Progress with tracing organic matter and nutrient sources using isotopic techniques

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Our involvement in applying various isotope tools to several past, current, and soon-to-start CALFED-funded projects:

DO TMDL-related projects:

- Kratzer's 2000-2001 study: “Sources of nutrients, organic matter, and Chl A to the lower SJR”
- Kendall’s Task 7 of Stringfellow’s Upstream DO TMDL project: “Biological Oxygen Demand (BOD) isotope studies”
- Kendall’s PIN 700 study: “Determination of sources of organic matter and nutrients in the SJR”
- Kratzer’s PIN 755 study: “Groundwater nitrate inputs to the SJR”

Other Drinking Water Quality Program projects:

- Bergamaschi’s 1999-2002 study: “Sources of DBPs to the Delta”
- Bergamaschi’s 2004-2005 study: “Sources of DBPs to the SWP”
- Bergamaschi’s PIN 396 study: “Management of DOC, DBP, and nutrient release from major agricultural land uses”
- Harter’s PIN 708 study: “Risk of dairies and other non-point sources to groundwater”

Our different approaches for investigating the causes of low DO conditions in the SJR

As part of 4 started (or soon to start) projects, we plan to do the following over the next 2 years:

- **Add a complete suite of isotope measurements to the DO TMDL monitoring program, to evaluate the spatial and seasonal patterns biweekly for 2+ years at ~20 sites on the SJR and major tribs, and ~20 main sub-watersheds periodically.**
- **Conduct quarterly transects along the entire SJR-Delta-Bay system (30-40 sites), coordinated with the DO TMDL monitoring.**
- **Add isotopes to detailed evaluation of the source of nitrate in groundwater that is leaking into the SJR, using transects and multi-level samplers (Kratzer)**
- **Add isotopes to detailed investigations of N sources and sinks at dairies at different locations, to better characterize the isotopic signature of dairy waste (Harter)**
- **Test some relatively new isotope techniques in the DWSC for "added value":**
  - **mapping DO sources and sinks in the Stockton channel with DO-$\delta^{18}O$ and other isotope tracers,**
  - **analyzing the isotopes of the bacteria that are respiring the decayed algae in the channel to determine which specific types and sources of the algae are the ones most responsible for the low DO conditions.**

Other recent "isotope-related" activities in the SJR Basin

Field experiments:

Diel and spatial changes in the DWSC (piggybacked on Fleenor's field experiment August 2004)

Diel changes in the SJR at Crow's Landing (piggybacked on Dahlgren's field experiment August 2005)

Papers:

McLaughlin, K., Kendall, C., Silva, S.R., et al. (2006) Phosphate oxygen isotope ratios as a tracer for sources and cycling of phosphate in North San Francisco Bay, California, Journal of Geophysical Research, Biogeosciences, in press.

Wankel, S.D., Kendall, C., et al. (2006) Nitrogen sources and cycling in the San Francisco Bay Estuary: A nitrate dual isotopic composition approach, Limnology & Oceanography, in press.

Ohte, N., Silva, S.R., Kendall, C., et al., Sources and transport of algae and nutrients in the San Joaquin River upstream of Vernalis, California, in colleague review.

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.

Isotopic Tools for Nutrient-related Studies

- **Nitrate: $\delta^{15}N$ and $\delta^{18}O$ ($\delta^{17}O$).**
- **POM (particulate organic matter): $\delta^{15}N$ and $\delta^{13}C$ ($\delta^{34}S$).**
- **Water: $\delta^{18}O$ and $\delta^{2}H$ (T, $^{3}H/^{3}He$, CFCs).**
- **DIC (dissolved inorganic carbon): $\delta^{13}C$.**
- **DOC (dissolved organic carbon): $\delta^{13}C$.**
- **DON (dissolved organic nitrogen): $\delta^{15}N$.**
- **Ammonium: $\delta^{15}N$.**
- **Phosphate: $\delta^{18}O$ (DIP and DOP).**
- **Sulfate: $\delta^{34}S$ ($\delta^{18}O$, $\delta^{17}O$).**
- **O_2 (DO = dissolved oxygen): $\delta^{18}O$.**
- **Biota (algae, invertebrates, fish): $\delta^{15}N$ and $\delta^{13}C$ ($\delta^{34}S$, also $\delta^{18}O$ and $\delta^{2}H$).**

How isotopes are used to trace sources of nitrate:

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

Ratios of $^{15}N/^{14}N$ are reported as $\delta^{15}N$. These ratios are pronounced "delta 15-N" or "delta N-15".

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

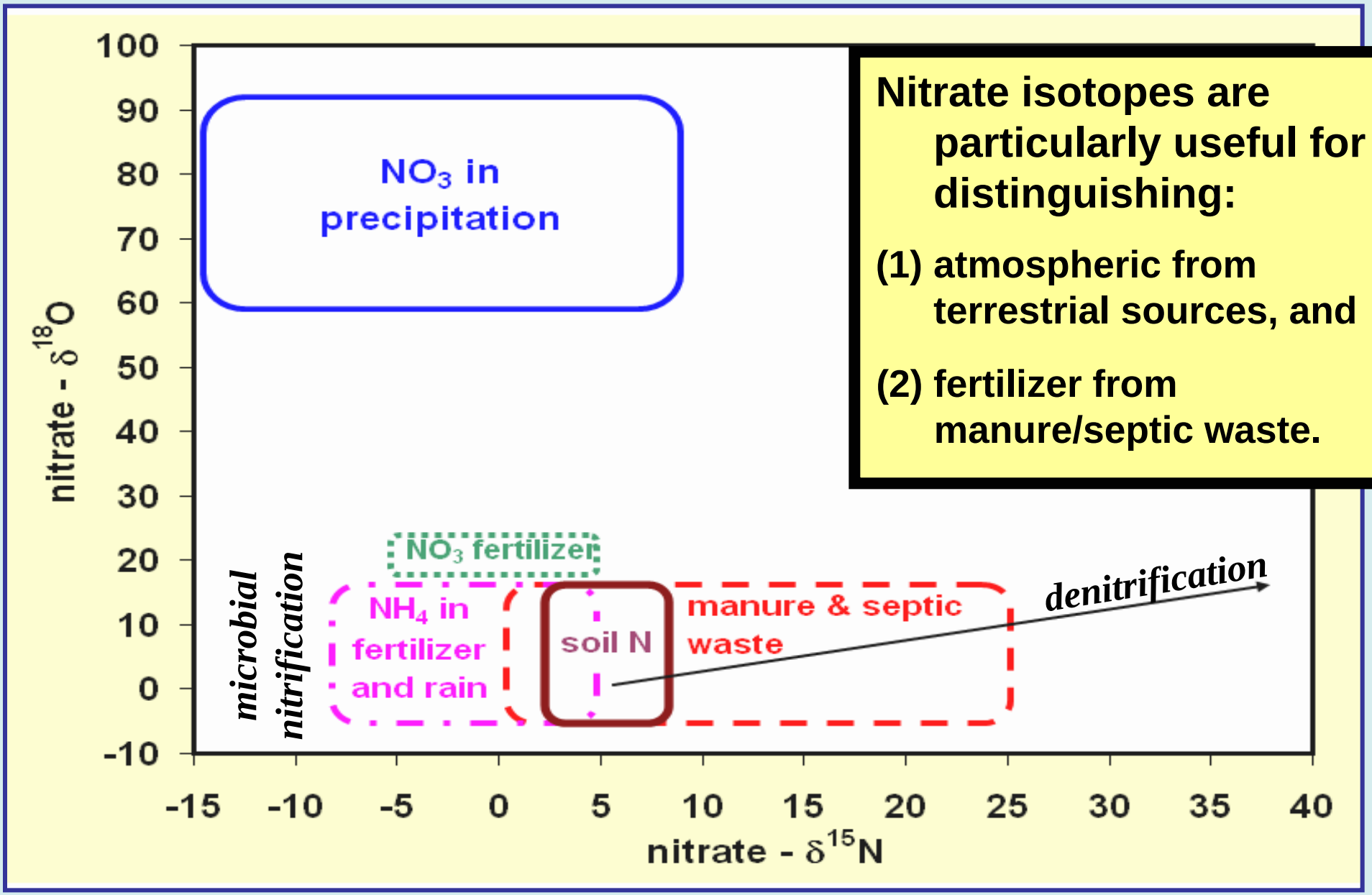
Ratios of $^{18}O/^{16}O$ are reported as $\delta^{18}O$.

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

"δ values" are reported in units of permil = ppt = ‰ because the ratios are usually in the range of 1:1000.

Example: **if different sources of nitrate have different $\delta^{15}N$, $\delta^{18}O$, or $\delta^{17}O$ values, we can sometimes determine how much nitrate comes from the different sources.**

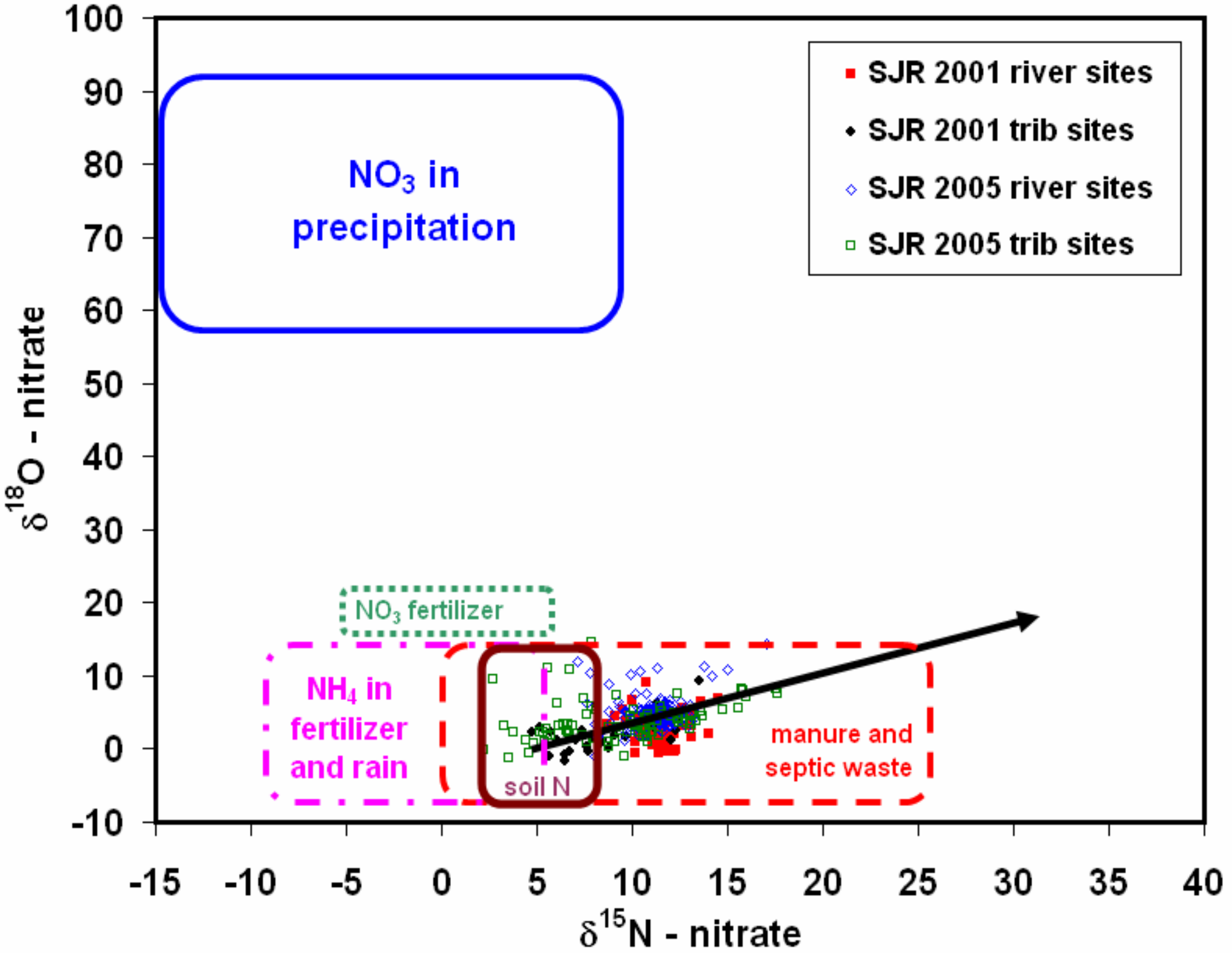
How can nitrate isotopes (nitrate $\delta^{15}N$ and $\delta^{18}O$) help determine the dominant source of nitrate?



