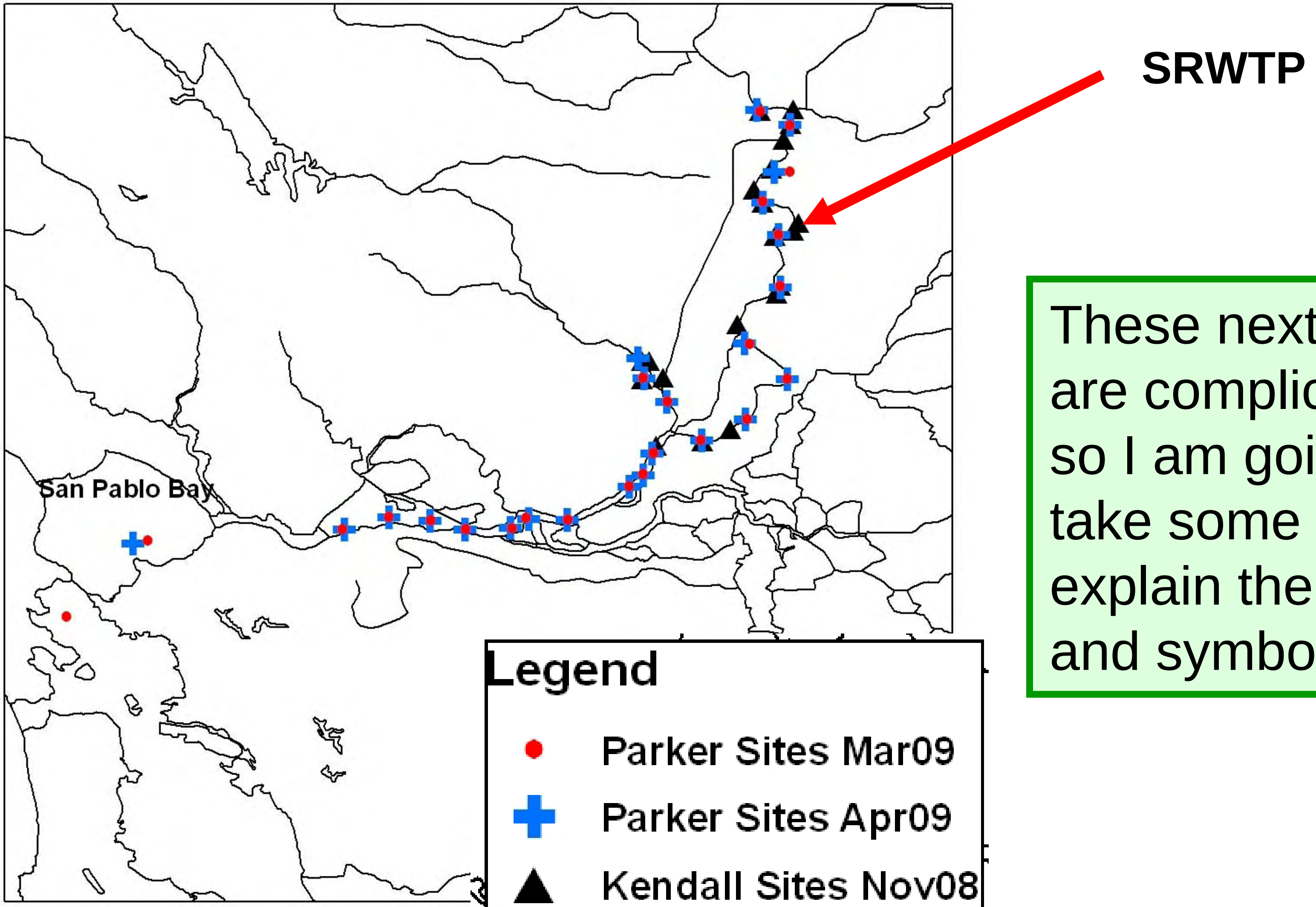
# Why do we want to analyze NH4-$\delta^{15}$N?

1) **To see if NH4 from different sources have distinctive $\delta^{15}$N values.**

2) **To determine the spatial and temporal variability in the sources of NH4.**

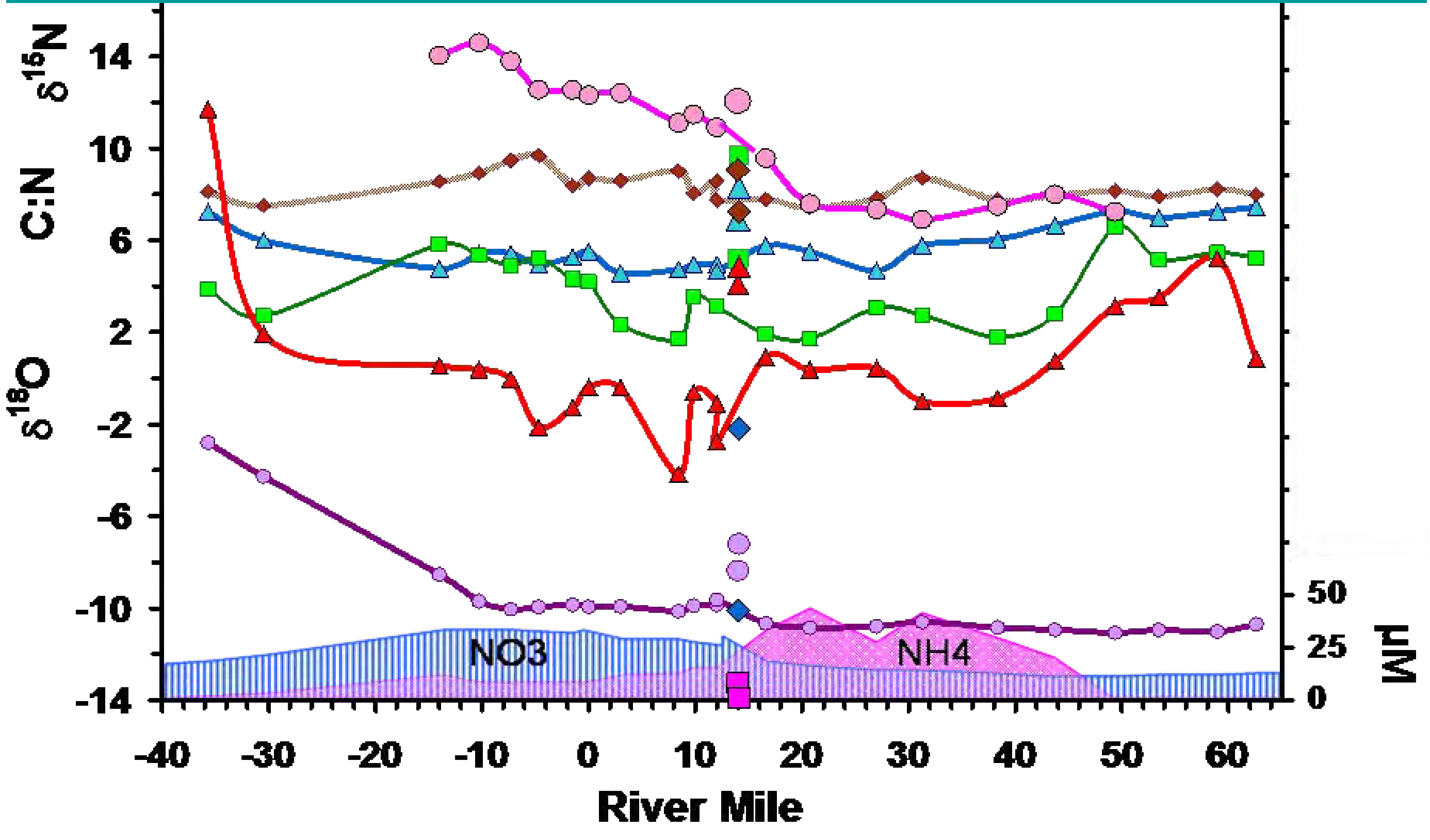
3) **So that we can use NH4- $\delta^{15}$N along with NO3-$\delta^{15}$N and $\delta^{18}$O (and our other data) to calculate the temporal and spatial variability in N sources to phytoplankton, as an independent test of the model developed by the Dugdale et al group based primarily on $^{15}$N-additions.**

The next few slides show isotope and chemical data from two 100-mile transects that piggybacked on the Dugdale-Parker sampling in late March and late April 2009.



