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2) Some of the data presented in this talk are from ongoing projects. Final interpretation of these results is still subject to change upon project completion and publication.

3) Full citations for all published and reported data included in this talk are listed on the final slides.

4) Funding sources and primary collaborators are listed after the title slide.

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Using a Multi-Isotope Approach to Understanding Nutrient Sources and Cycling in Surface- and Groundwater

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Adina Paytan, UC Santa Cruz

Mike Singleton, Lawrence Livermore National Laboratory

William Stringfellow, U. of the Pacific

Funding Sources

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CALFED Proposition 50 Drinking Water Program Grants

California State Water Contractors grant

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Where did those nutrients come from?

How stable isotopes can answer your nutrient questions

I. The Menlo Park Isotope Tracers Project

II. Overview of stable isotopes

III. Established isotope methods: case studies in surface and groundwater

IV. New isotope method: oxygen isotopes of dissolved phosphate

Isotope Tracers Project

USGS Water Resources Discipline

Menlo Park, CA

Carol Kendall, Project Chief

Steve Silva, Assistant Project Chief

Utilize multiple stable isotopes to identify nutrient sources and trace physical and biological processes which alter nutrient distributions throughout aquatic systems and food webs

Past and Present Conditions

- Rivers
- Estuaries
- Sediments
- Lakes
- Groundwater
- Food webs

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Capabilities

Standard Analyses:

Nitrate: $\delta^{15}N$ and $\delta^{18}O$

Water: $\delta^{2}H$ and $\delta^{18}O$

Organic matter & sediments: $\delta^{15}N$, $\delta^{13}C$, C:N ratios

Dissolved Organic & Inorganic Carbon: $\delta^{13}C$

Additional Analyses:

Ammonium: $\delta^{15}N$

Phosphate: $\delta^{18}O$

Sulfate: $\delta^{34}S$ and $\delta^{18}O$

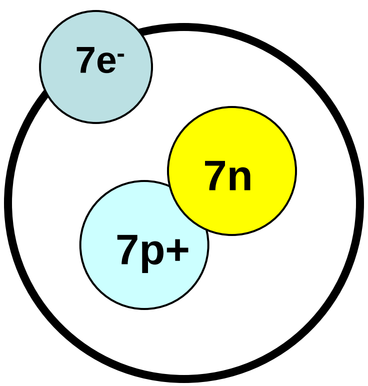
Organic matter: $\delta^{34}S$

Dissolved Oxygen: $\delta^{18}O$

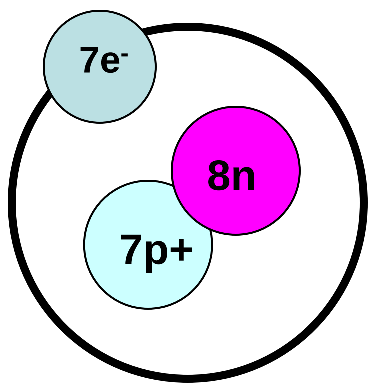
Isotope Notation

Isotopes are forms of the same element that have different numbers of neutrons

N (nitrogen): 7 protons, 7 electrons



^{14}N: 7 neutrons



^{15}N: 8 neutrons

Biological and non-biological processes can change the distribution of these isotopes

Isotope notation- Reported as a ratio

+100 ‰

more of the heavy isotope

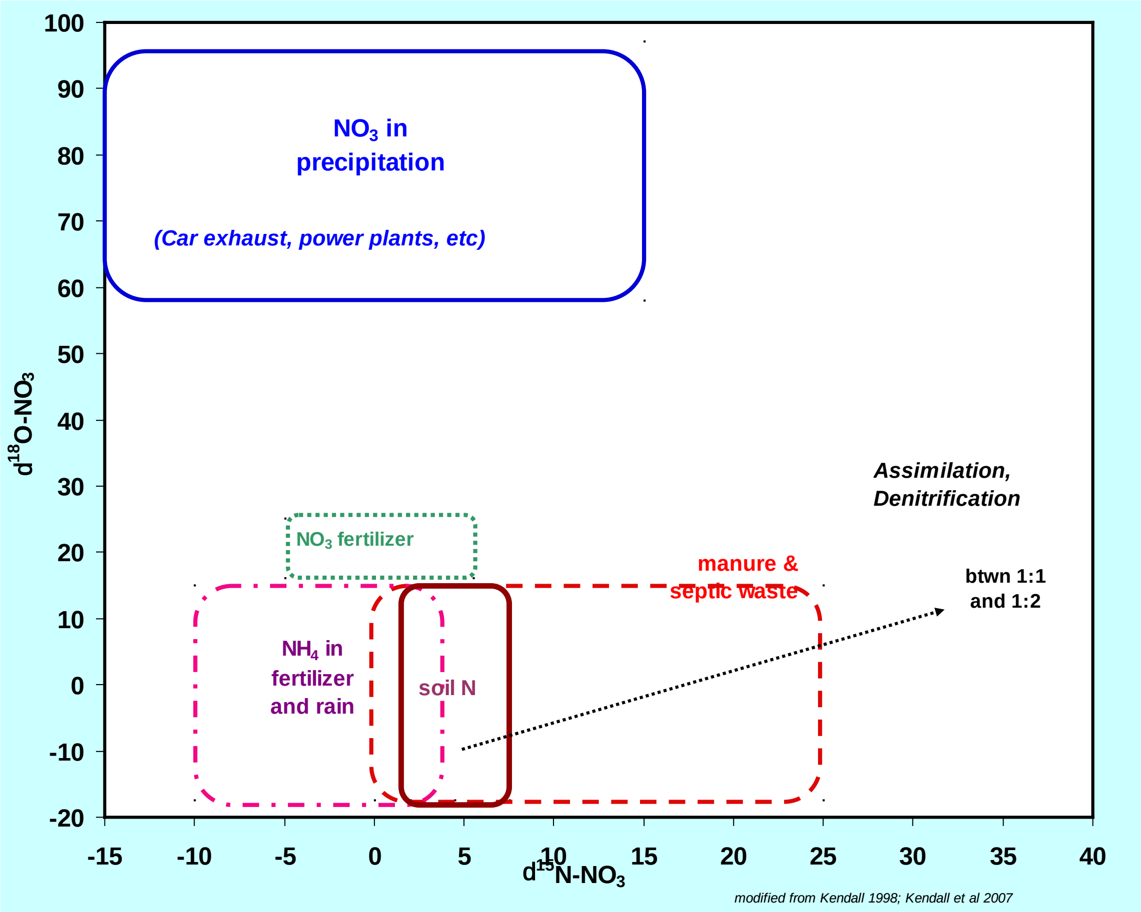
0 ‰

Chosen standard (air, seawater, etc)