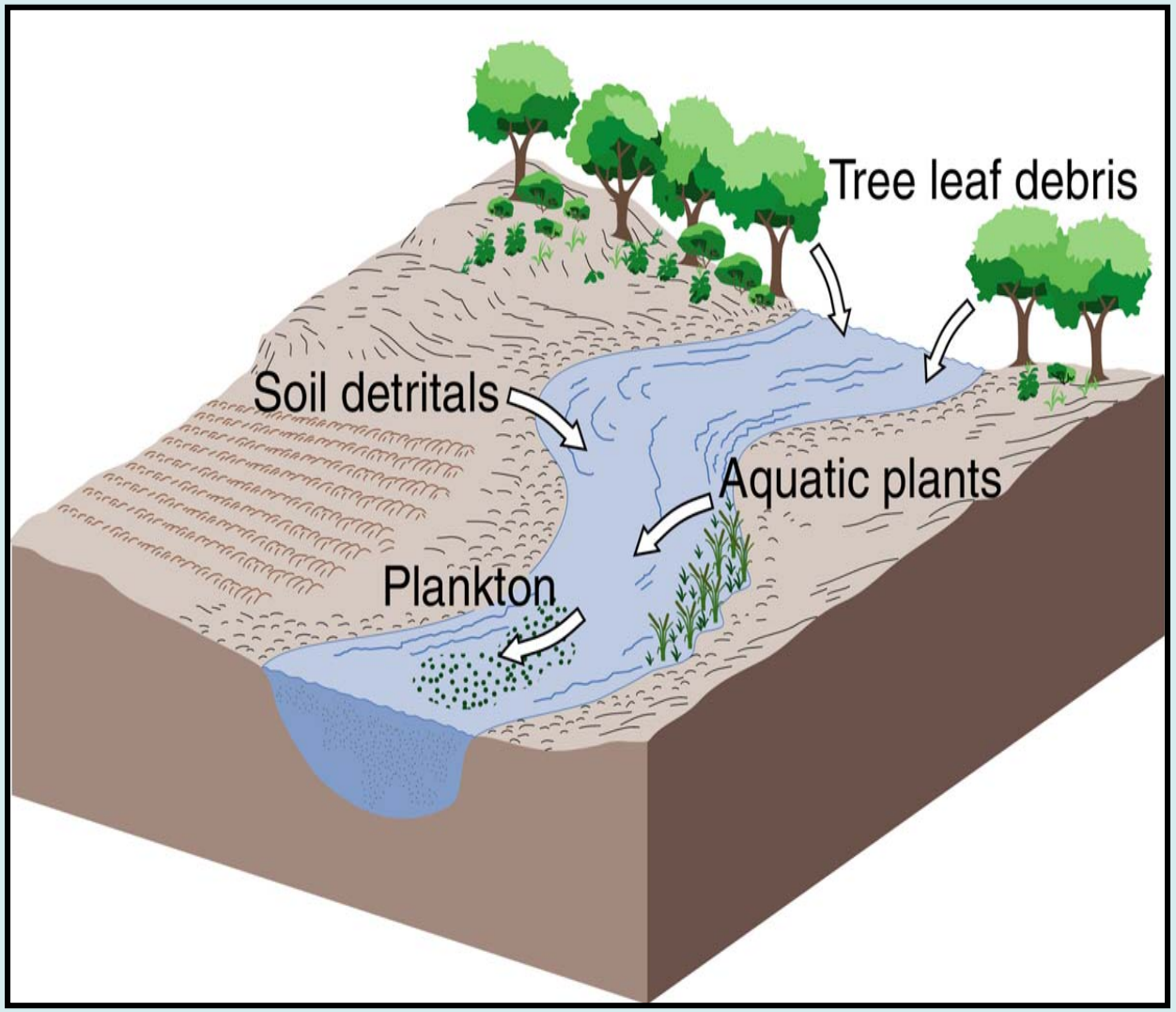
Nitrate isotopes are particularly useful for distinguishing:

(1) atmospheric from terrestrial sources, and

(2) fertilizer from manure/septic waste.


SJR 2001 river sites
SJR 2001 trib sites
SJR 2005 river sites
SJR 2005 trib sites
NO3 in precipitation
NO3 fertilizer
NH4 in fertilizer and rain
soil N
manure and septic waste
δ18O - nitrate
δ15N - nitrate
100
90
80
70
60
50
40
30
20
10
0
-10
-15
-10
-5
0
5
10
15
20
25
30
35
40

How do isotopes help determine the source of the particulate organic matter (POM)?



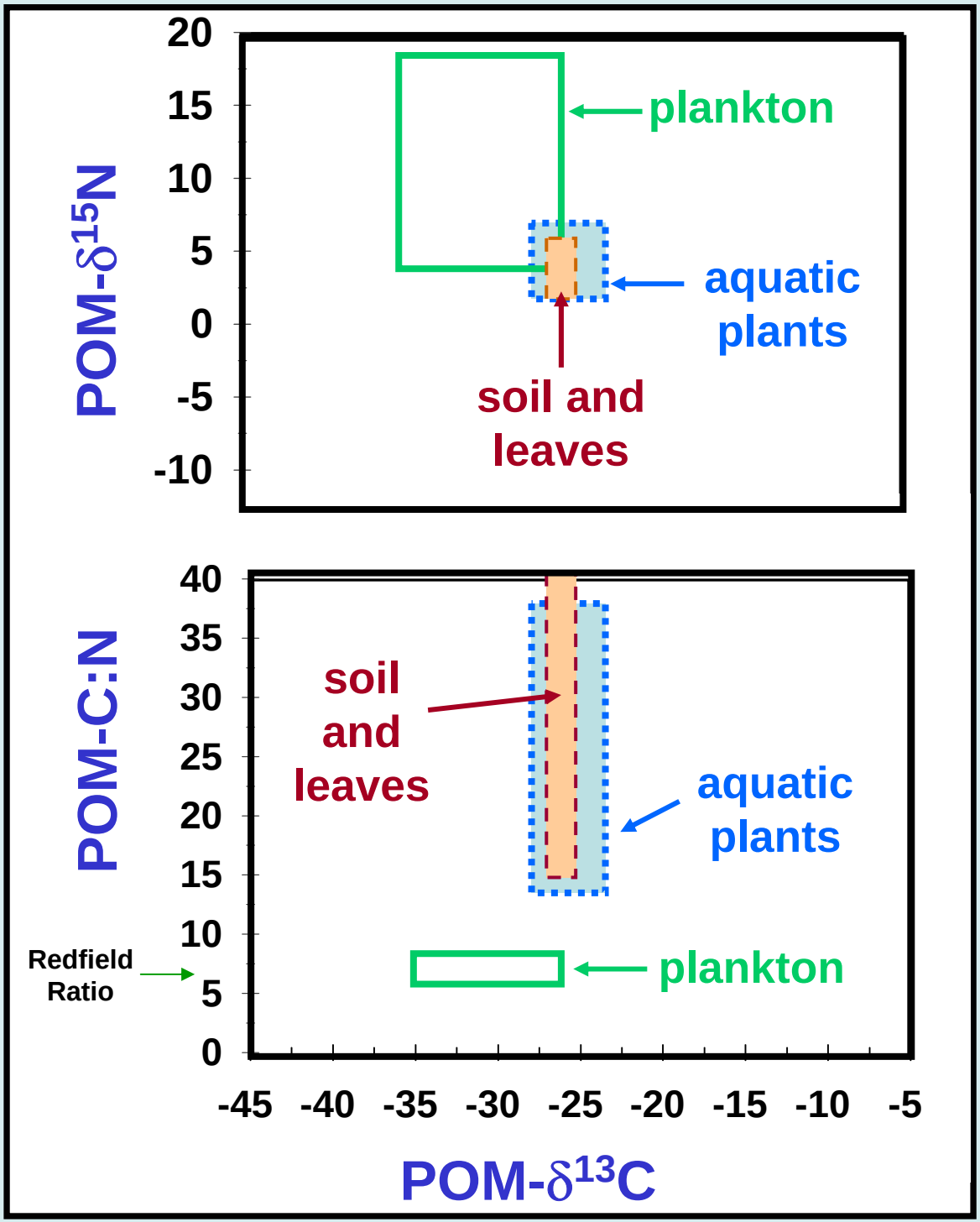
There are 4 main sources:

2 of these sources are terrestrial: leaves and soil.

2 are formed in-situ: plankton (consisting of algae and bacteria), and aquatic plants (consisting of hydrilla, cattails, etc).

These sources can often be distinguished when analyzed for C:N, $\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$, and C:S.

Compositions of different POM sources in the SJR



POM= particulate organic matter

Plankton = algae and bacteria

Since the values for plankton (algae) show little overlap with the ranges of the other POM sources, the combined use of isotopes and C:N ratios should be a very effective tool for determining the source of the POM.

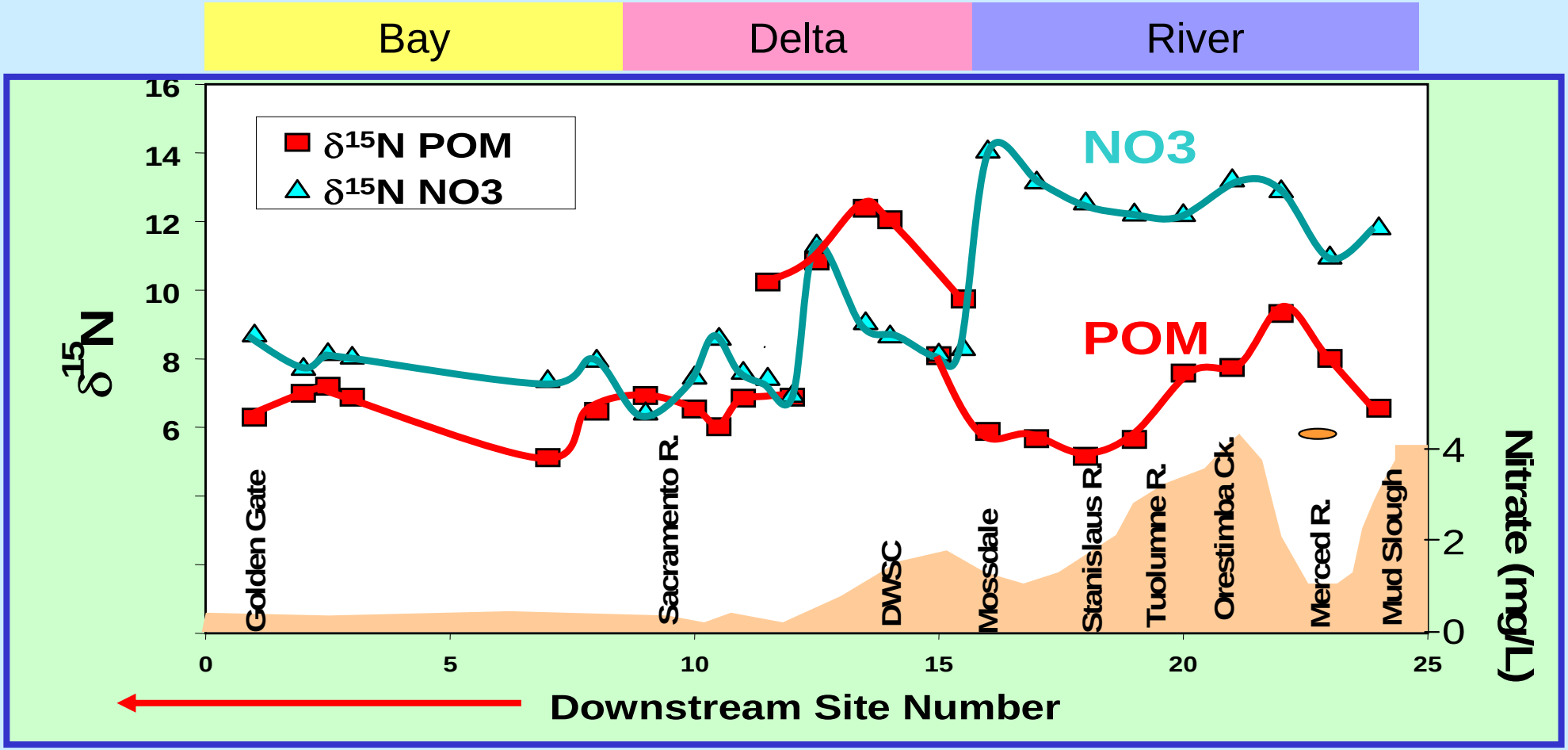
While waiting for our new project funding to start, we conducted several small pilot studies in the SJR and SFB to test out new isotope methods and applications

Examples:

- Diel and spatial studies of O2 sources and sinks in the DWSC.
- Diel studies of O2 sources and sinks in the SJR.
- Tracing sources of nitrate in the SFB with nitrate-$\delta^{18}O/\delta^{15}N$.
- Tracing sources of P in the SFB with phosphate-$\delta^{18}O$.