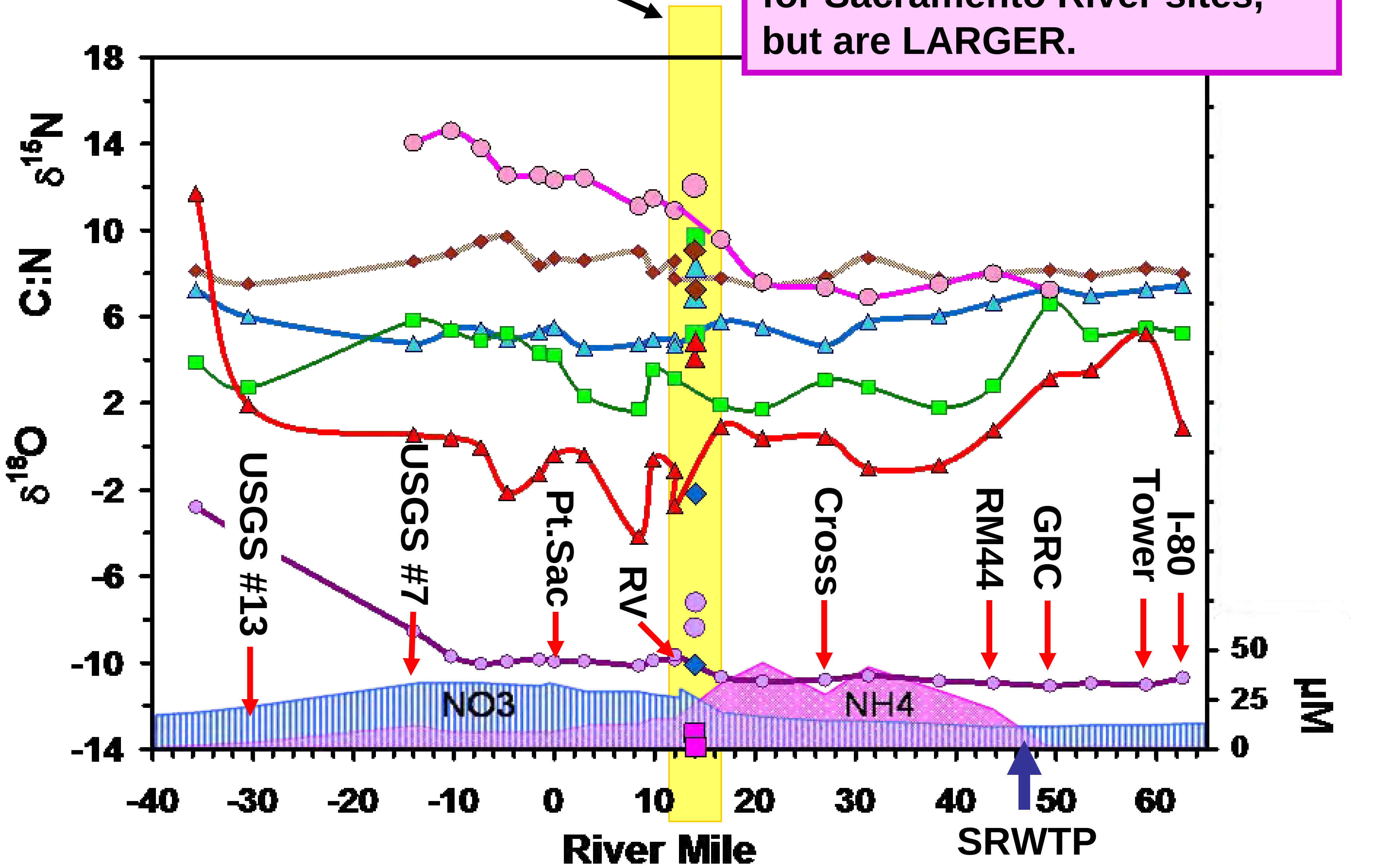

These next slides are complicated, so I am going to take some time to explain the formats and symbols….

We see large spatial differences in NO3 and NH4 concentrations -- and in the “natural abundance” stable isotopic compositions of NO3, NH4, POM, and H2O -- from samples collected during the late March 2009 transect.