more of the light isotope

-100 ‰

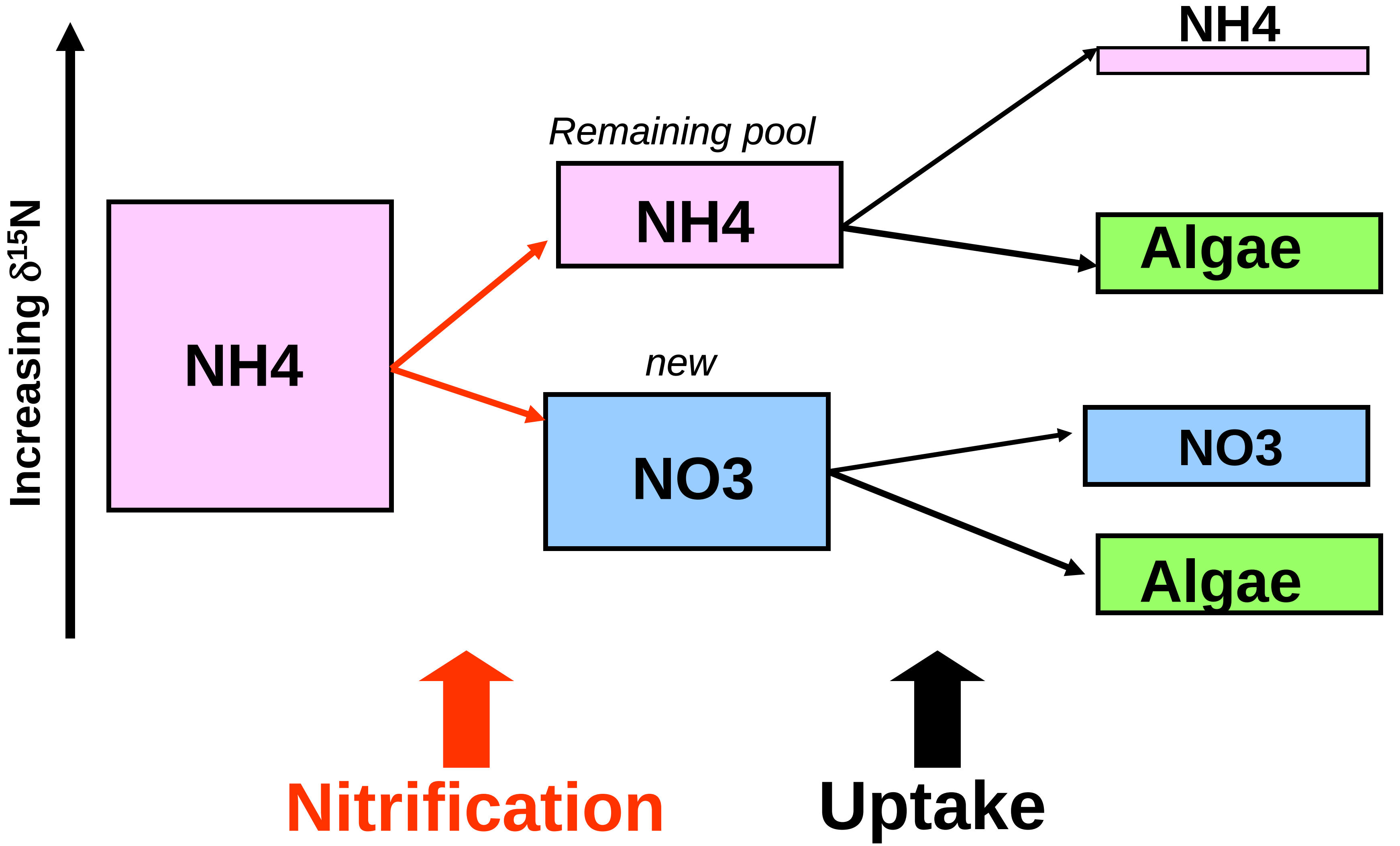
Sources and Processes



Biological & physical processes can change the isotopic composition of the remaining nitrate

Consumption processes such as denitrification and assimilation may cause a range of fractionations, but will always result in a linear increase in both $\delta^{15}N$ and $\delta^{18}O$ in the remaining nitrate pool in a closed system.

Biological processes can alter isotope composition



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Slide courtesy of Carol Kendall