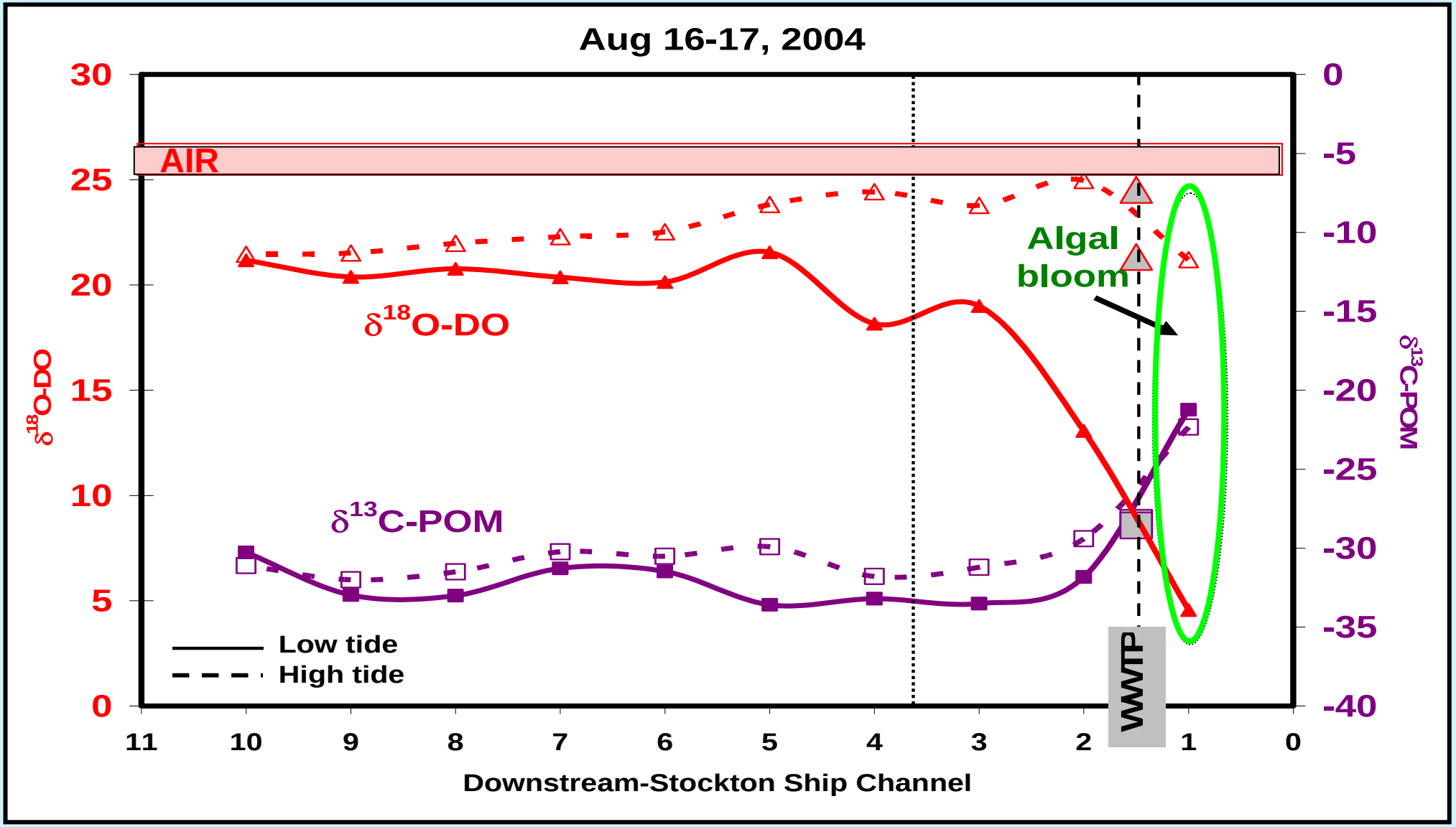
Longitudinal transect showing changes in the $\delta^{15}N$ of NO3 and POM caused by downstream changes in nitrate sources (August 2004).

The $\delta^{15}N$ of the river POM (which is largely algal) tracks the $\delta^{15}N$ of nitrate.

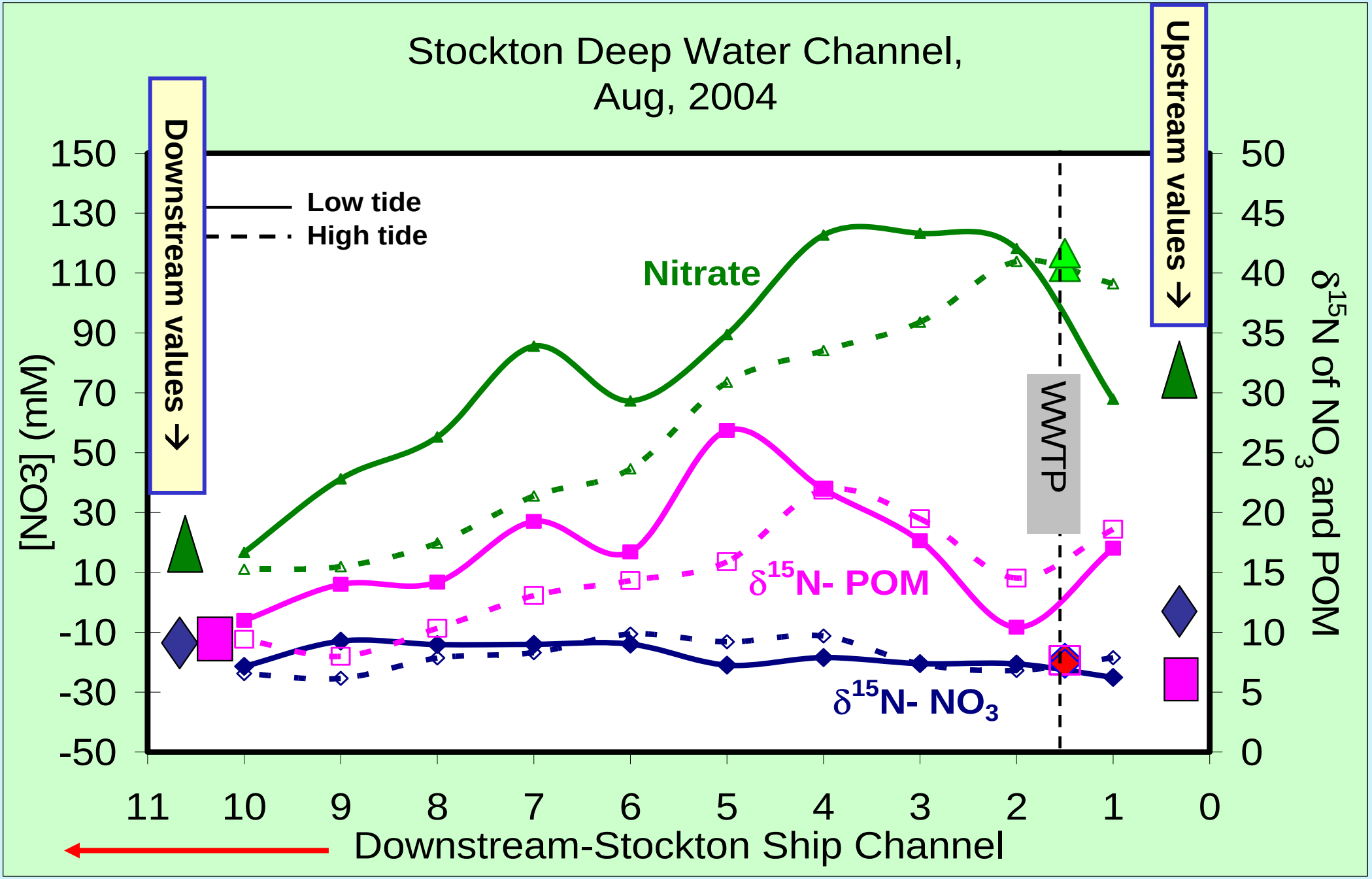


What is going on in the shipping channel?

During our field experiment, there was a huge blue-green algae bloom near the WWTP that strongly affected river chemistry