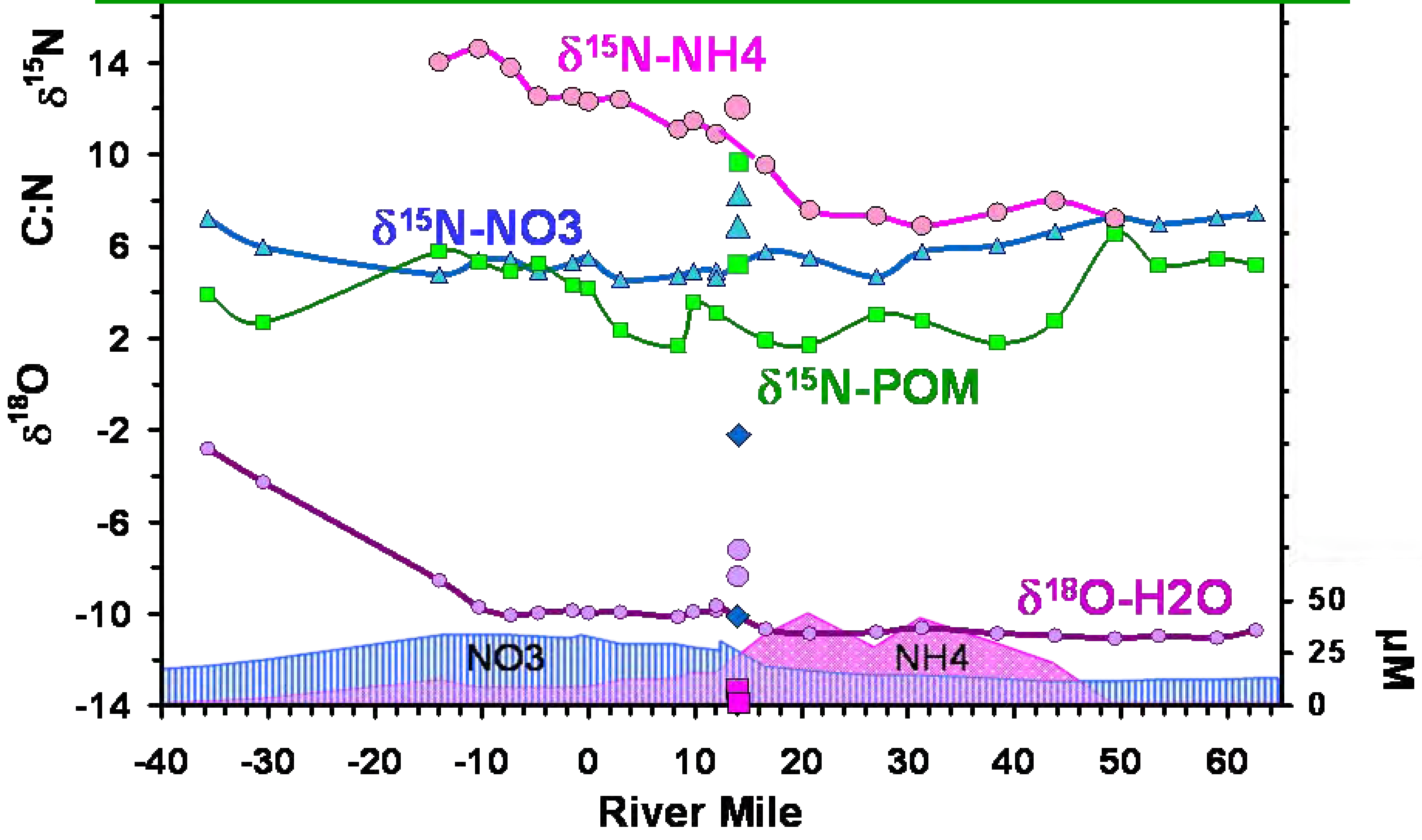


## 2 (3) sites in the Cache Slough Complex

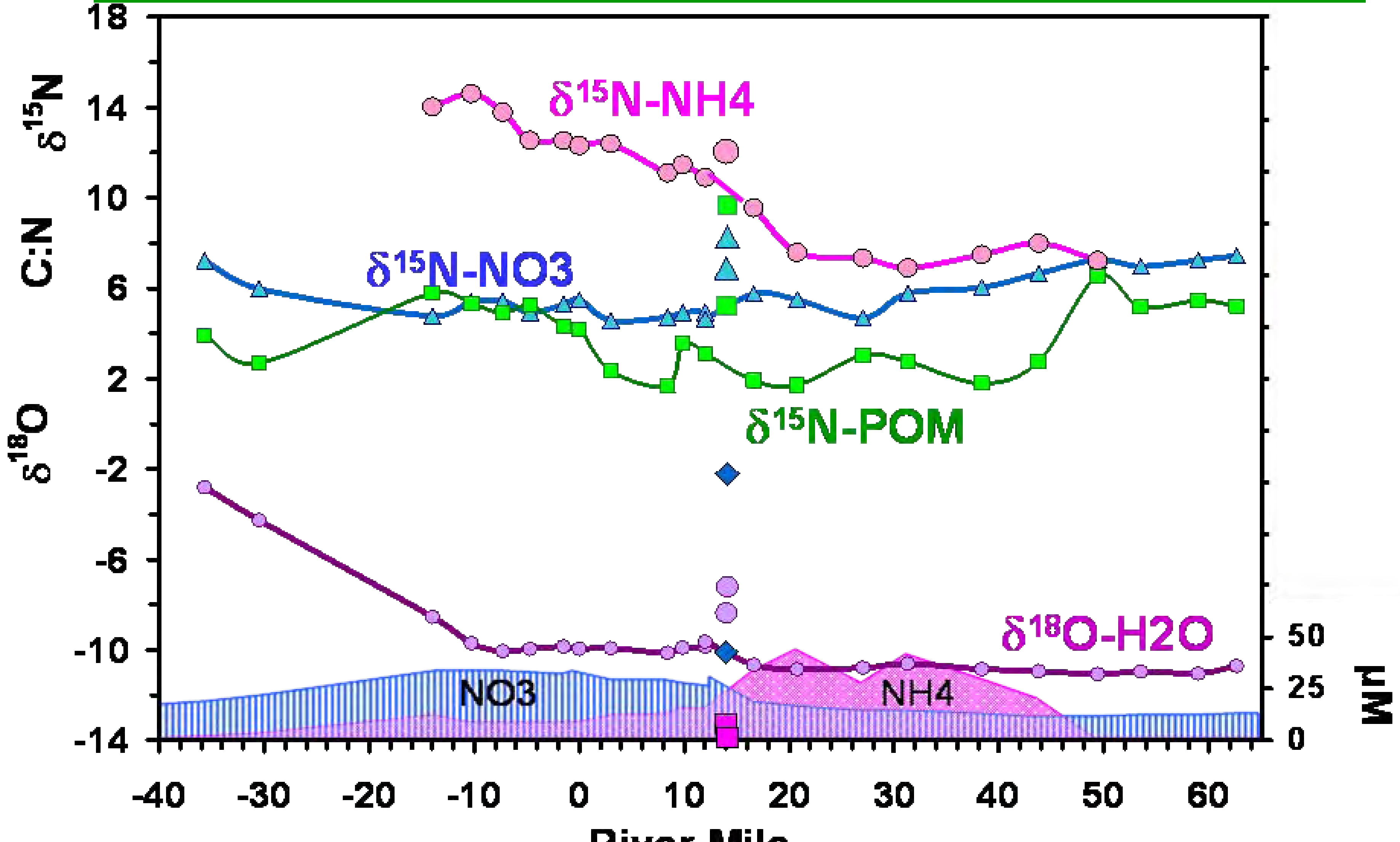
**The tributary symbols are the same shapes and colors as for Sacramento River sites, but are LARGER.**



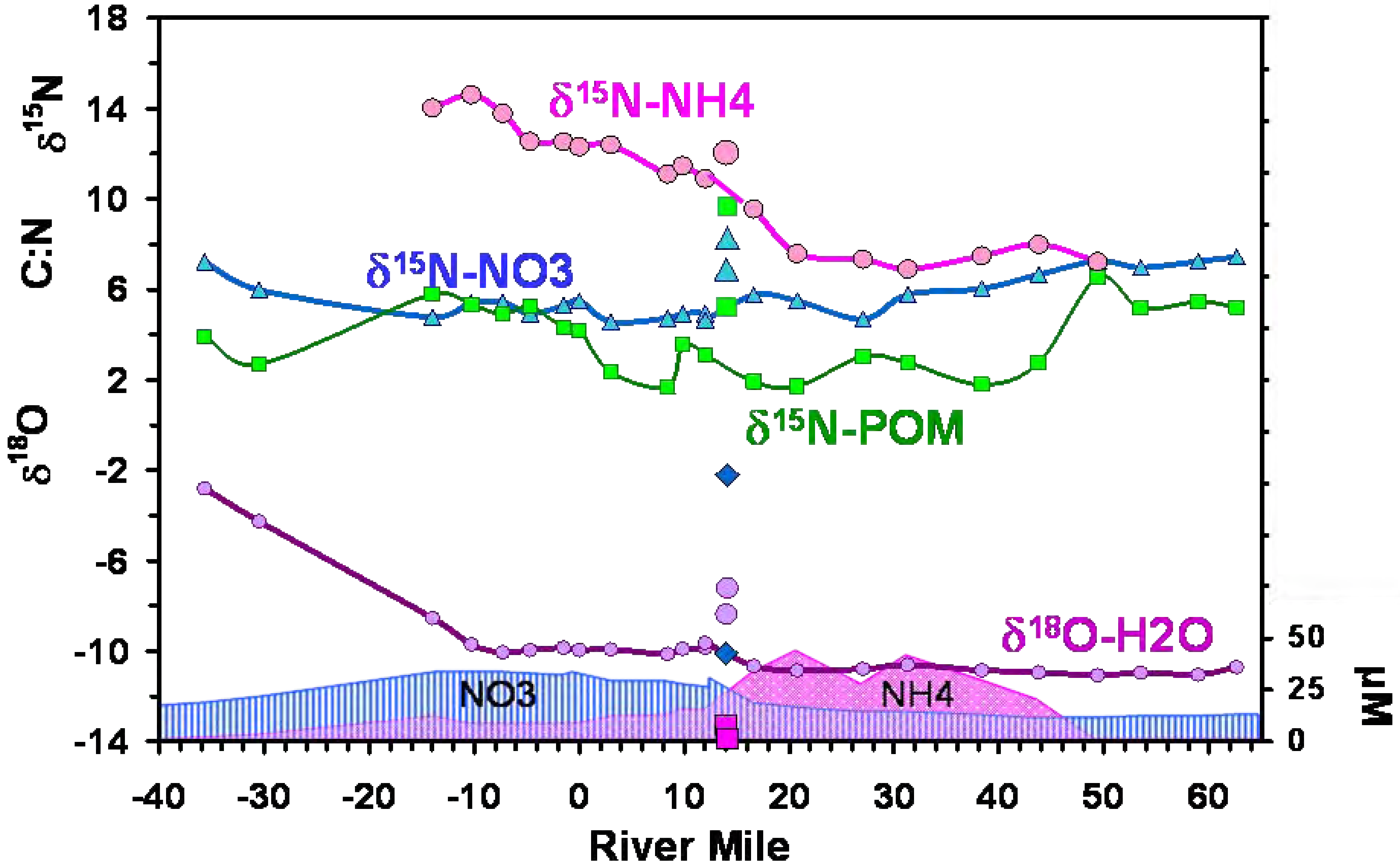
One main finding is that δ15N of NH4 shows a dramatic increase downstream as NH4 decreases and NO3 increases due to nitrification, providing a distinct isotopic signature for WWTP-derived NH4.



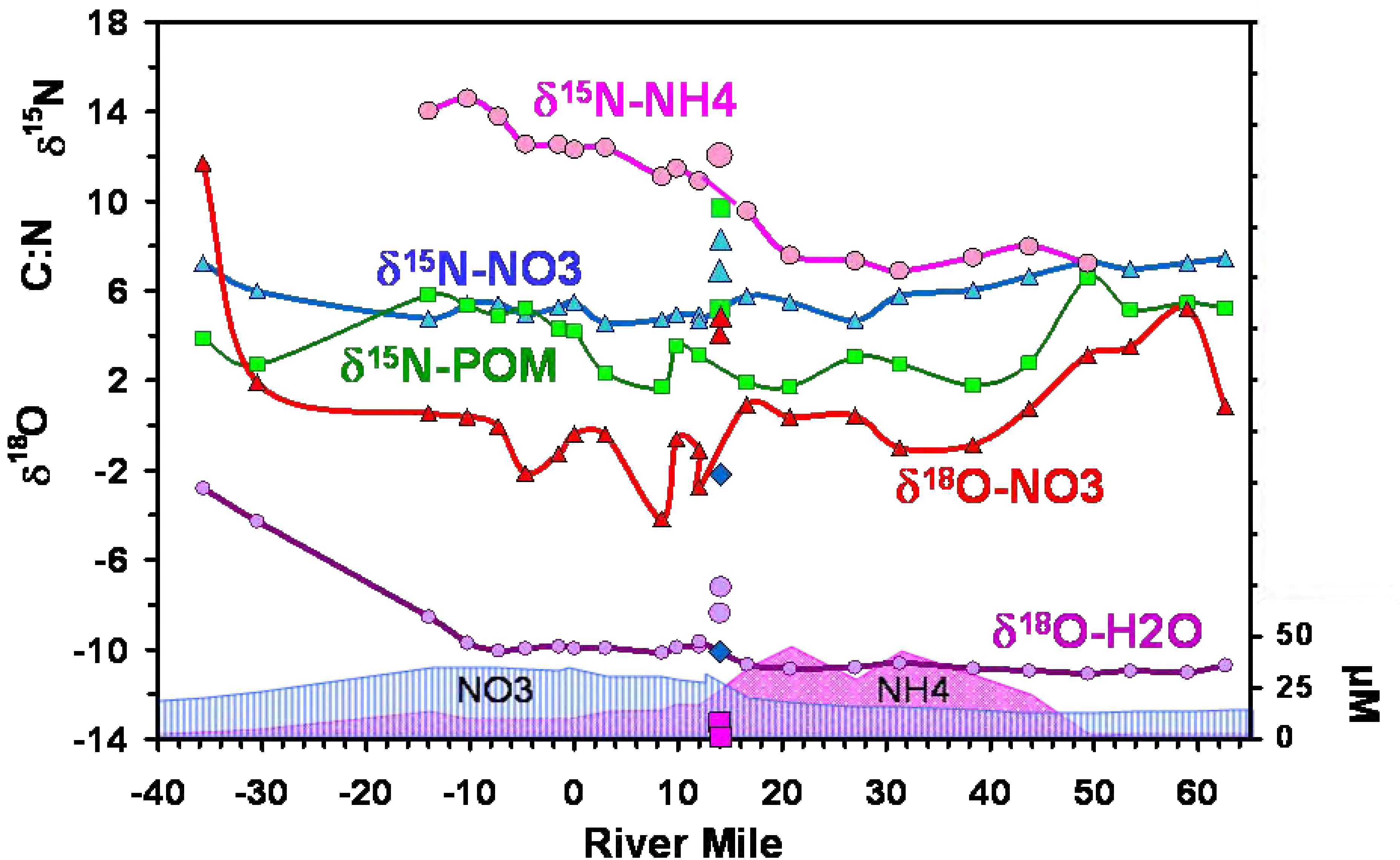
As NO3 increases gradually downstream, δ15N-NO3 decreases. Starting at ~RM20, NH4 rapidly decreases and NO3 increases, and the δ15N-NO3 levels off. Downstream of RM -15, δ15N-NO3 increases as residual NH4 with high-δ15N is nitrified.