Water Sources for San Francisco Bay & Delta

Sacramento River

Supplies most of the fresh water to the north Bay

Low chl-a concentrations

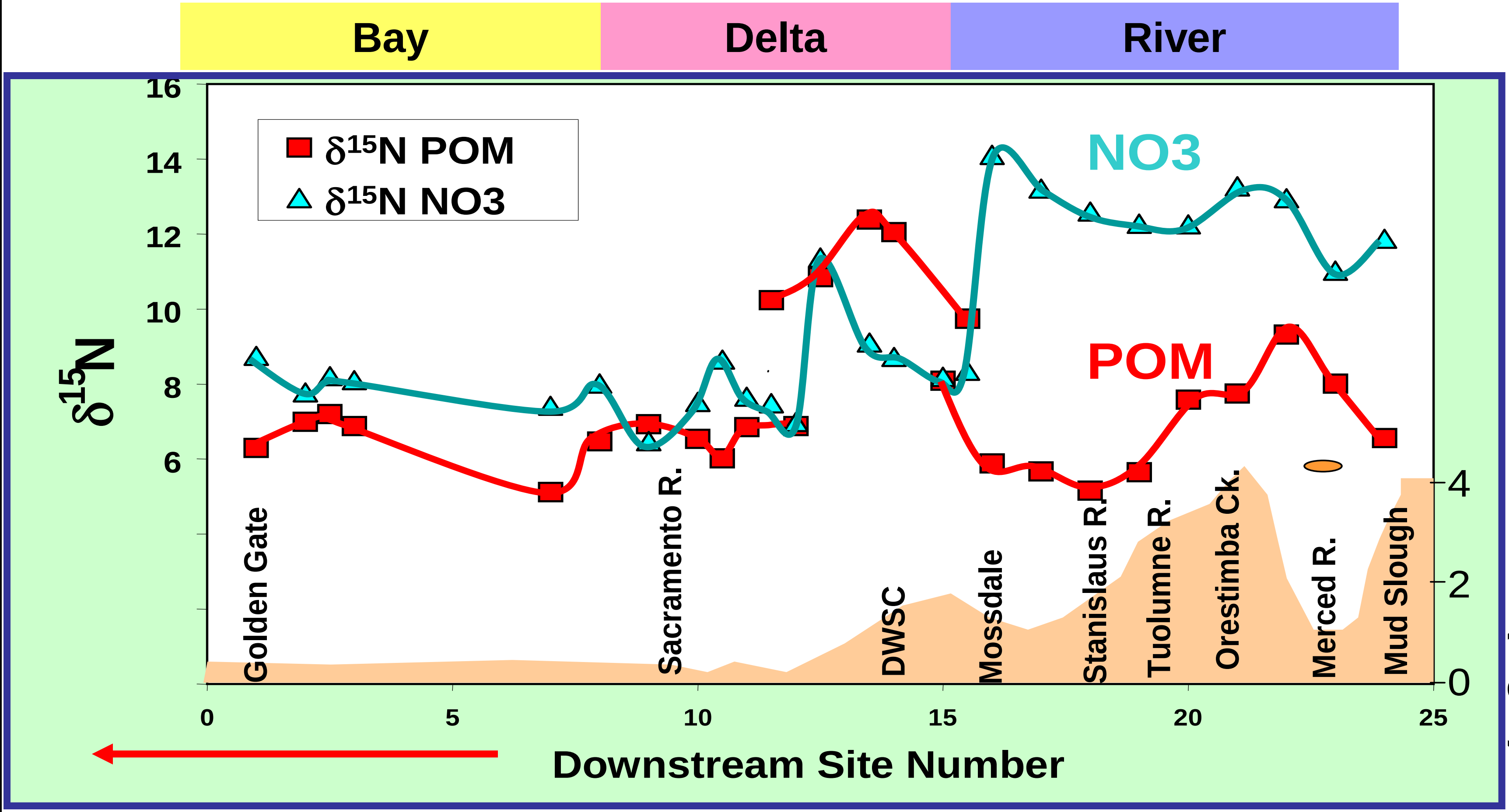
San Joaquin River

Water is diverted south out of the Delta

High nutrients, very high algae growth

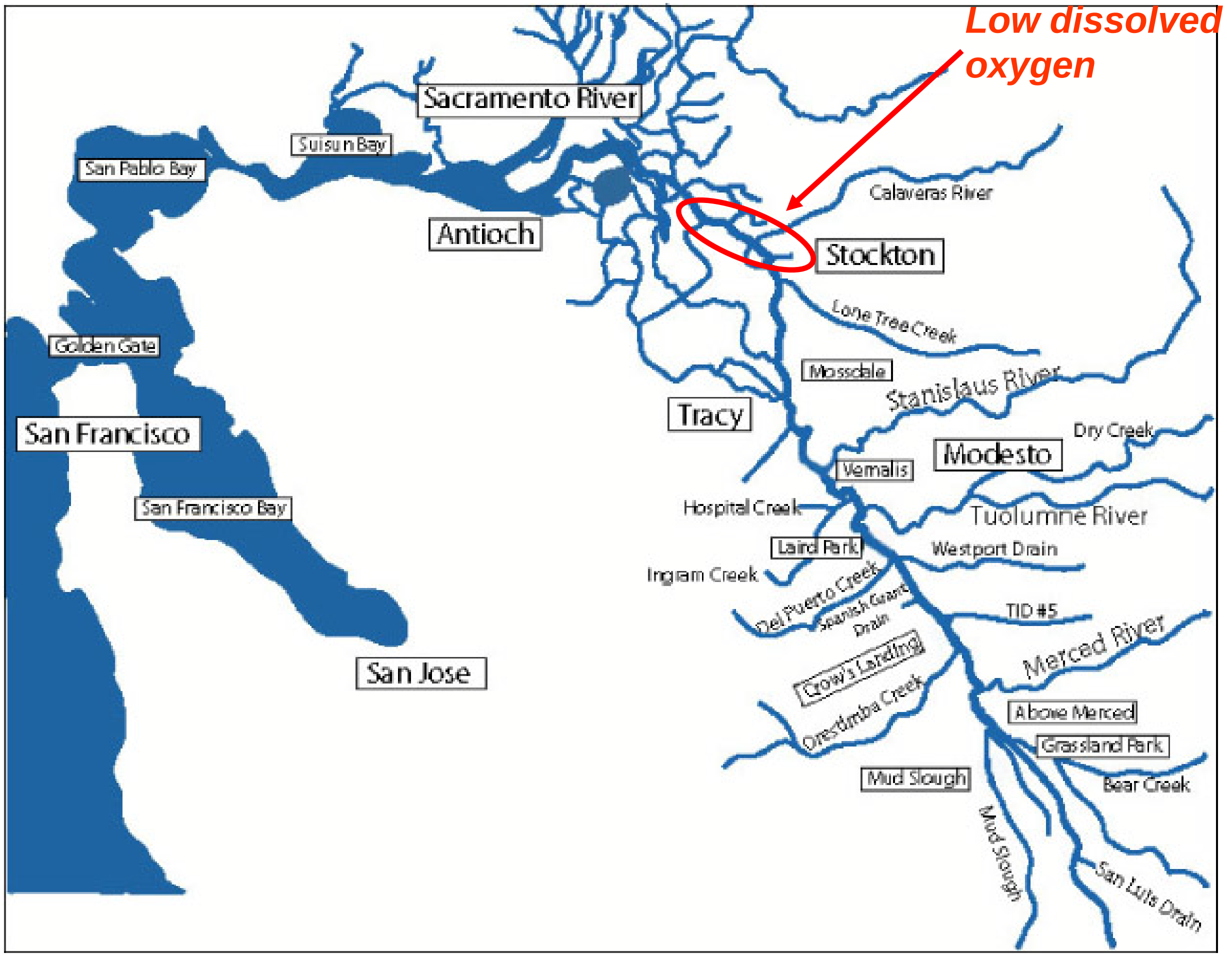
Algae (as particulate organic matter) & nitrate