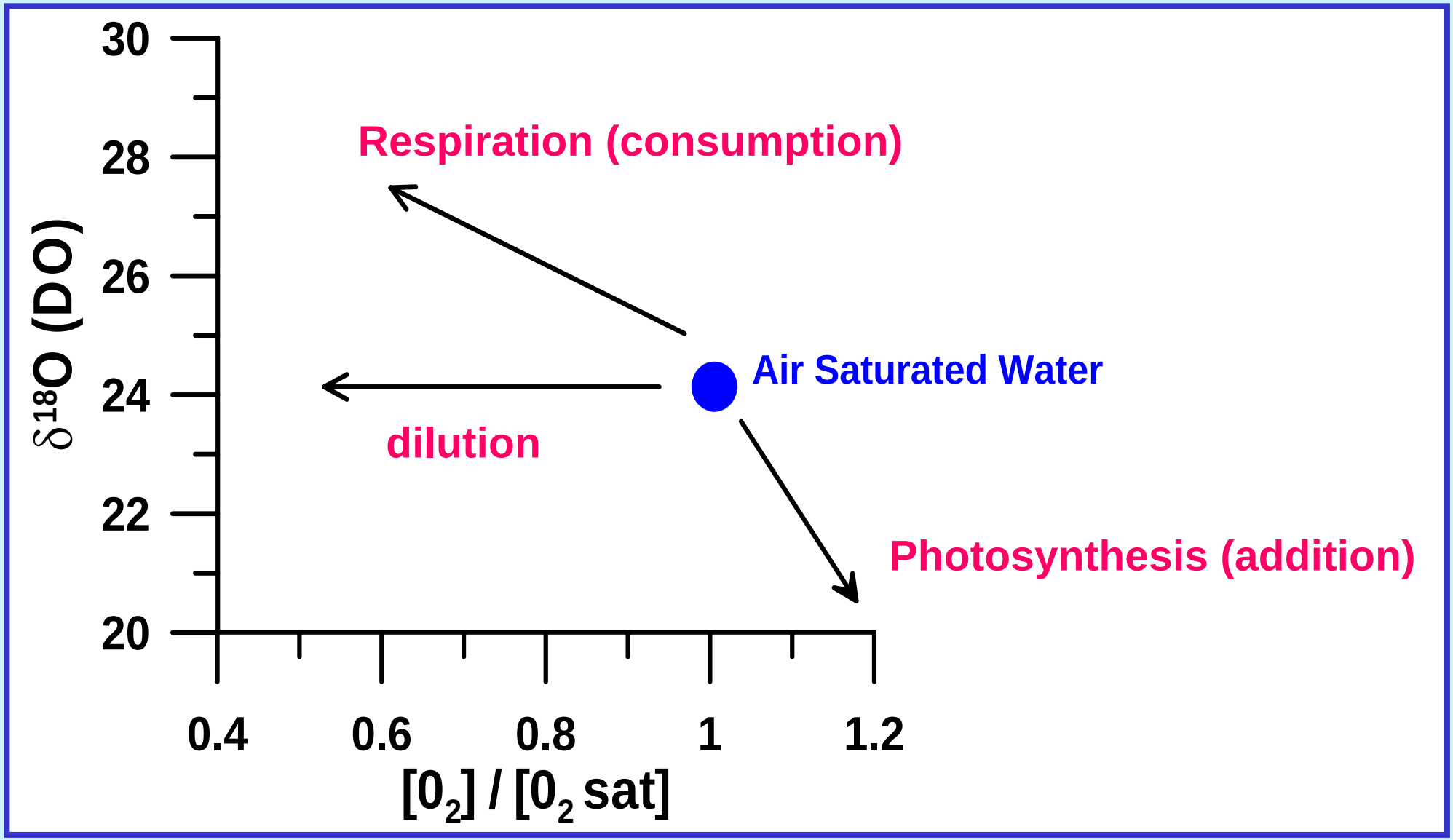


The decrease in the $\delta^{18}O$ of DO and the increase in the $\delta^{13}C$ of DIC near the WWTP reflect algal photosynthesis in the bloom area.

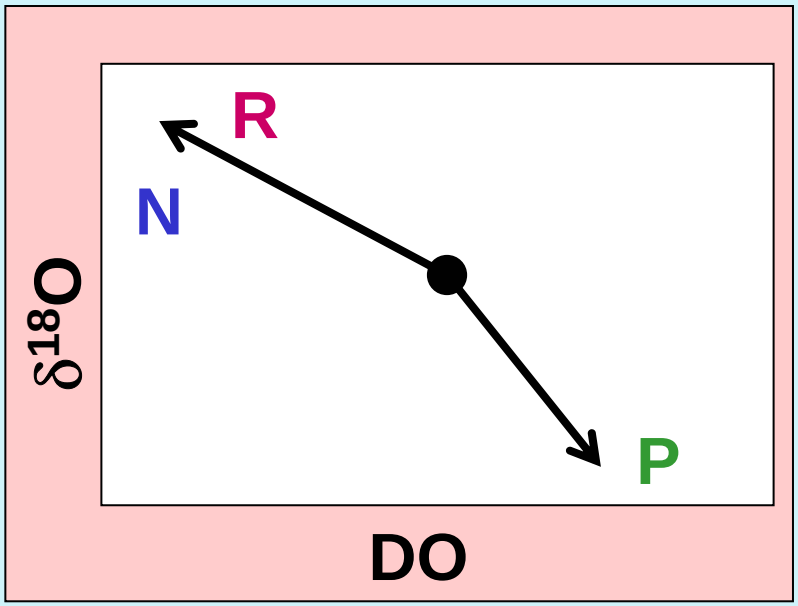


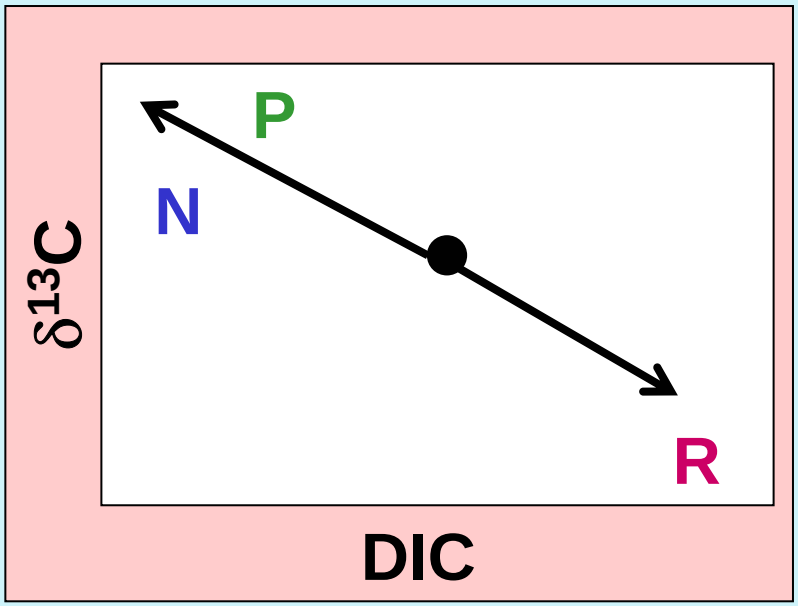
These data suggest NH4 from WWTP is immediately nitrified and then the residual NH4 is uptaken by algae

Algal blooms add a lot of O2 (DO) to the water column. The $\delta^{18}O$ of DO can be used to estimate the ratio of productivity to respiration in the water column



The $\delta^{18}O$ of DO and the concentration of DO change on a daily cycle as O2 is produced during the day and consumed at night.





How to tease out the main controls on DO:

Photosynthesis (P)

Respiration (R)

Nitrification (N)

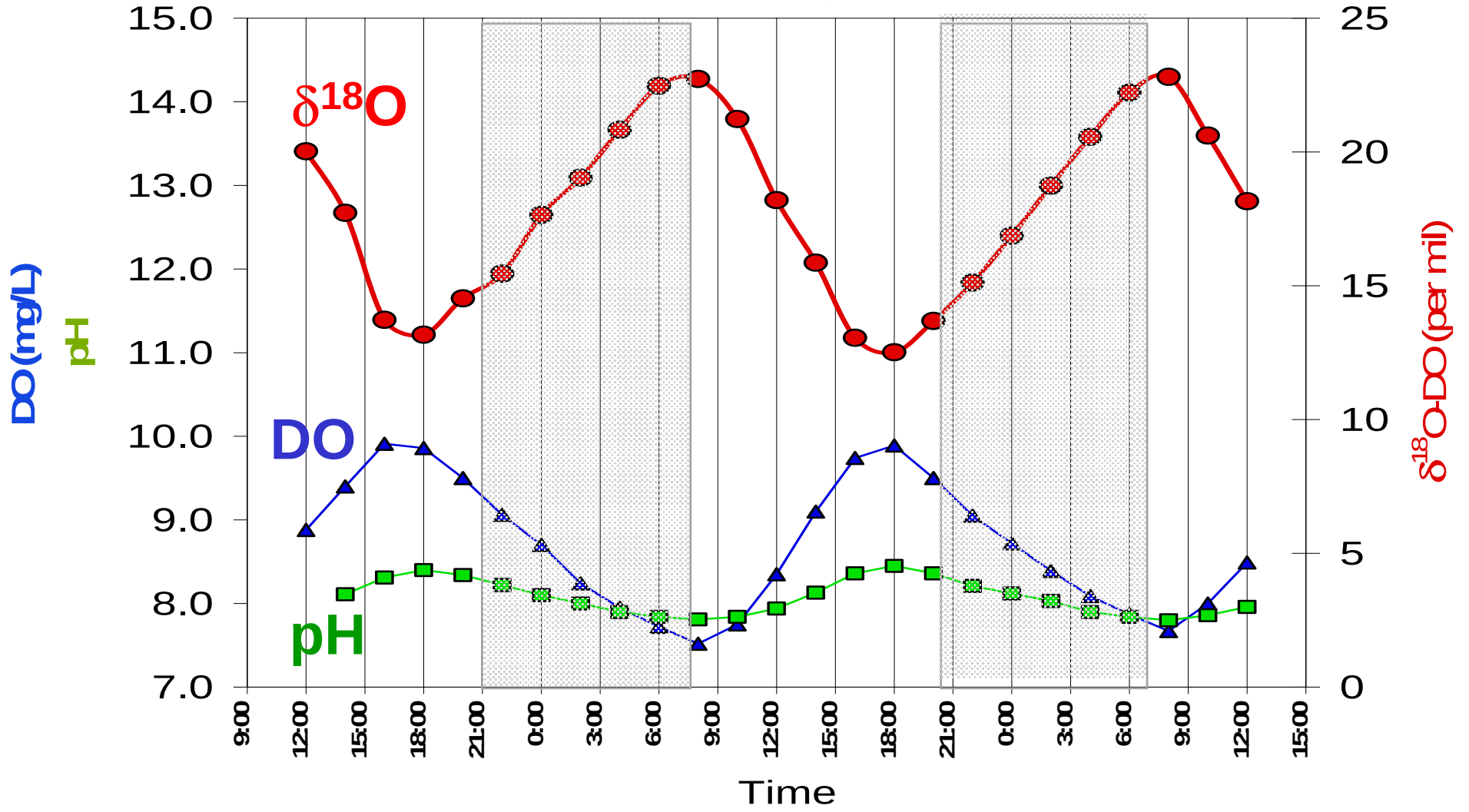
One way is by $\delta^{13}C$ analysis of the DIC (as shown).

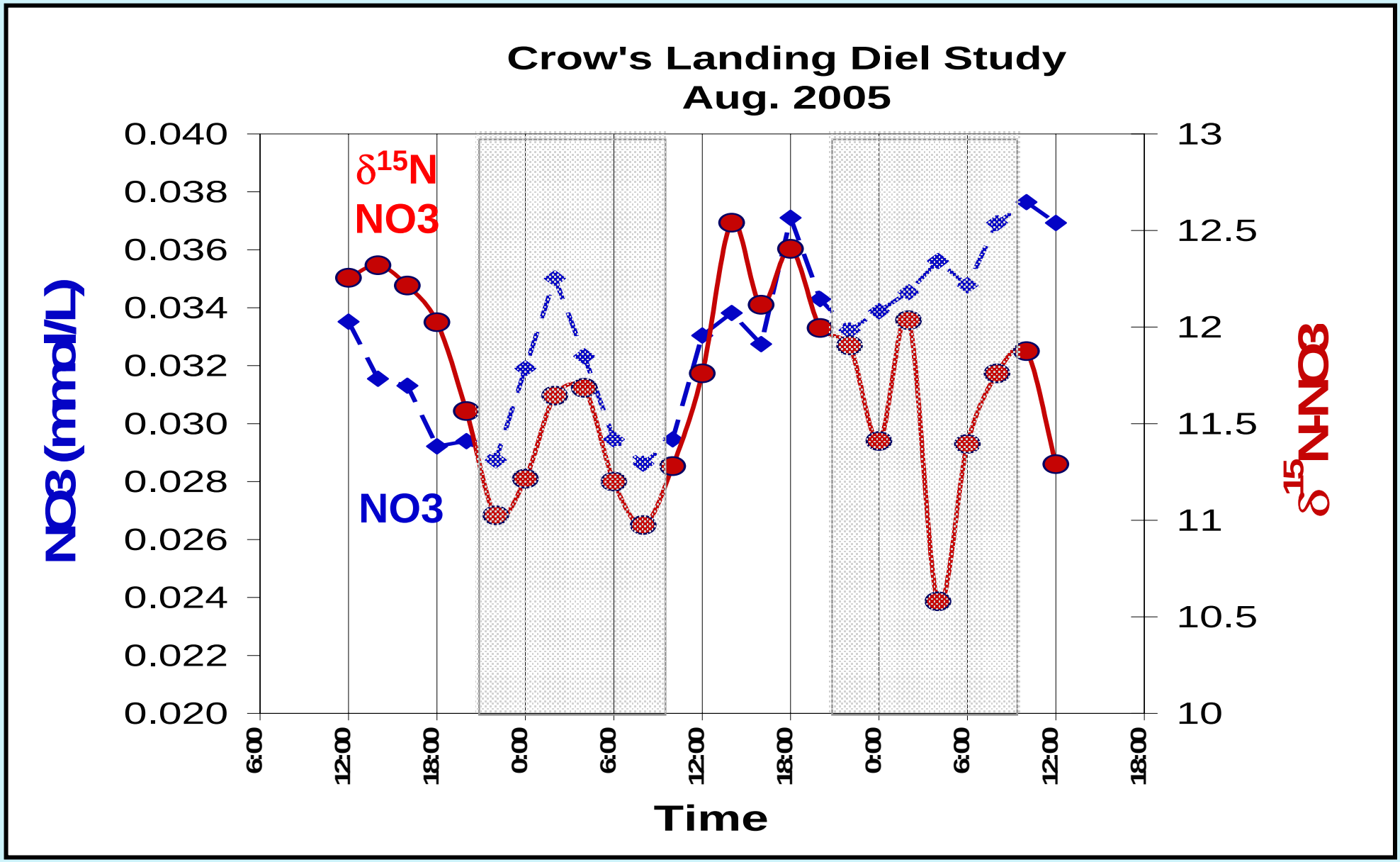
Other isotope analyses can also be useful because these processes often cause diagnostic changes in the $\delta^{18}O/\delta^{15}N$ of nitrate and the $\delta^{15}N/\delta^{13}C$ of POM

Next – a diel experiment to investigate the effect of algal blooms on stream chemistry.