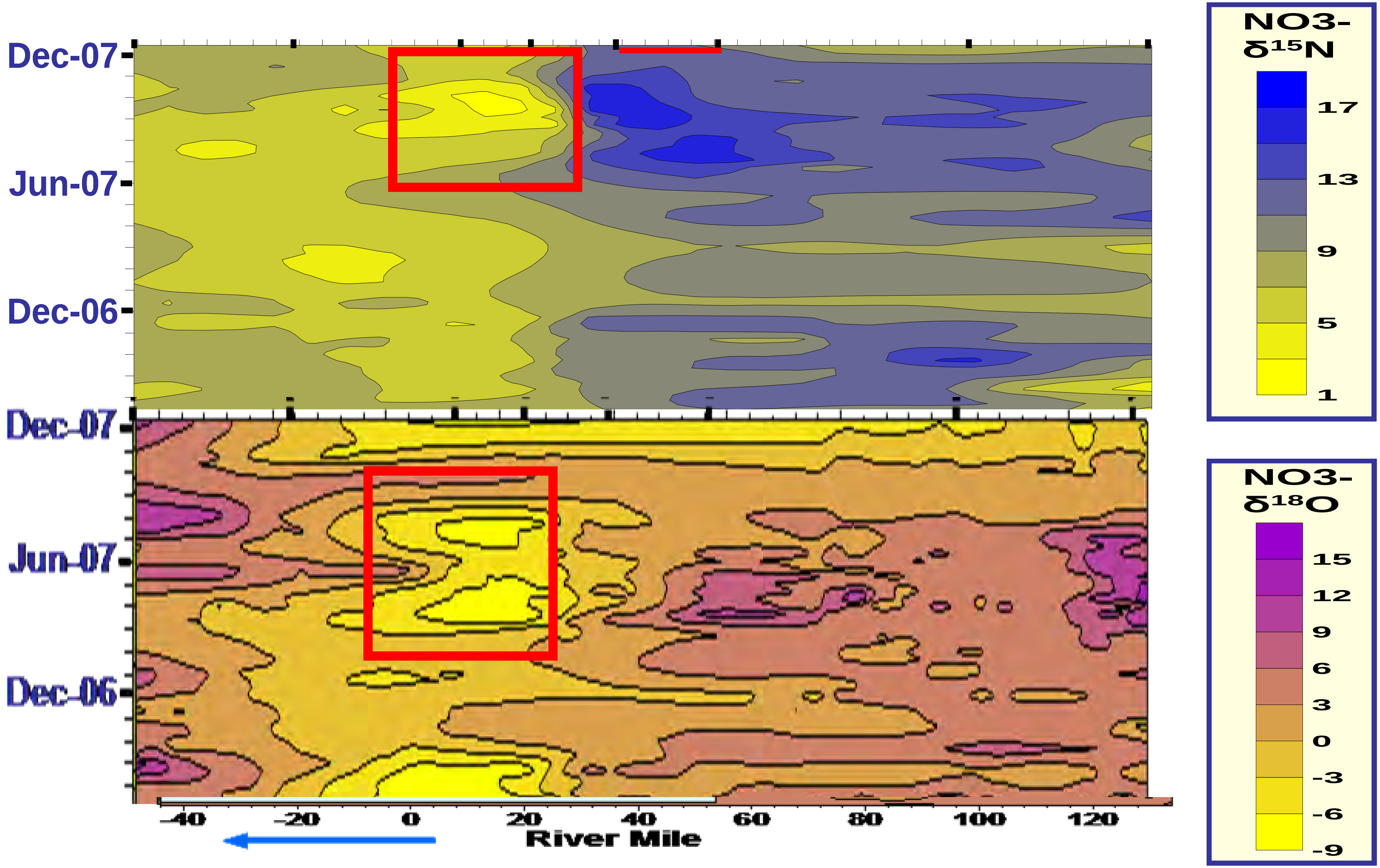
The related downstream changes in δ¹⁵N of NH4 and NO3 are consistent with massive amounts of nitrification.



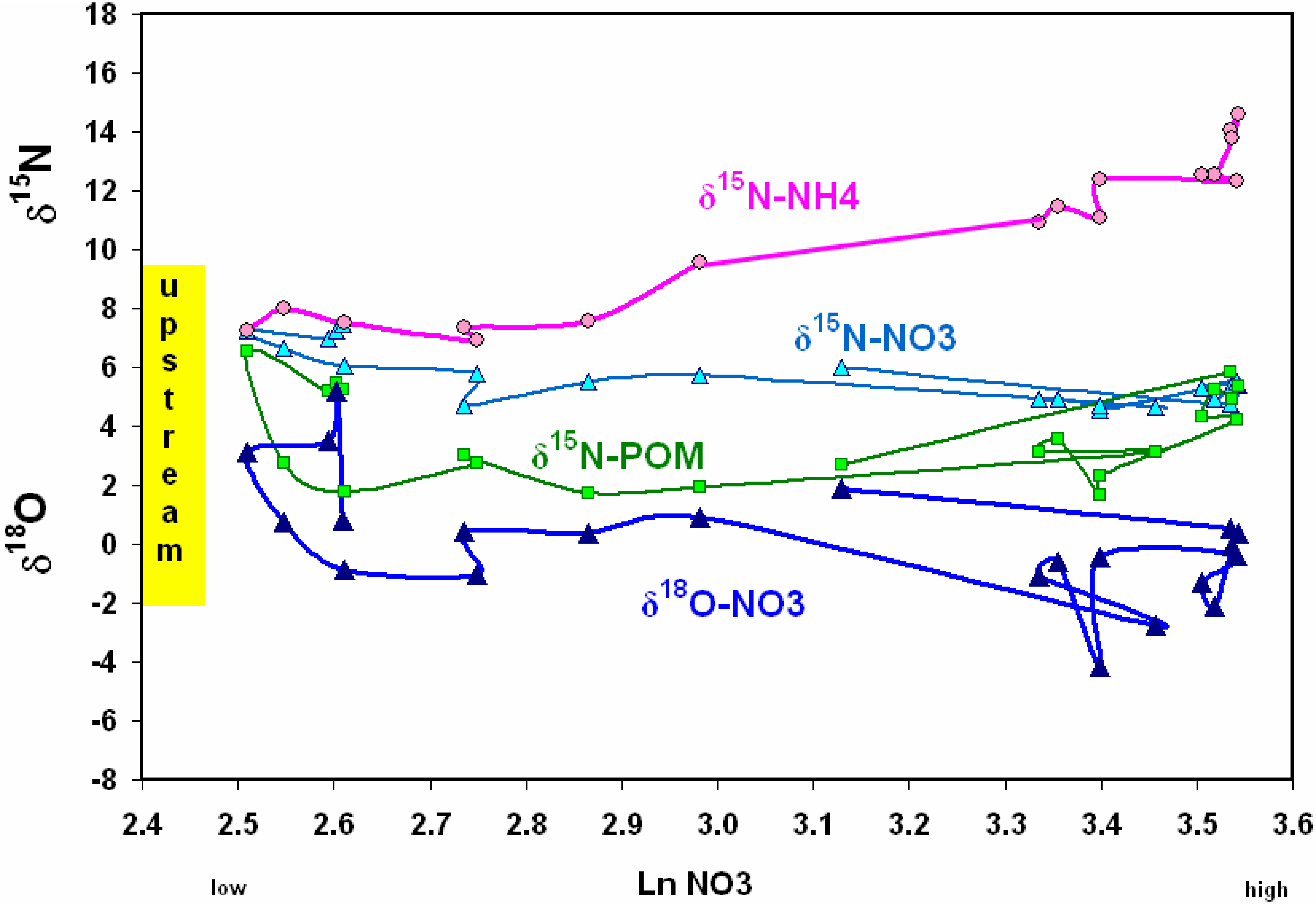
The related downstream changes in $\delta^{18}O$ of NO3 are also consistent with nitrification.