Nitrate is the primary source of N for algae in the San Joaquin



Slide courtesy of Carol Kendall

San Joaquin River & low dissolved oxygen



Organic matter (algae) travels down the SJR

Enters the Turning Basin of the Deep Water Ship Channel

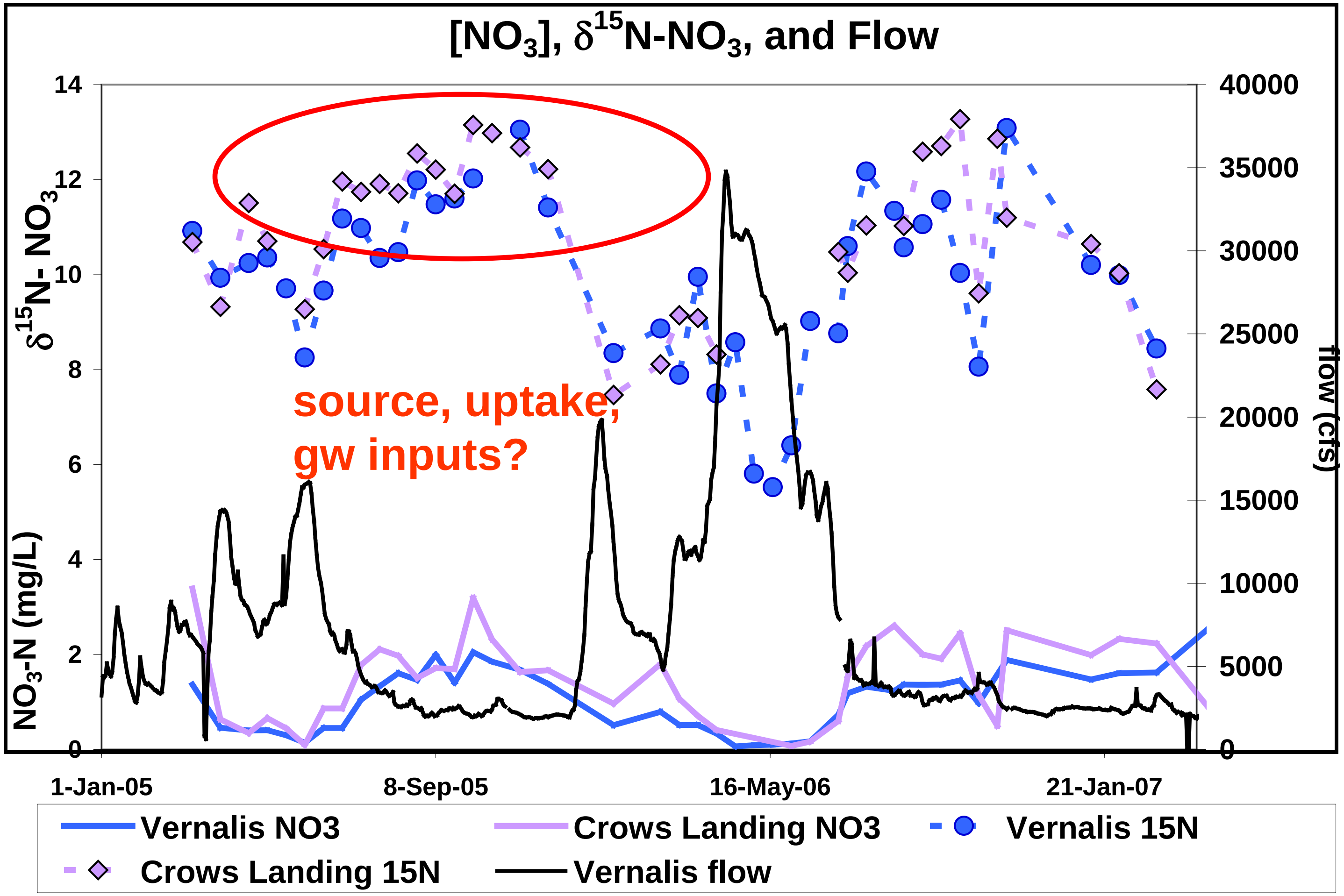
Decays and consumes oxygen- potentially interferes with fish migration

San Joaquin Isotope Study Questions

Three year study to look at nutrient & organic matter cycling, and provide a baseline for establishing a DO TMDL

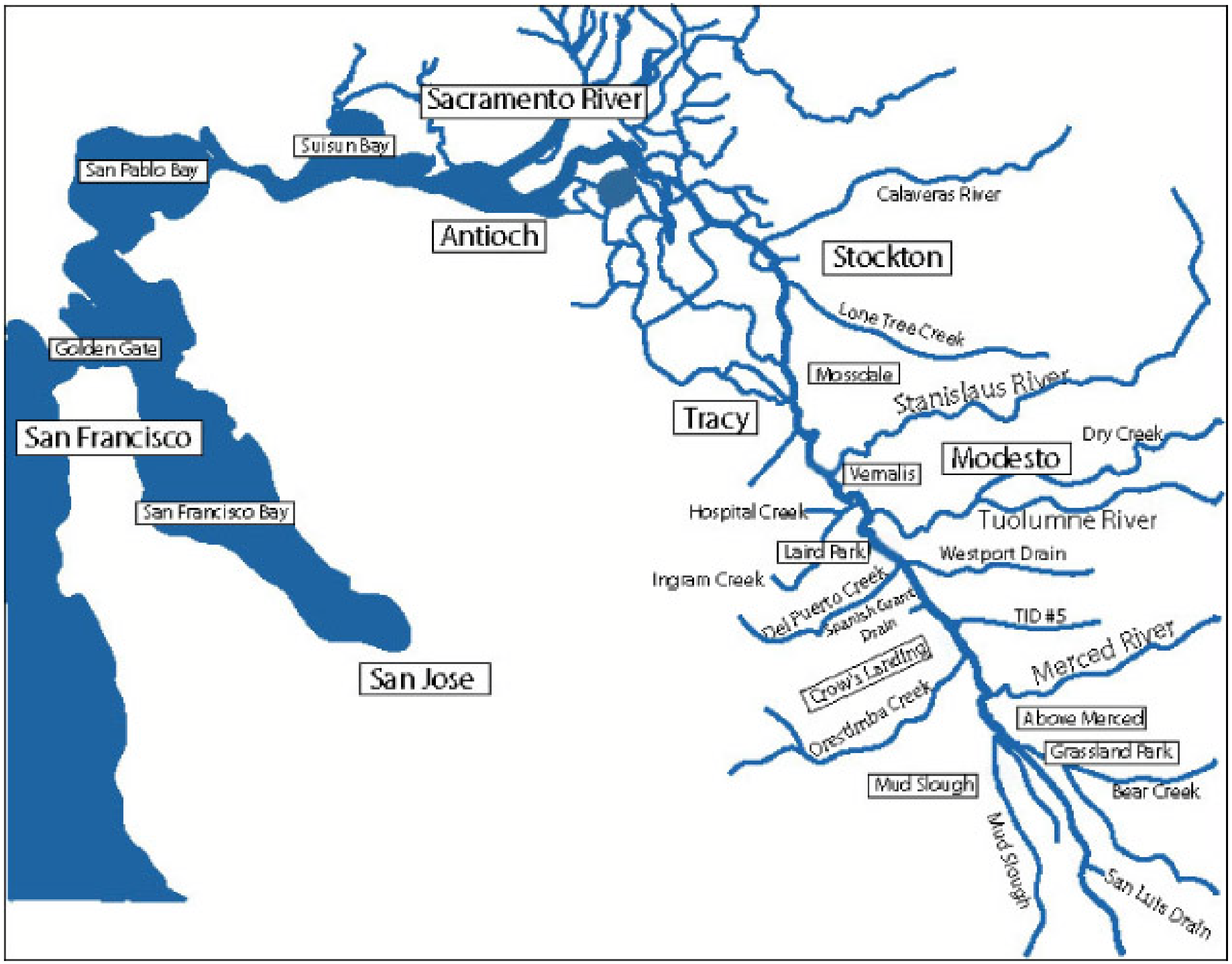
- Do stable isotopes provide distinct signatures for tributaries with different dominant land uses?
- What is controlling the temporal changes in $\delta^{15}N-NO_3$ values?

Nitrate, Nitrate Isotopes, and Flow



Large variations in nitrate concentrations and isotopic composition- what is driving these changes?