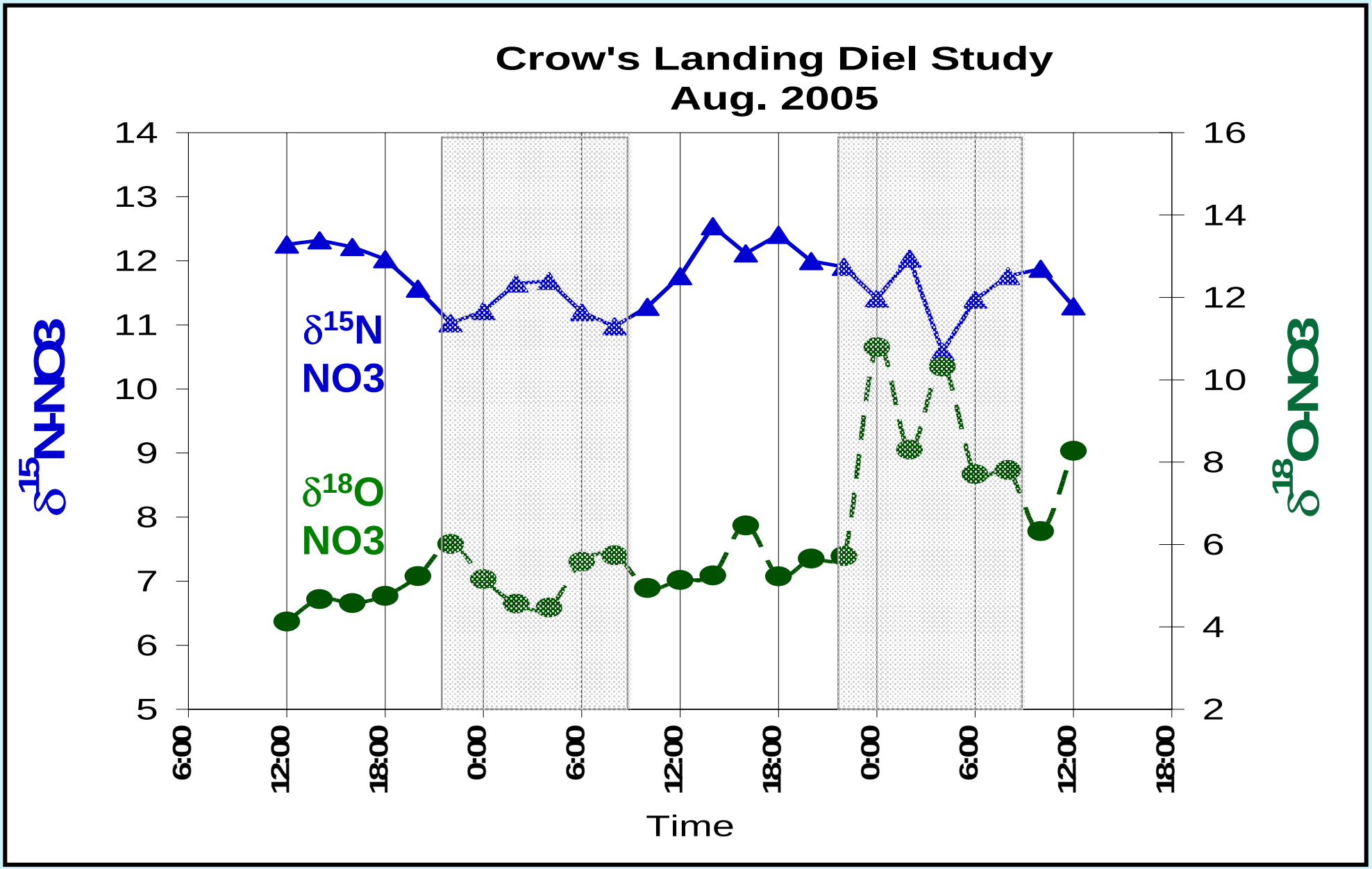
48-Hour Diel Cycle of DO concentrations and DO-$\delta^{18}O$

San Joaquin River

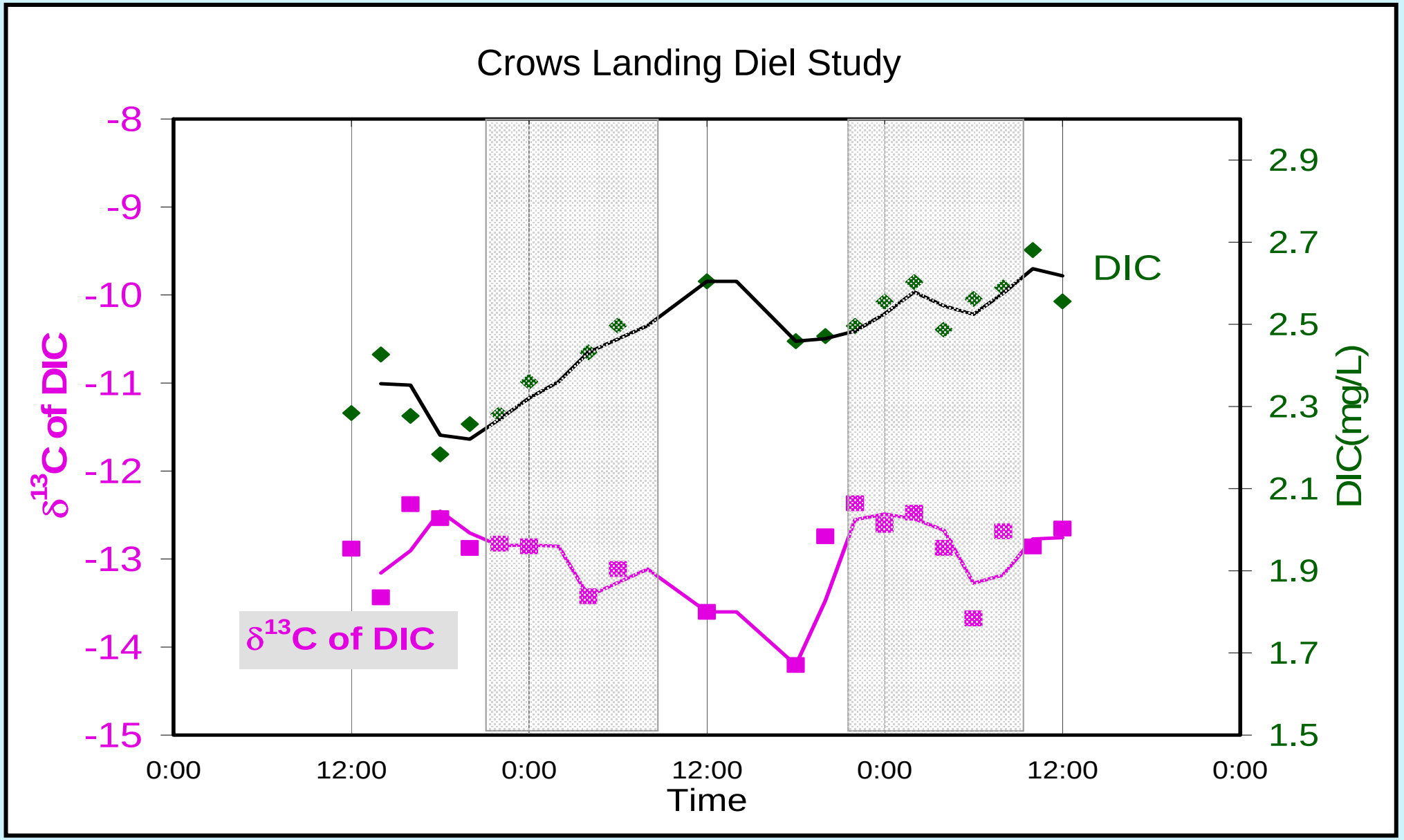




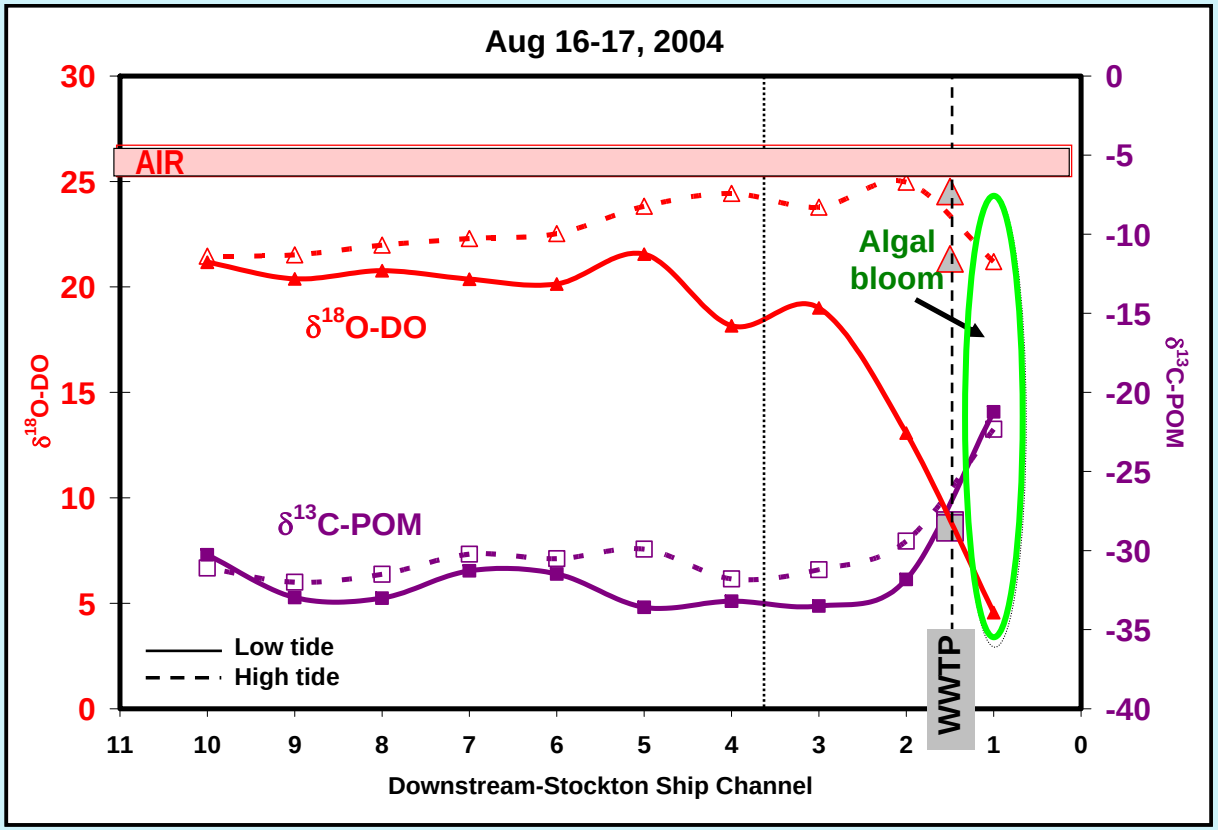
Since the $\delta^{15}N$ tracks the NO3 during the first day, these diel changes reflect either mixing of 2 sources or some diel process. This question can be resolved with other information (next).