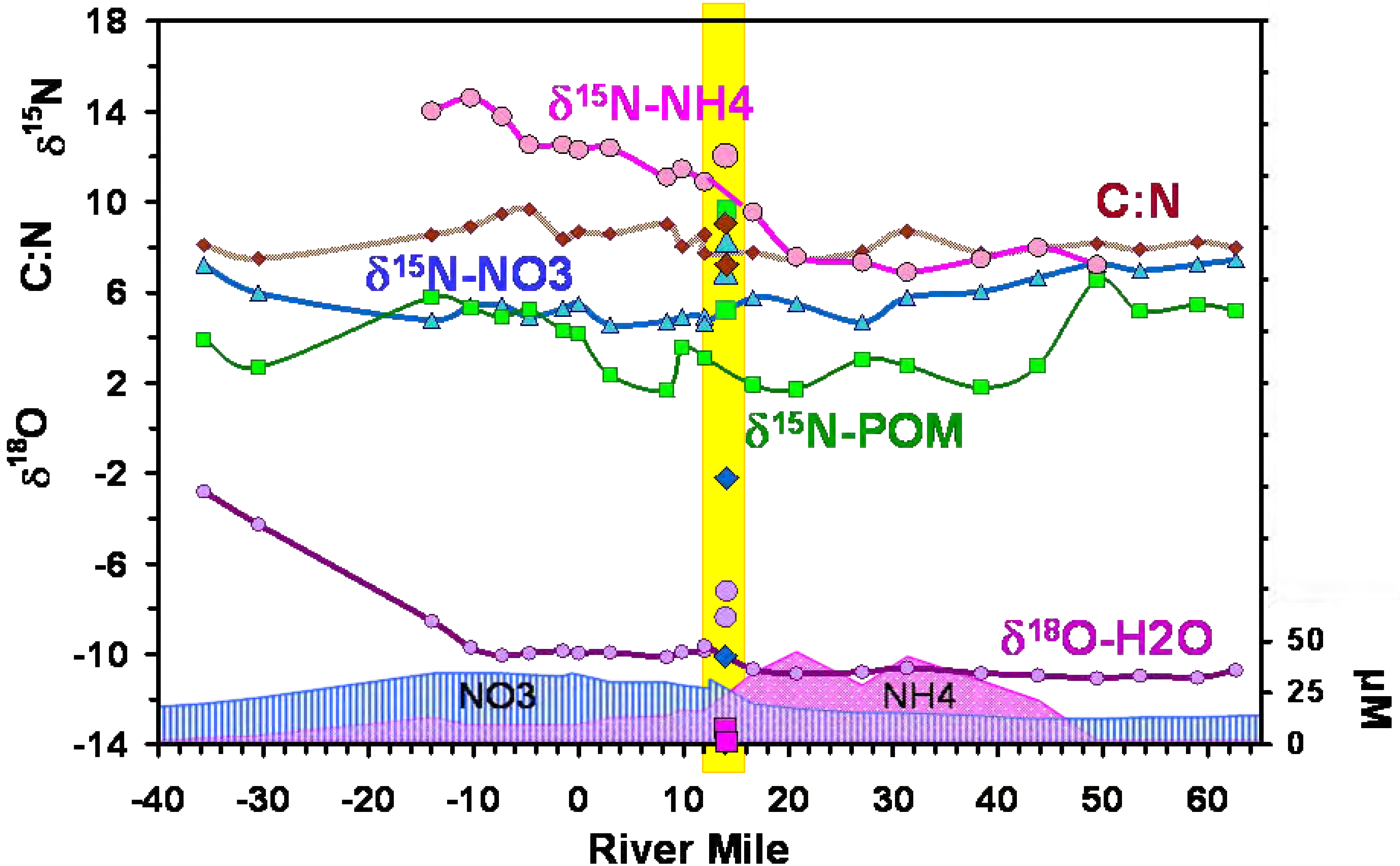
A good example of the usefulness of isotopes is that we had previously identified nitrification in the delta or Sacramento River as the likely cause of these isotope "hot spots" before we had collected any samples from upstream of Rio Vista.



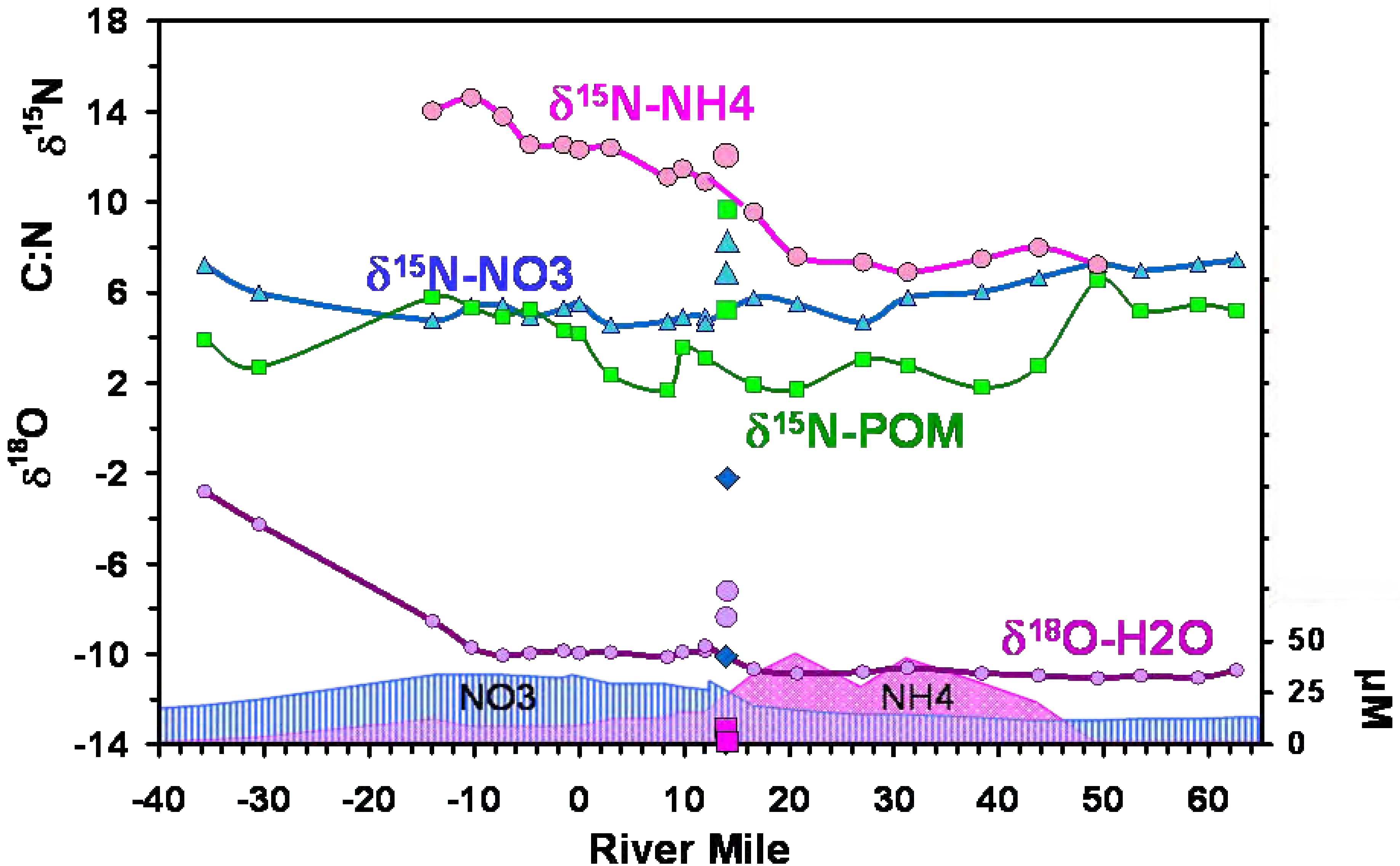
# The isotope trends are clean enough for isotope mass balance models and empirical derivation of isotope fractionations.