San Joaquin Tributaries



Sierran drainage

Agricultural drainage

Urban wastewater

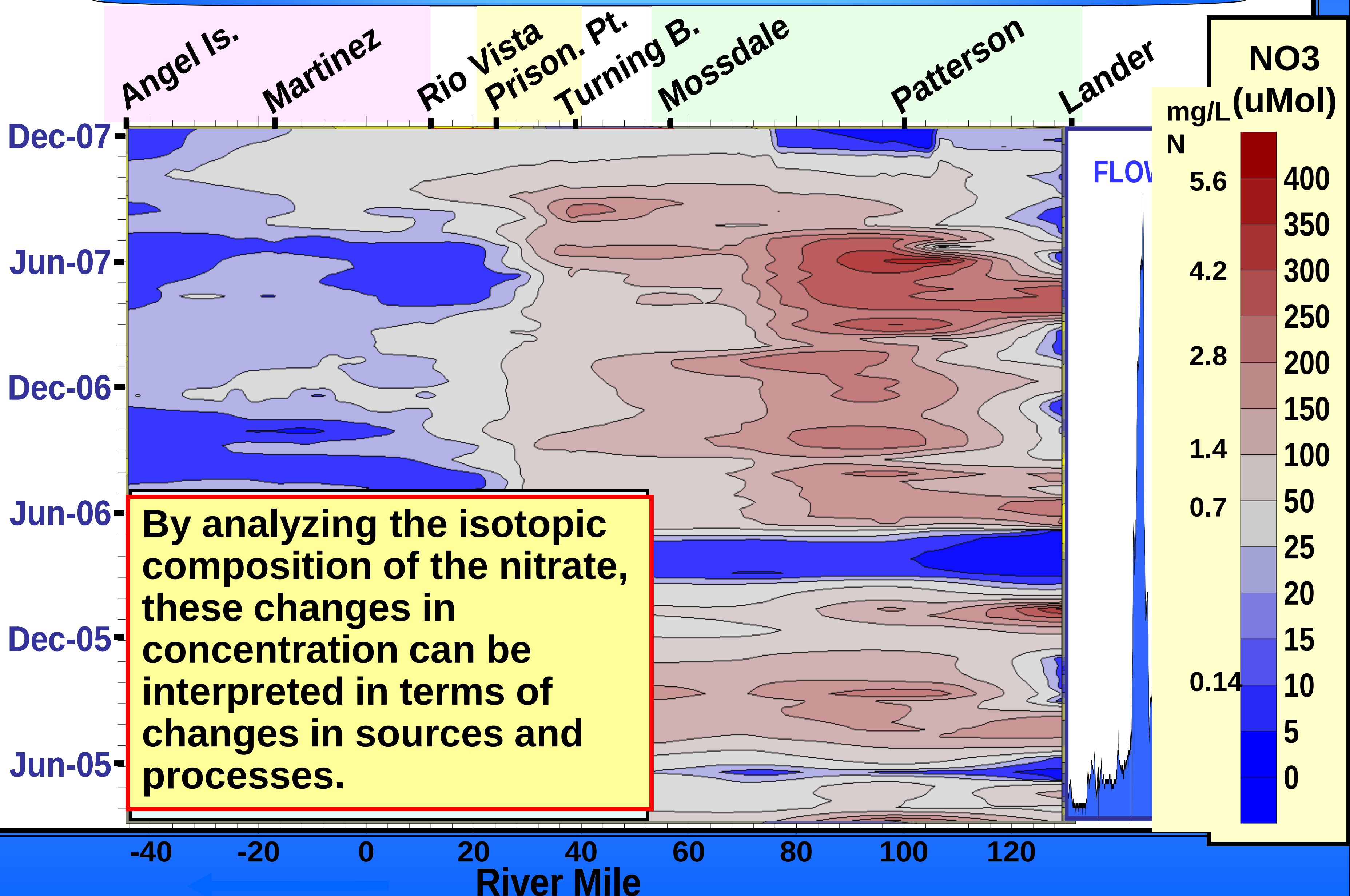
Wetland drainage

MIXED USE

Eastside vs Westside

Many small diversions and drains along the length of the river

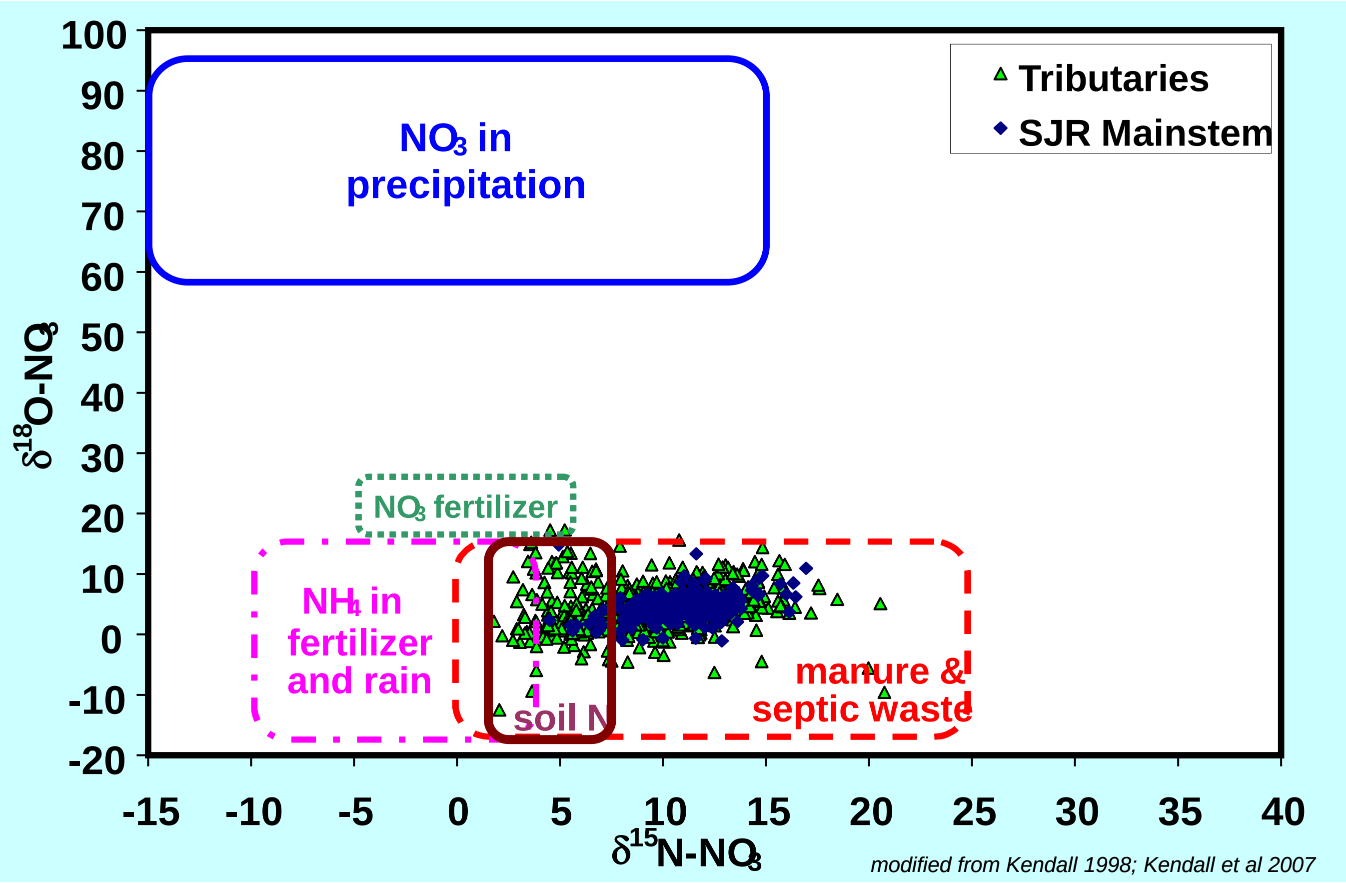
Looking at nitrate by distance and time



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

Nitrate Isotope Distributions