The strong inverse relationship between $\delta^{15}N$ of NO3 and $\delta^{18}O$ of NO3 is suggestive of nitrification not uptake as the main process affecting the nitrate.

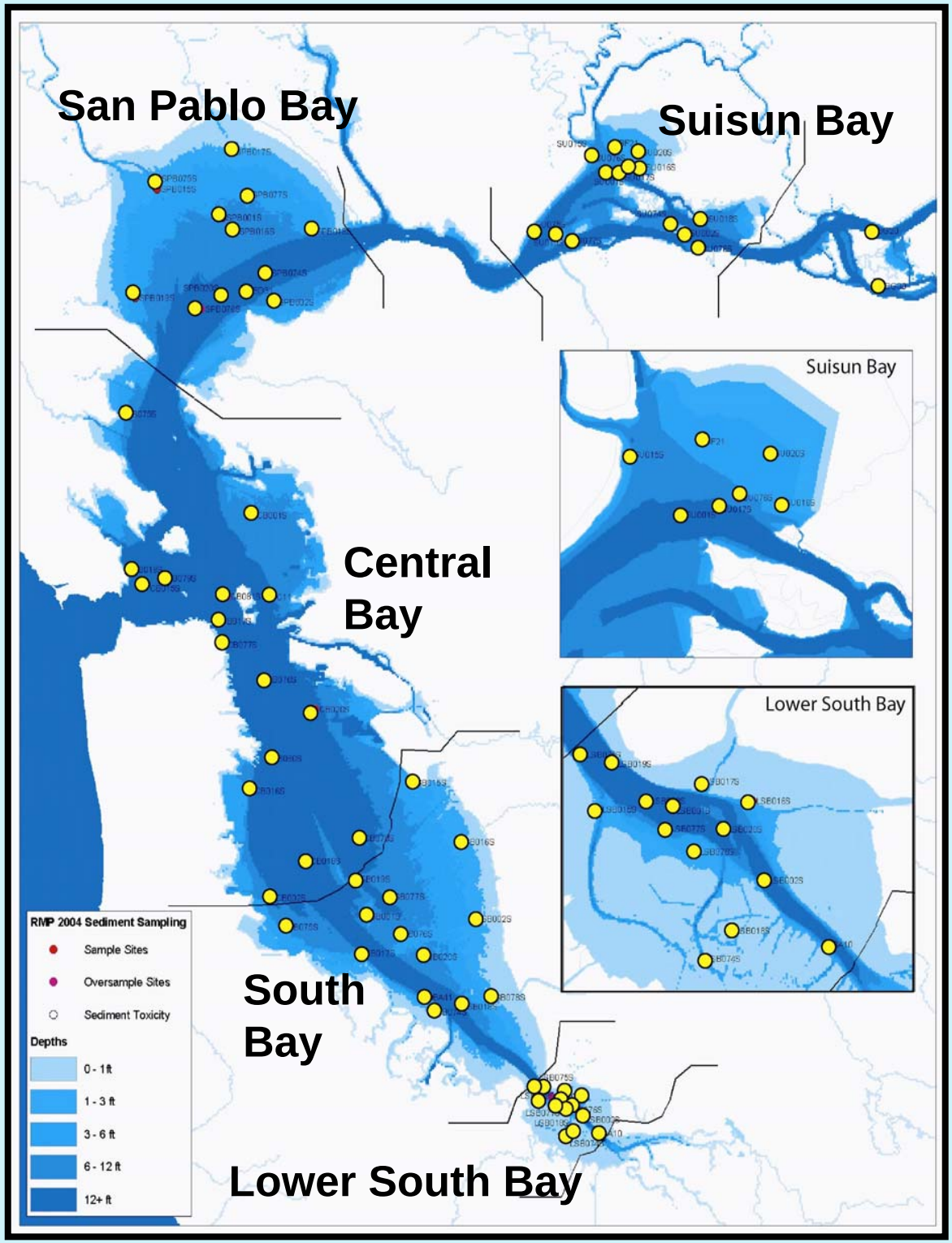


The inverse relation between DIC and δ^{13}C of DIC suggests that respiration at night has a larger effect on the δ^{13}C of DIC than does algal uptake.



Isotopes are likely to be very useful tools for assessing the success of the DWSC aeration experiment because they provide a very sensitive indicator of DO source and of the effect of aeration on the chemistry of the water column.

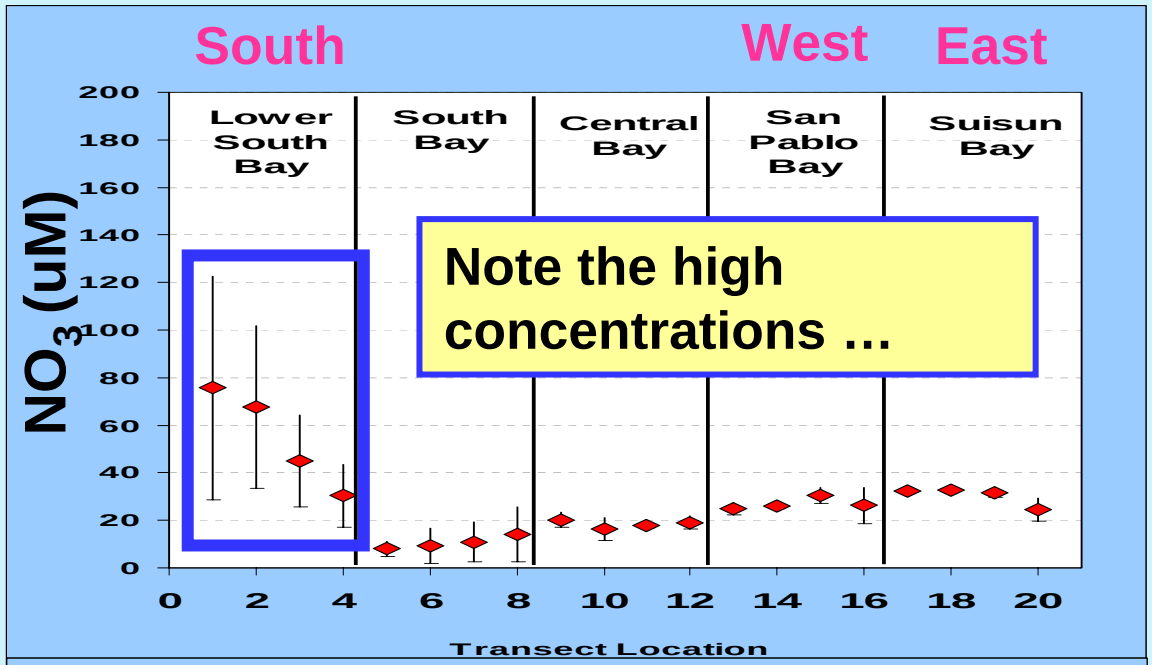
How can isotopes help assess success? Tank gas, since it is derived from air, probably has a DO-$\delta^{18}O$ near +24‰. Background DO-$\delta^{18}O$ values in the DWSC range from +5 to +25‰ (see above), with an analytical sensitivity of ~0.2‰. Hence, measurement of DO-$\delta^{18}O$ during aeration experiments could be used to quantify the amount of DO derived from "background" conditions versus DO derived from aeration. The natural diel changes in DO because of photosynthesis and respiration, combined with tidal mixing, will provide a natural "pulse" of DO compositions that will allow quantification of the temporal and spatial changes in DO derived from aeration vs natural processes.

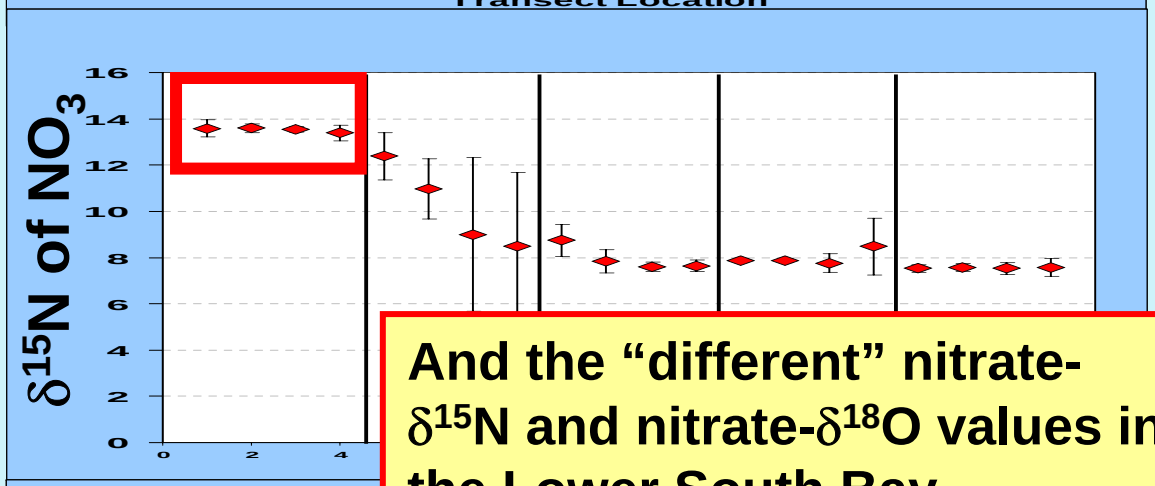


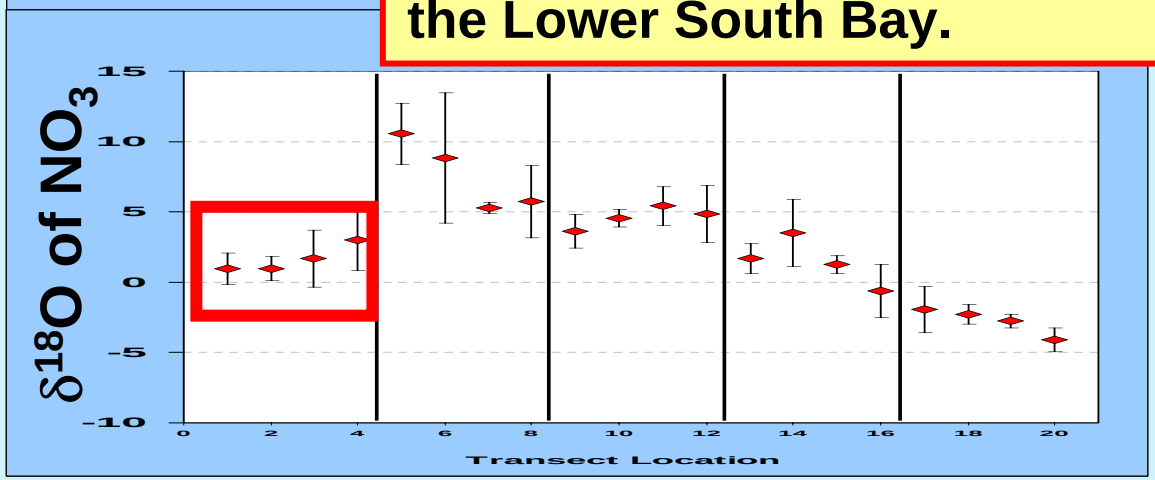
July 2004 transect

Main purpose: to determine the spatial variability in nitrate and organic matter sources to the Bay – and how this might affect our ability to use isotopes for identifying changes in food webs and pollution sources during restoration of wetlands along the shores.