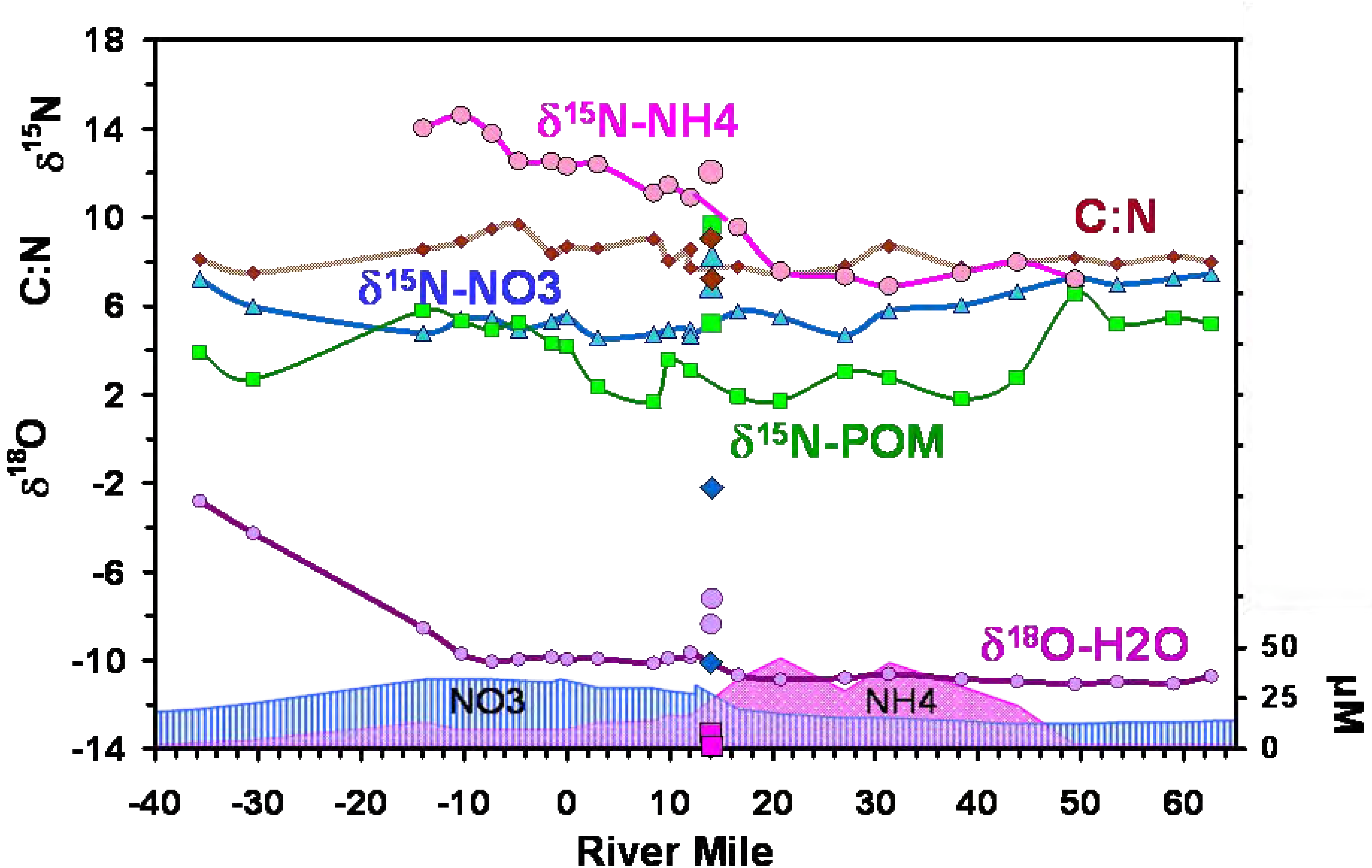
**The few NH4-δ15N values from Cache Slough are very similar to those from the WWTP. However, the Slough samples may have been adversely affected by tidal sloshing.**



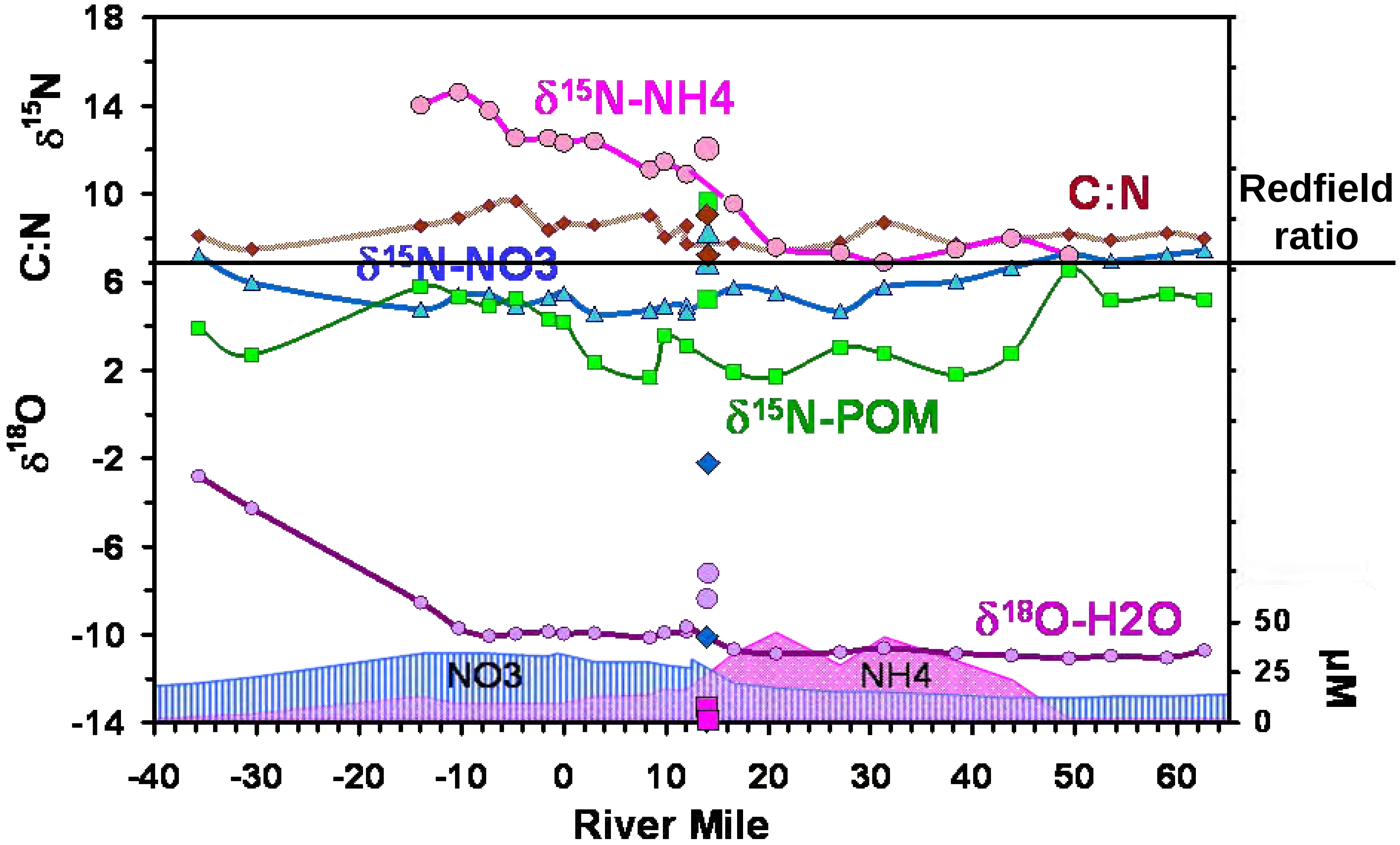
The NH4 from the WWTP is clearly isotopically labeled with increasingly high $\delta^{15}N$ as it is slowly nitrified. Can we distinguish this NH4 source from other NH4 sources?



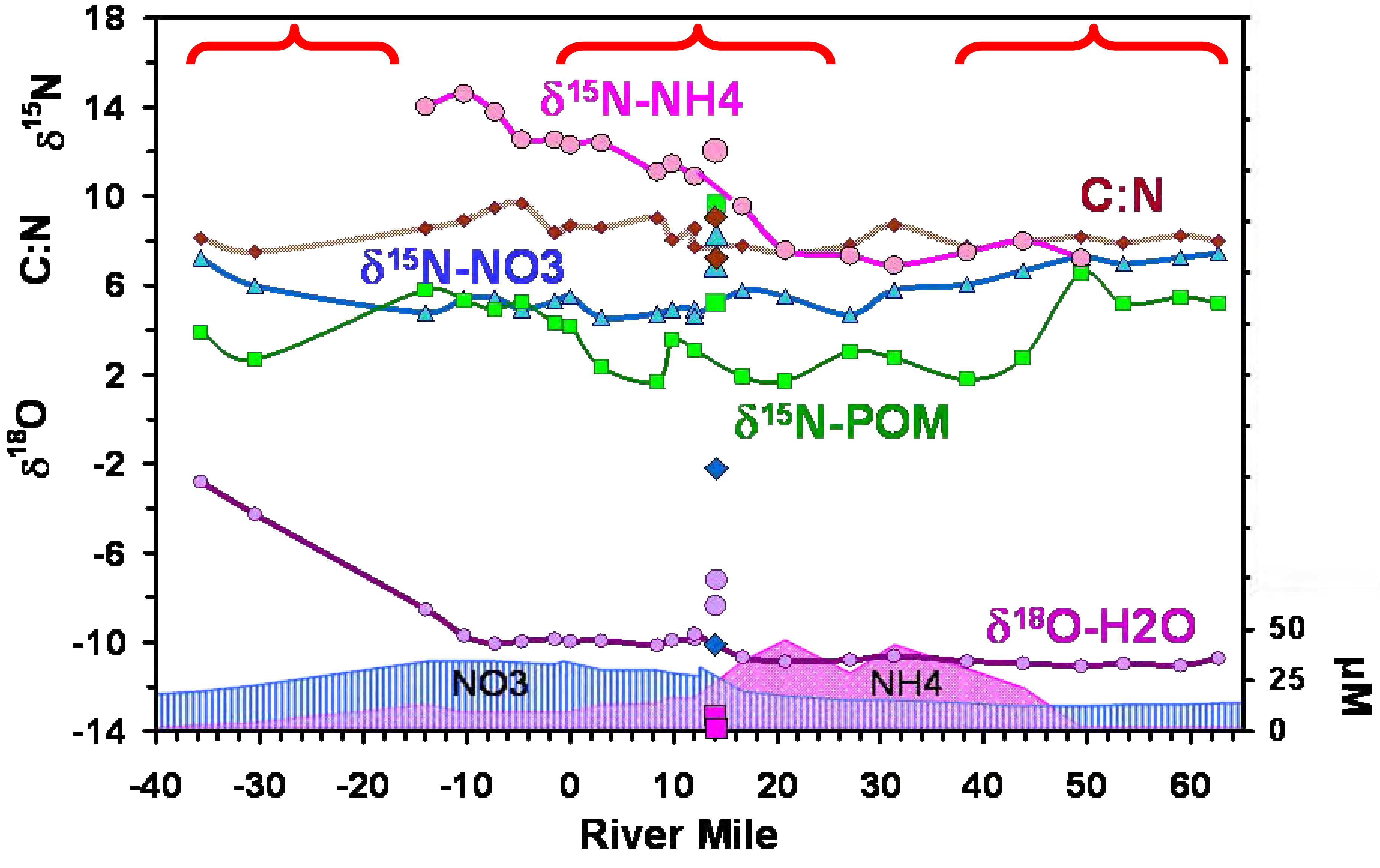
# $\delta^{15}N$ of NO3 begins to increase downstream at ~RM -15.