Participated in 3 year study to support the development of a DO TMDL



Wider range of nitrate isotopes in the tributaries in comparison to the mainstem

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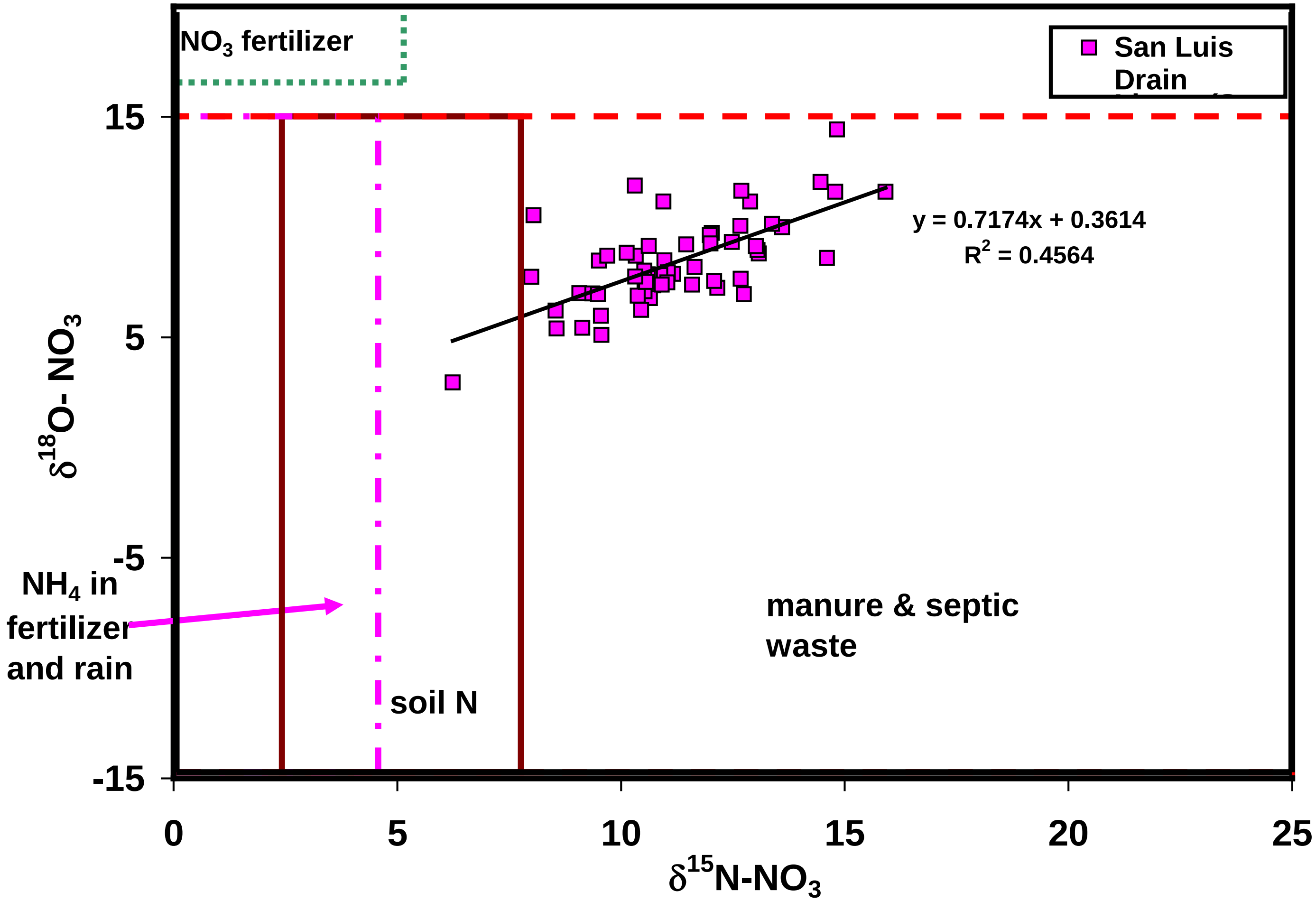
San Luis Drain- Most Simple System



- Agricultural drainage
- Concrete lined channel
- Well controlled system in comparison to other tributaries