(Wankel et al., 2006)

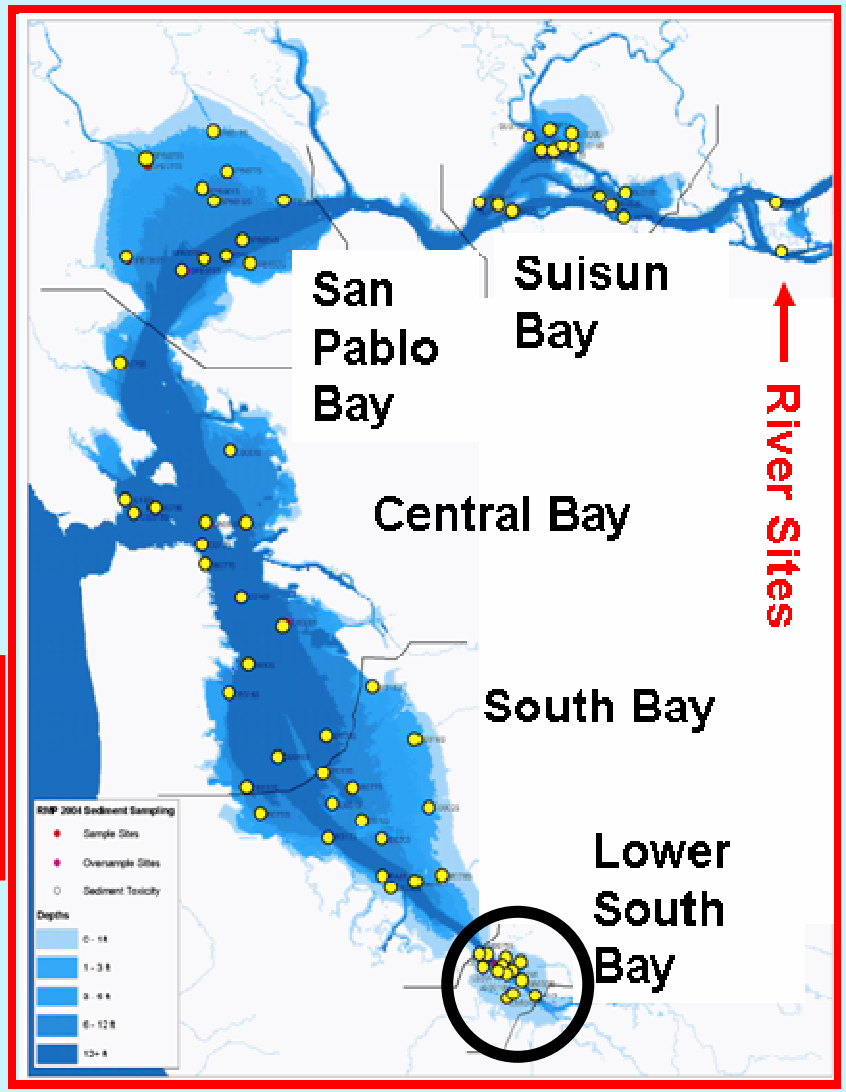






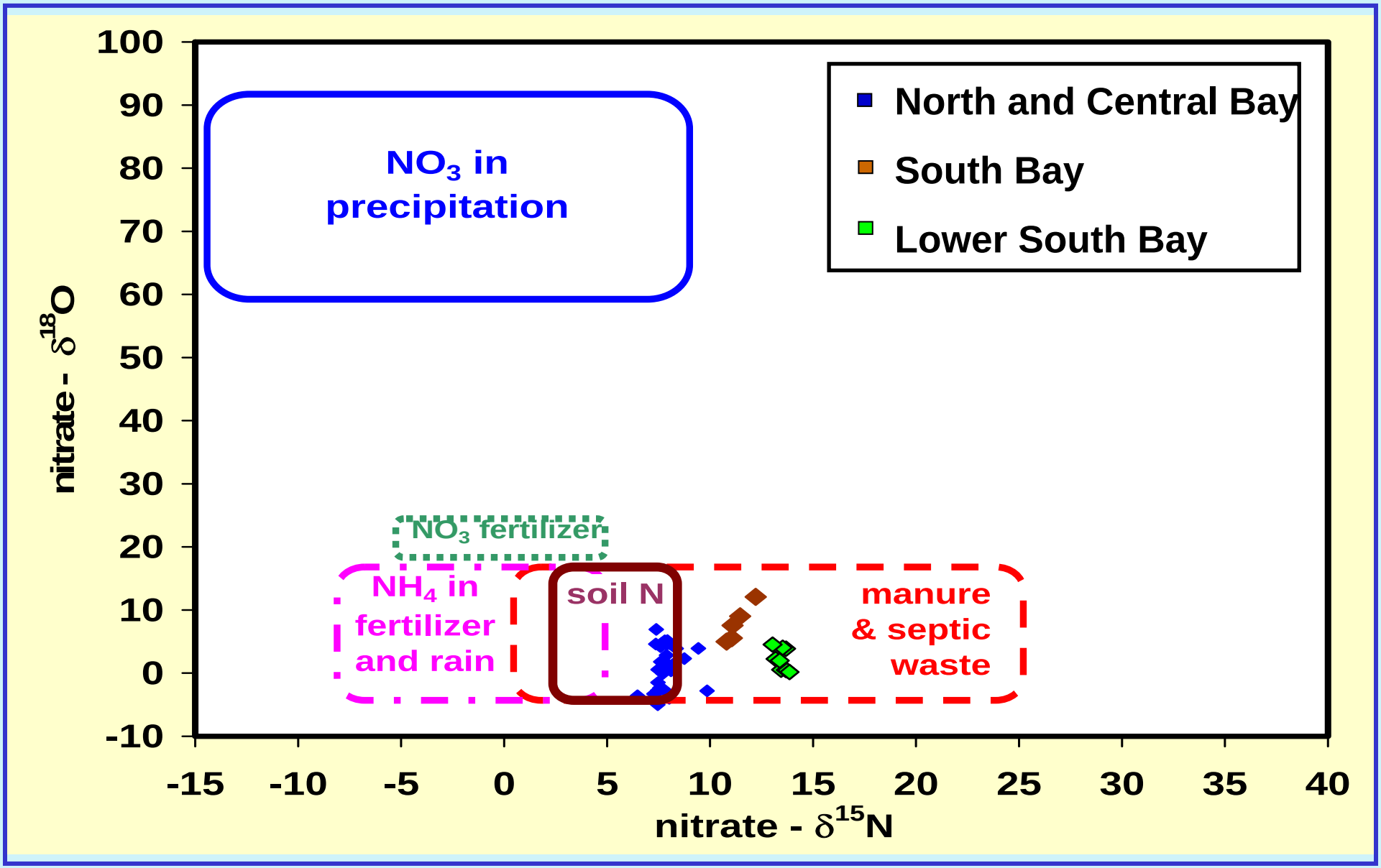
And the "different" nitrate-$\delta^{15}N$ and nitrate-$\delta^{18}O$ values in the Lower South Bay.

How much of the nitrate in San Francisco Bay is derived from septic waste?

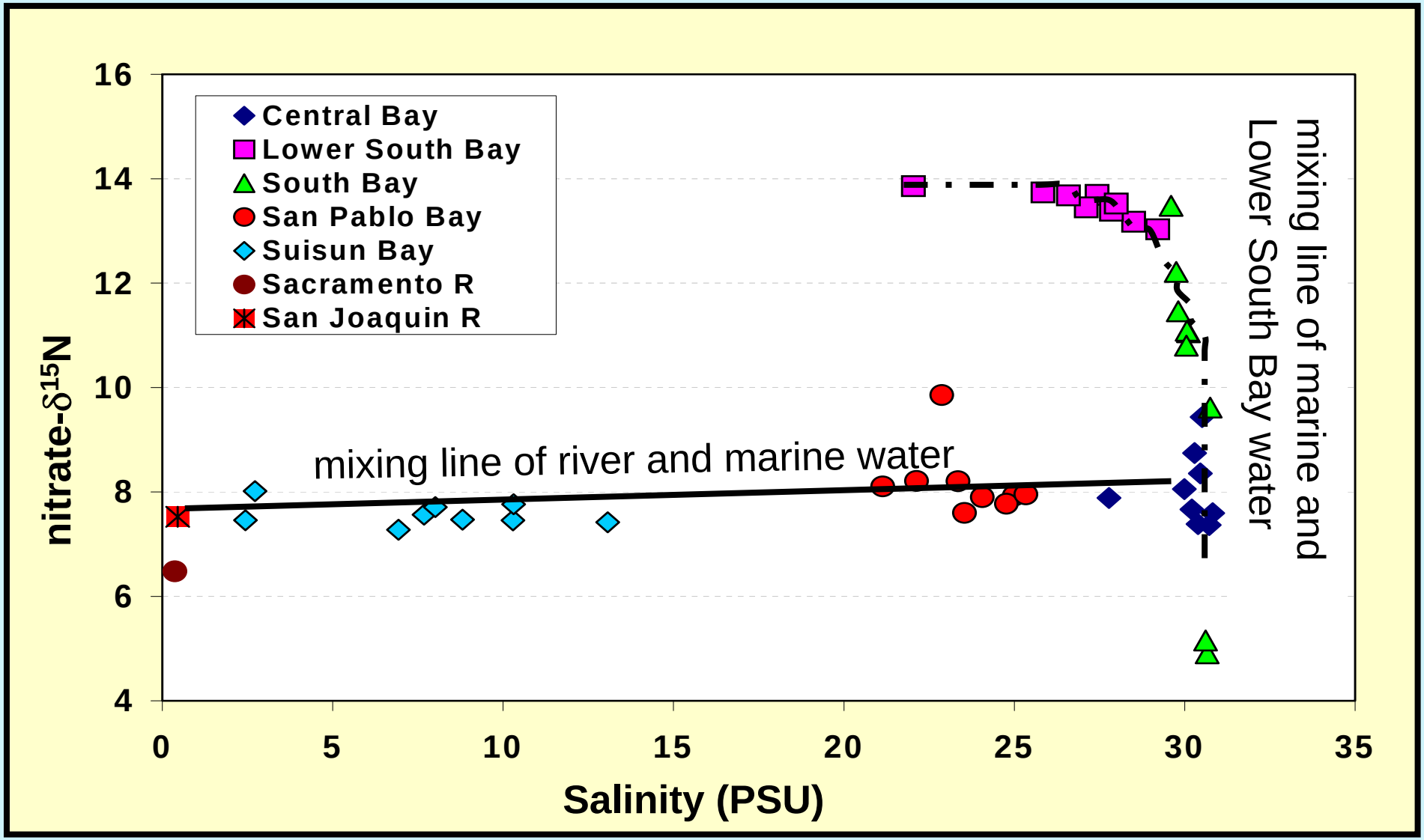


How much of the nitrate in the Bay is derived from septic waste?

The isotope data are consistent with a manure or septic source in the South and Lower South Bay. Several major cities export treated sewage into this poorly mixed section of the Bay.



Without isotopes -- and with only salinity, nitrate, and other chemical data -- we would not such convincing evidence that the additional nitrate source in the Lower South Bay was probably from sewage.