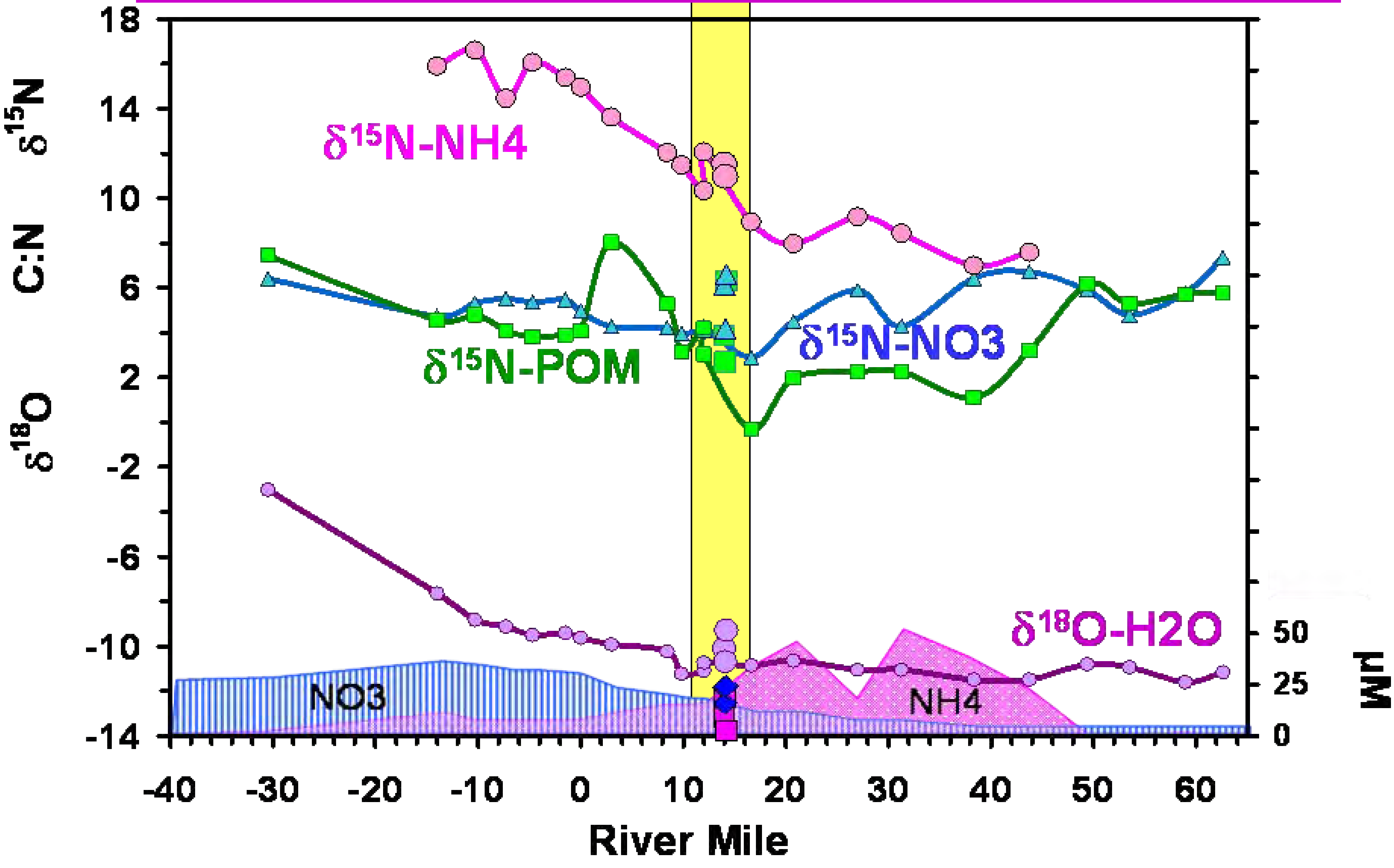
Decreases in C:N of POM suggest additions of algae and/or bacteria.



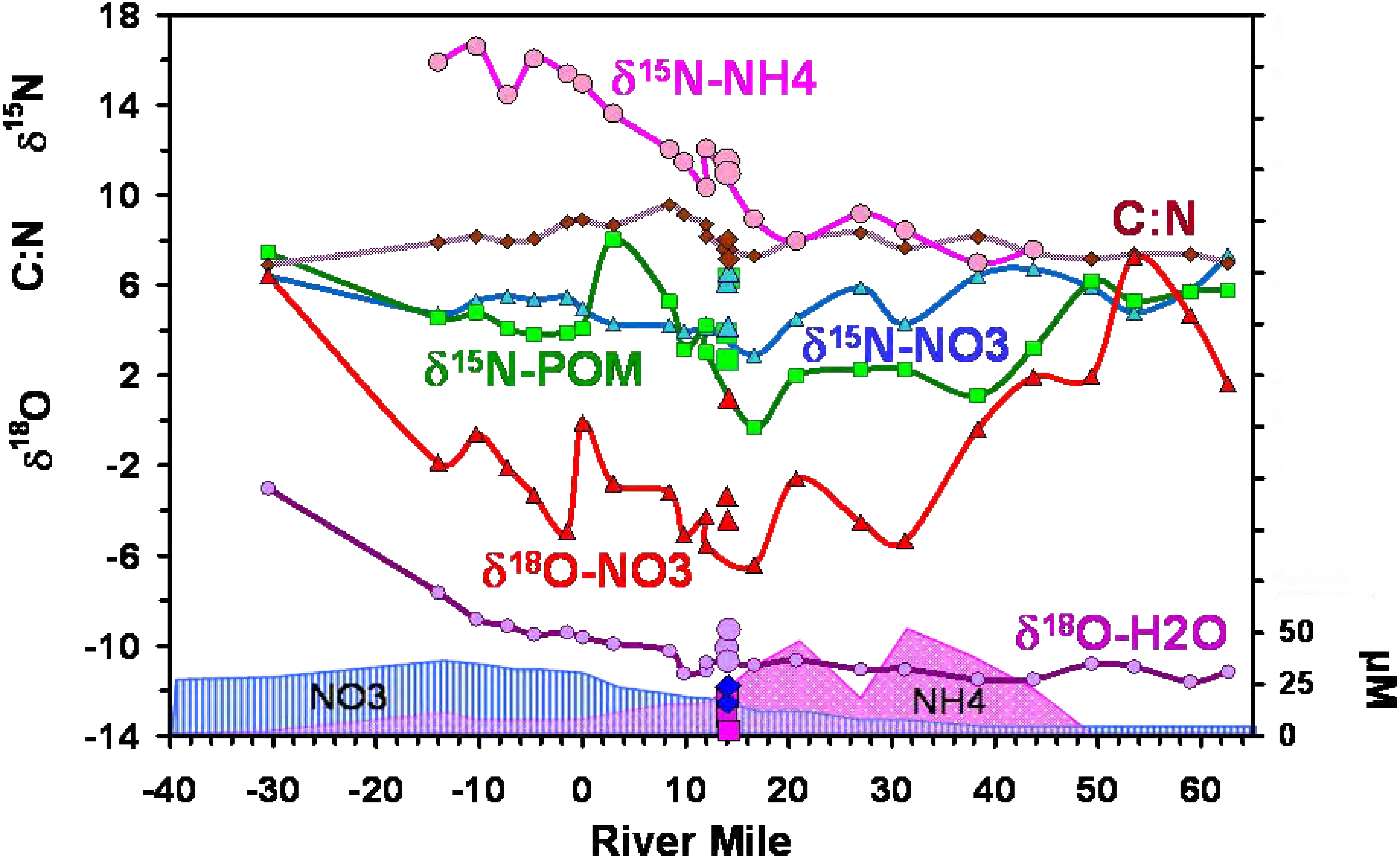
There are **3 locations** along the March transect with low C:N of POM, suggestive of increased contributions of new aquatic POM.