Clear relationship between $\delta^{15}N$ and $\delta^{18}O$

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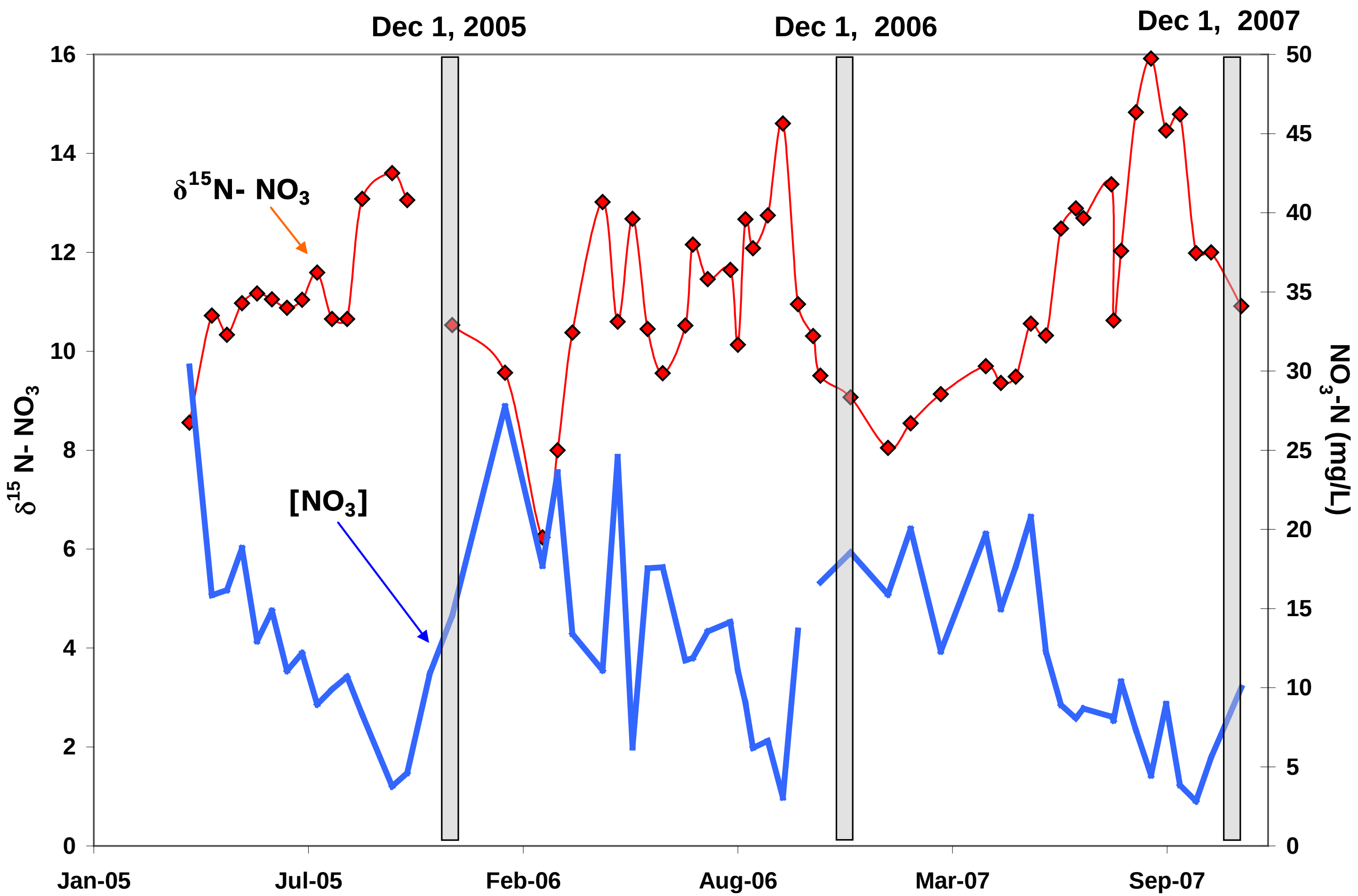
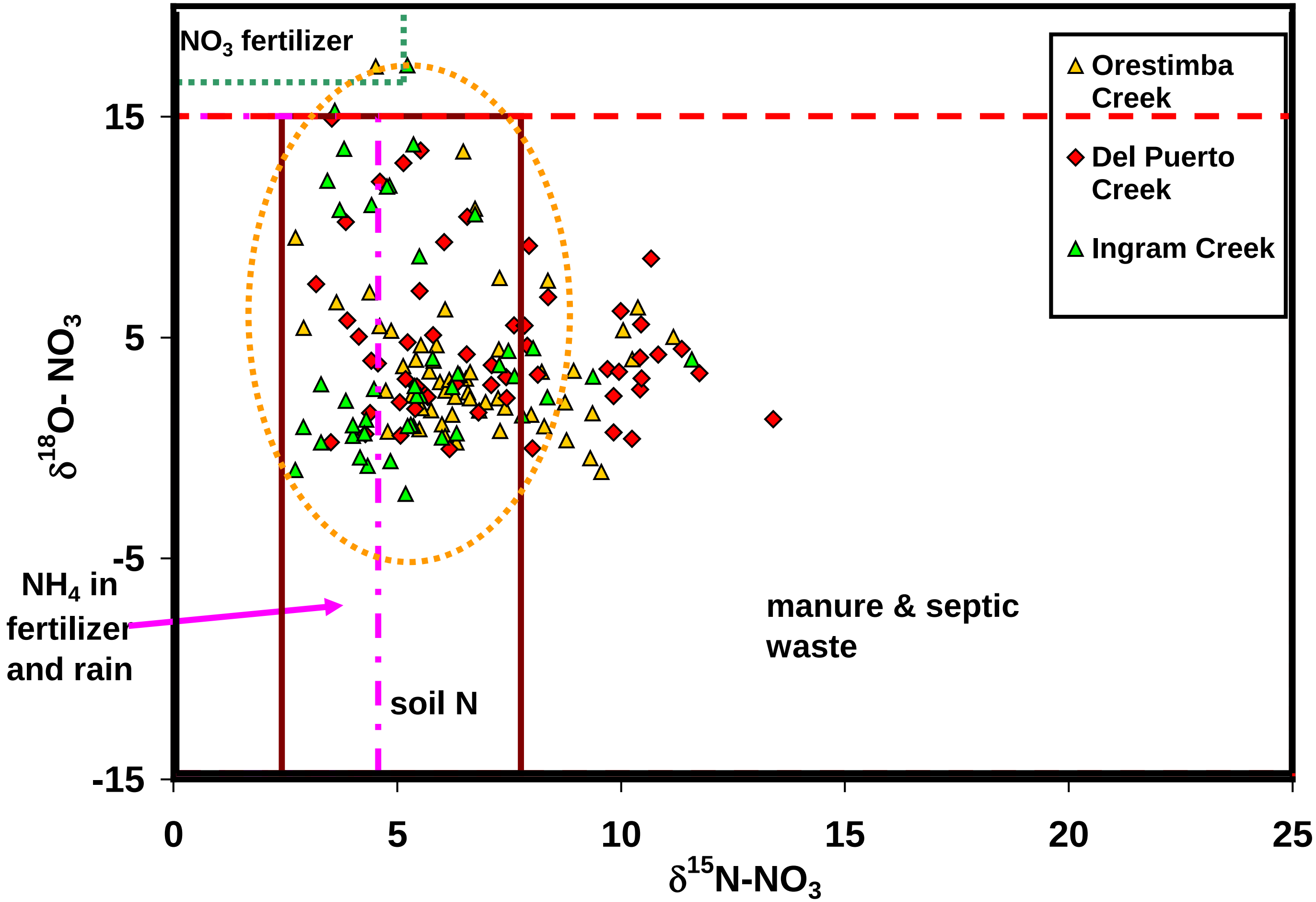
San Luis Drain- Most Simple System