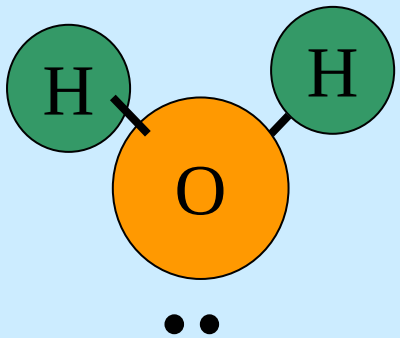


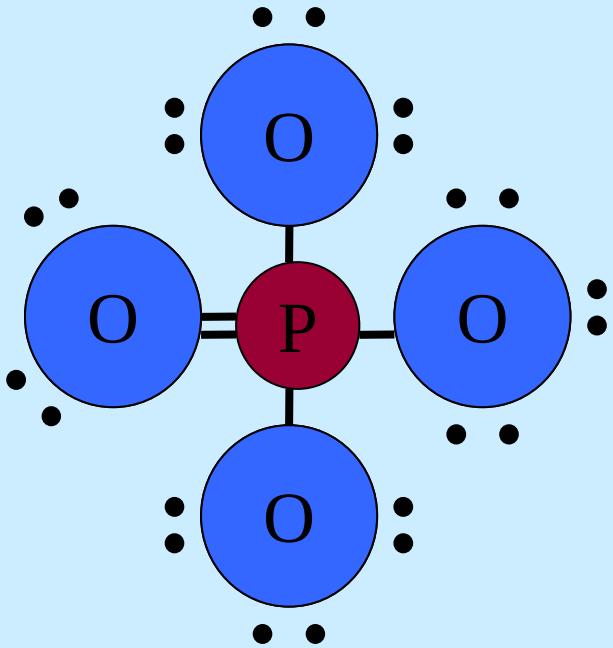
(from Wankel et al., 2006)

New isotope tool: the $\delta^{18}O$ 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.

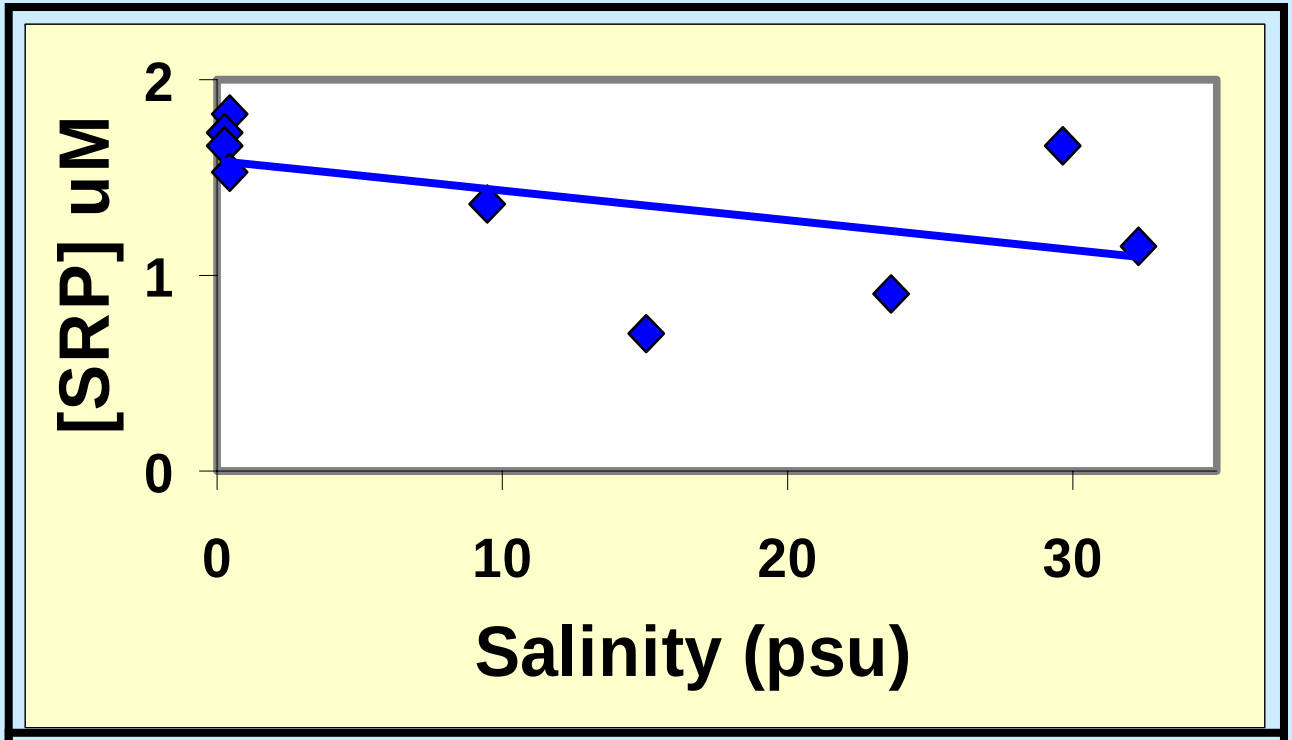
Therefore, PO_4-$\delta^{18}O$ is usually only a usable tracer in systems with excess PO4 where the <u>waters</u> associated with the two sources (e.g., waste vs natural) have $\delta^{18}O$ values that are **different by several ‰.**

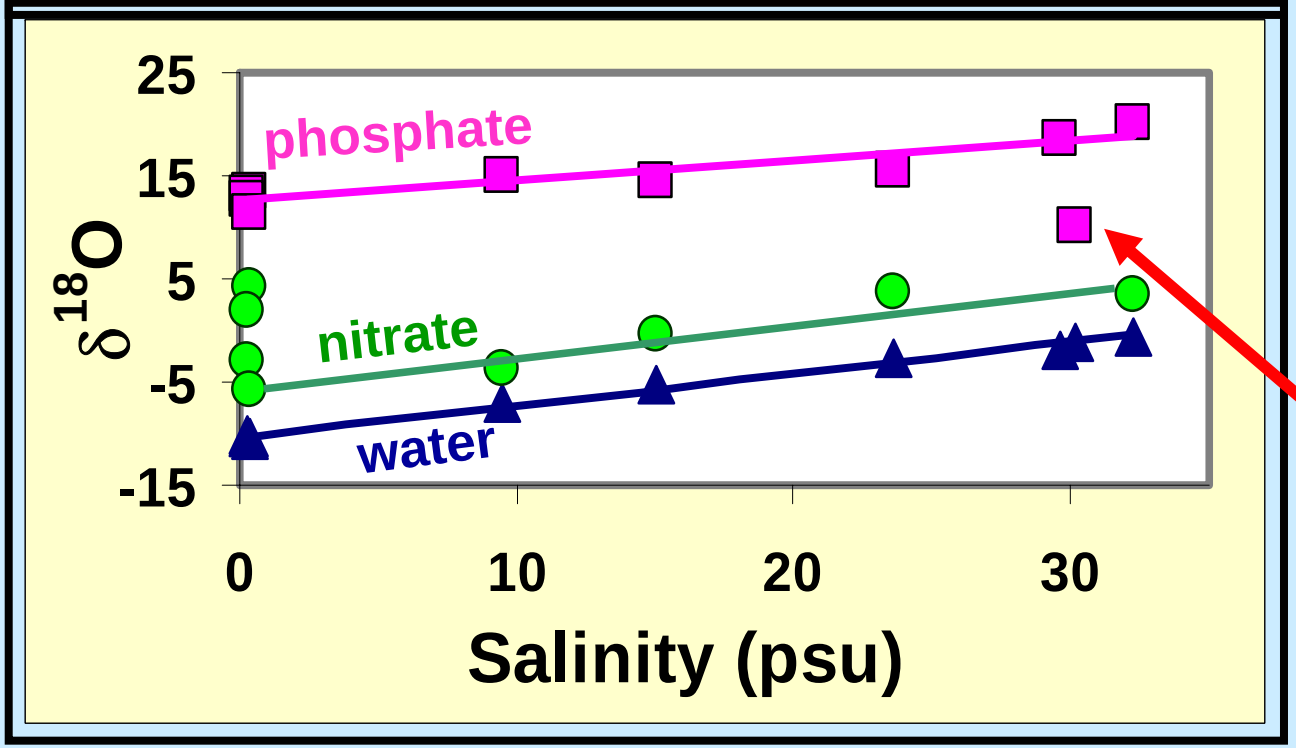




North Bay Transect, October 2002

Example of a high-P source





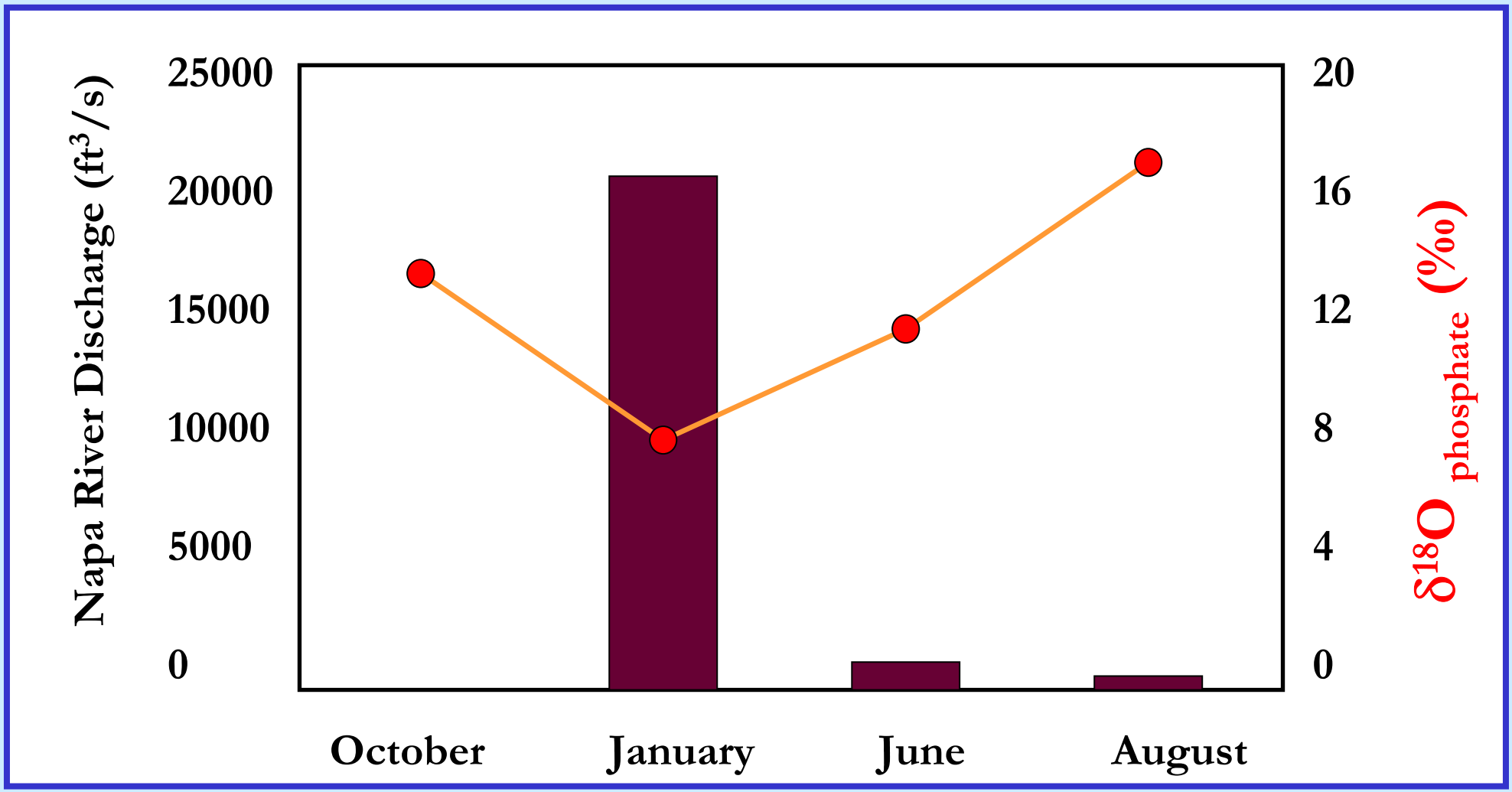
Question: what is the cause of the variability in P concentrations along the salinity gradient ?

Poor mixing of stratified waters?

Local point sources?

Anomalous site near the Napa River

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



(from McLaughlin et al., 2006)

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.

In summary:

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.**