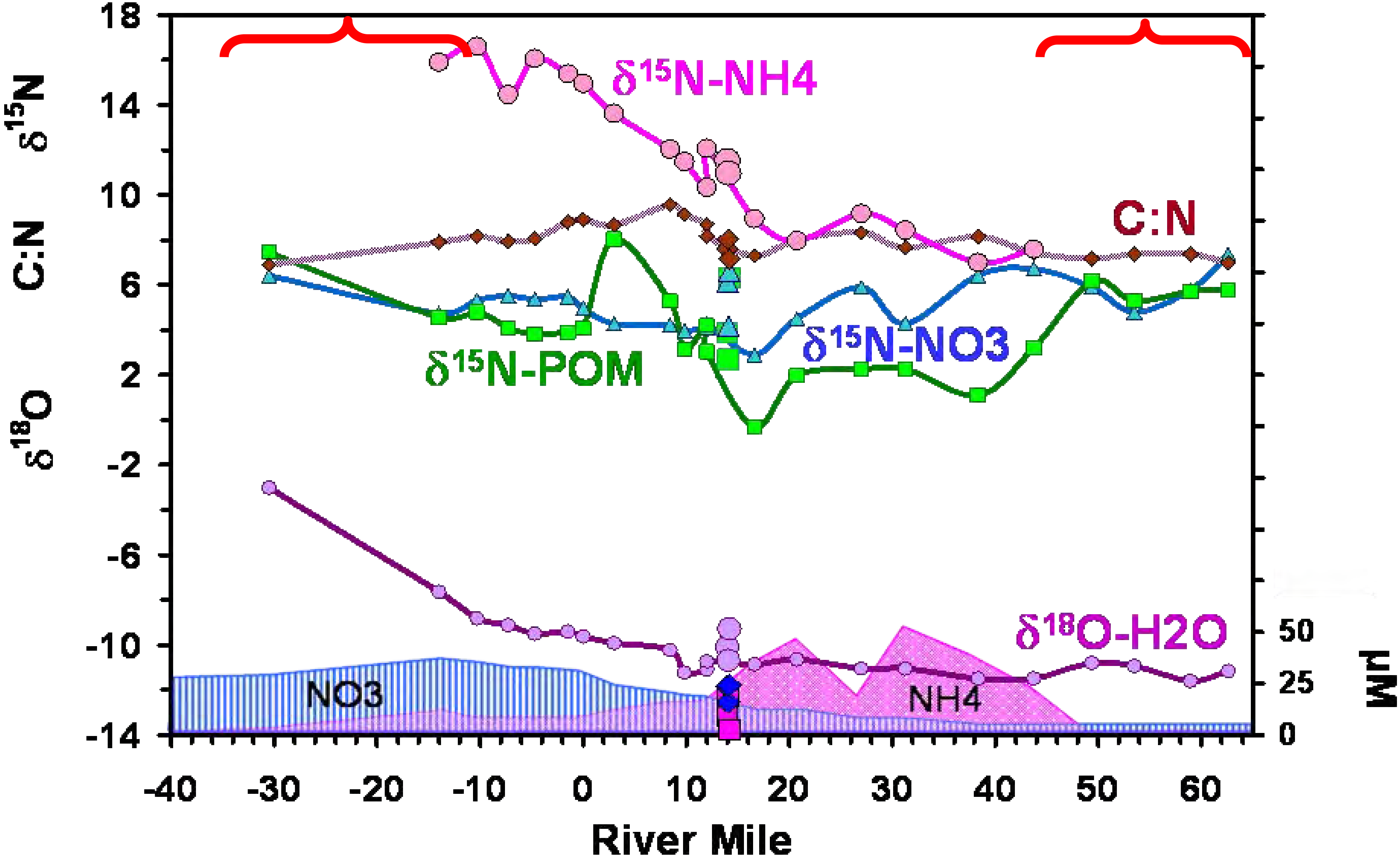
**The April 2009 transect shows very similar spatial patterns, with the downstream trends in δ$^{15}$N of NH4 and NO3 indicating massive nitrification.**



The April transect also shows a huge downstream drop in δ$^{18}$O-NO3 as NO3 increases, NH4 decreases, and δ$^{15}$N-NH4 increases -- indicative of nitrification.



**Again, the low C:N at both ends of the transect, as well as similarities in the $\delta^{15}N$ of POM and NO3, suggest uptake of NO3 by algae and/or bacteria.**



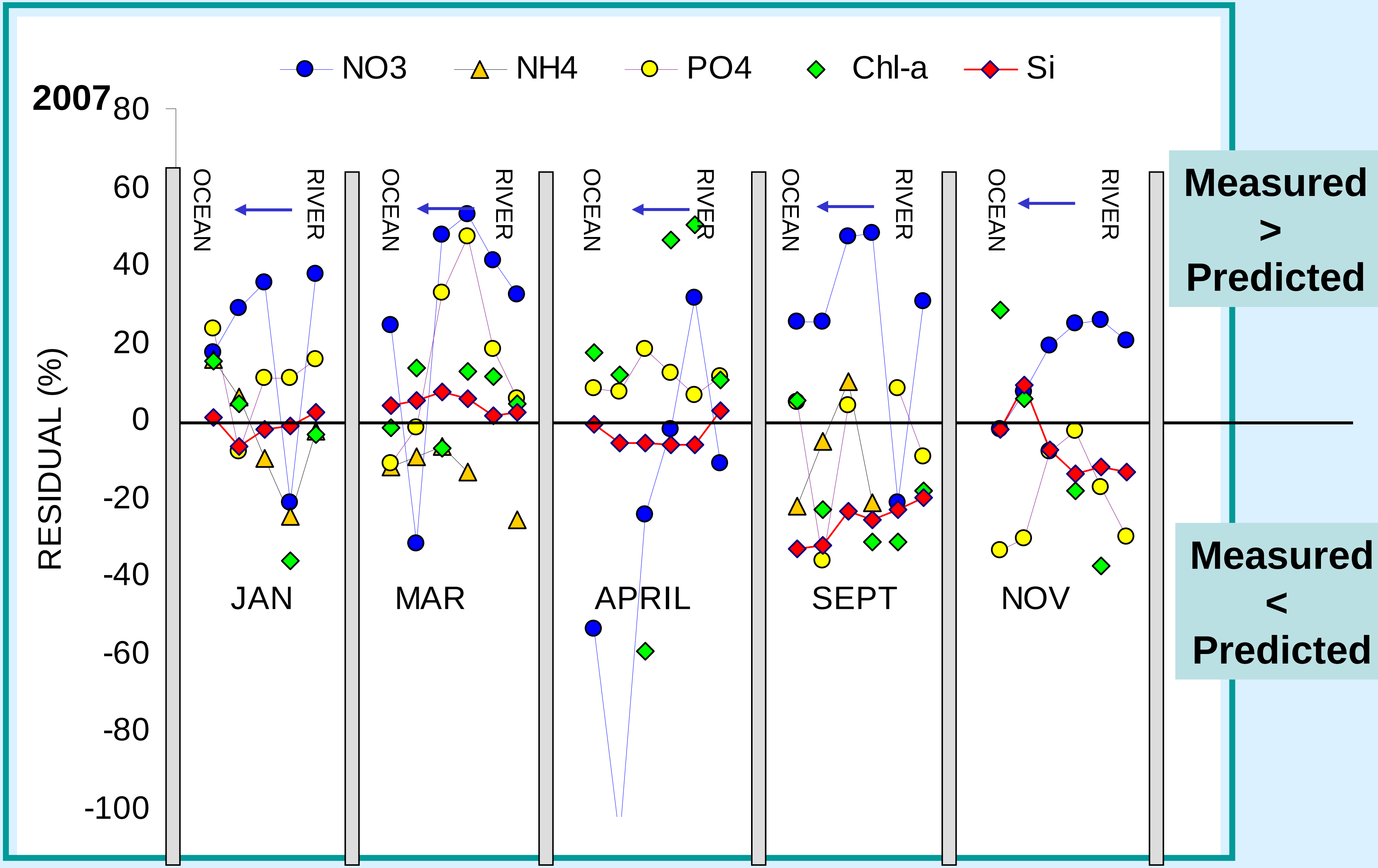
## MAIN QUESTIONS

**Can isotope techniques:**

1) **identify sources of NH4 and NO3 at key locations?**
2) **determine relative biogeochemical reactions rates of different nutrients at key locations?**

**Answering these questions is a work in progress. This collaboration started only a few months ago (just after the March NH4 meeting), and we have another year of study and 3+ papers to write before we will have all our pieces of the puzzle assembled.**

# NON-CONSERVATIVE MIXING (Measured ≠ Predicted)




**5 transects showing residuals from a 2-source mixing model.**

**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:**

- **a recent short-course at Oregon State University in June 2009 where I gave a few lectures: http://oregonstate.edu/groups/hydro/IsotopeWorkshop/IsotopeWorkshop.html (click on the Kendall links further down on the page).**
- **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://wwwrcamnl.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).**


Questions?