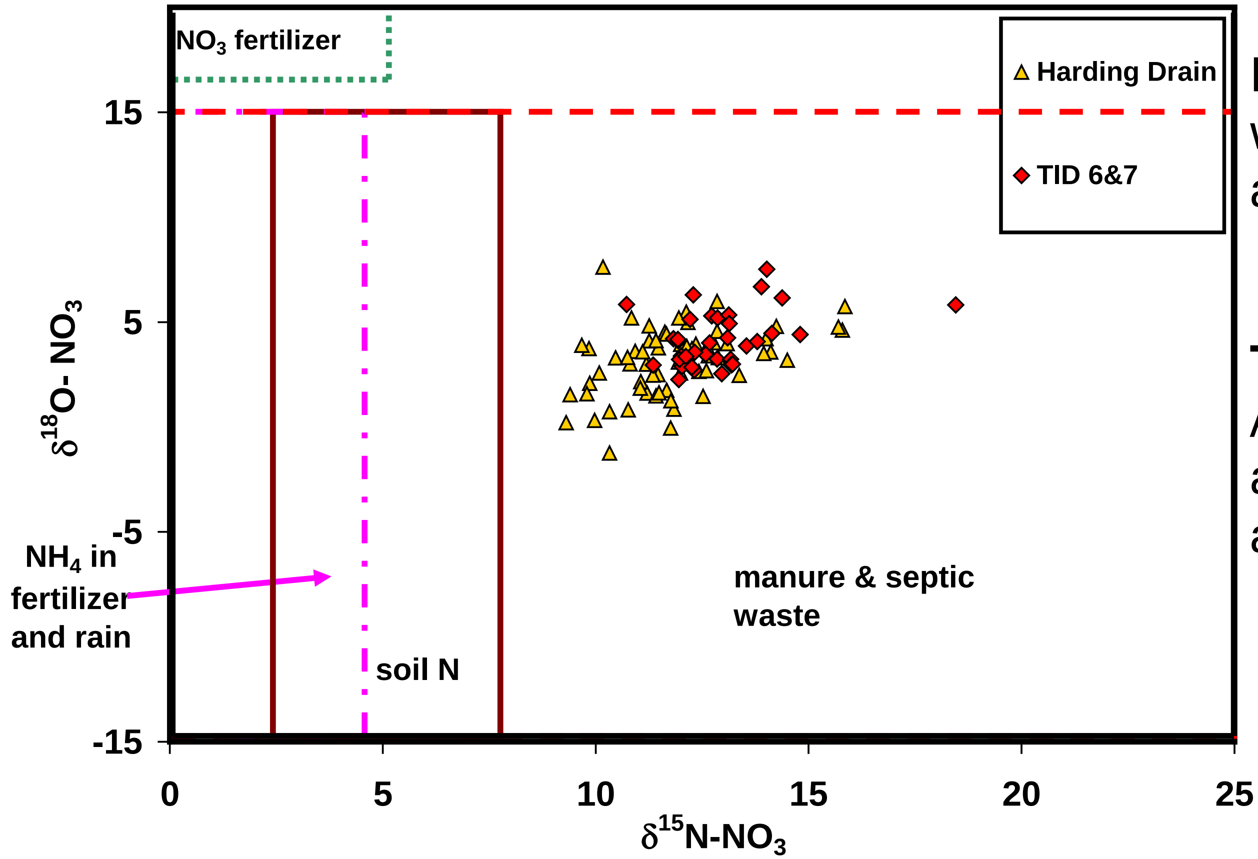
Nitrate assimilation by algae causes temporal shifts in $\delta^{15}N$, $\delta^{18}O$, and $[NO_3]$. Low $\delta^{15}N$ values occur in the winter/early spring, shift to high values in the fall.

1) Westside Agricultural tributaries



Fertilizer nitrate, possible soil nitrate, very little waste and/or assimilation or denitrification signature

2) Small Eastside Tributaries

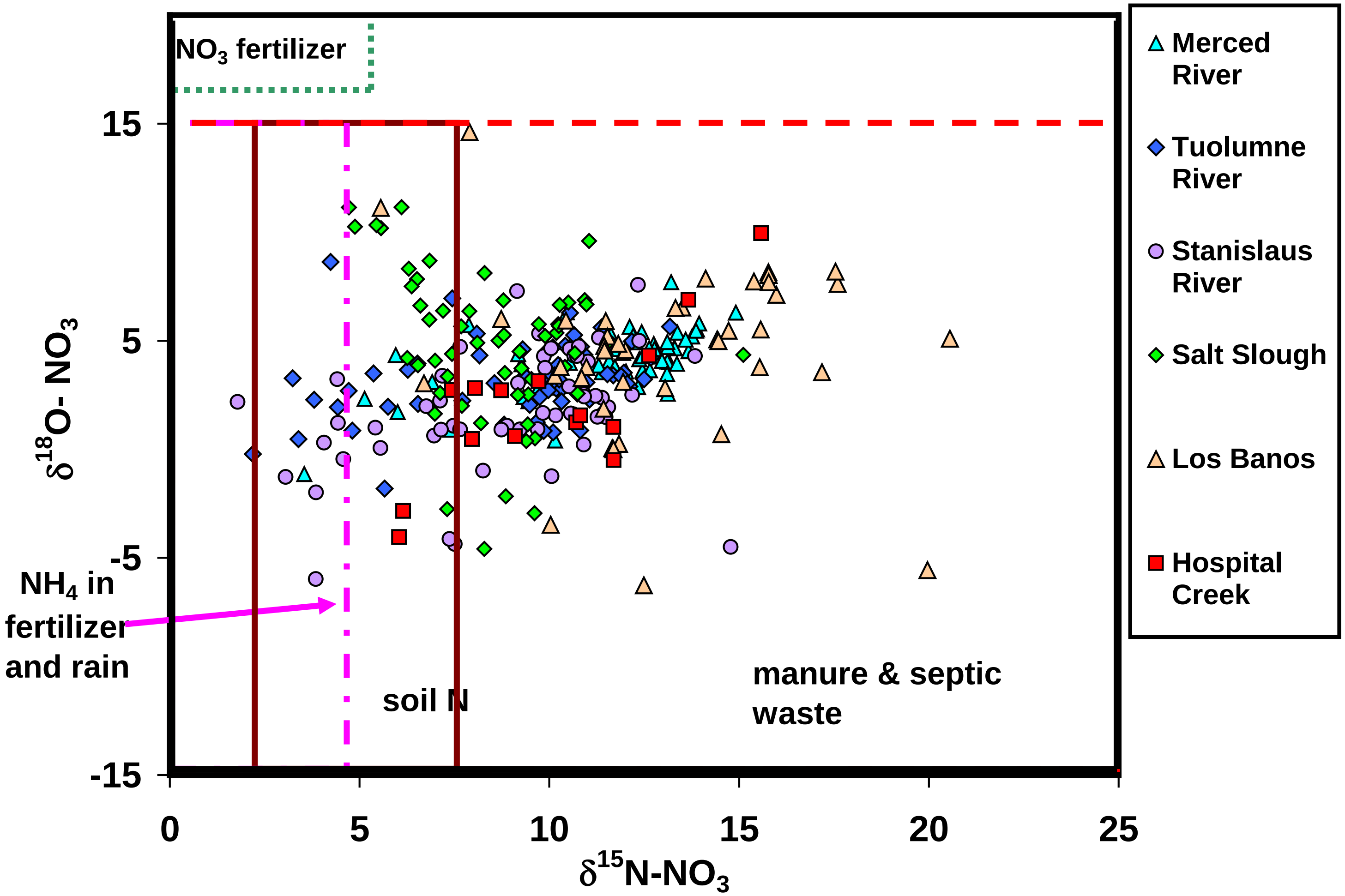


Harding: Known wastewater input & agricultural runoff

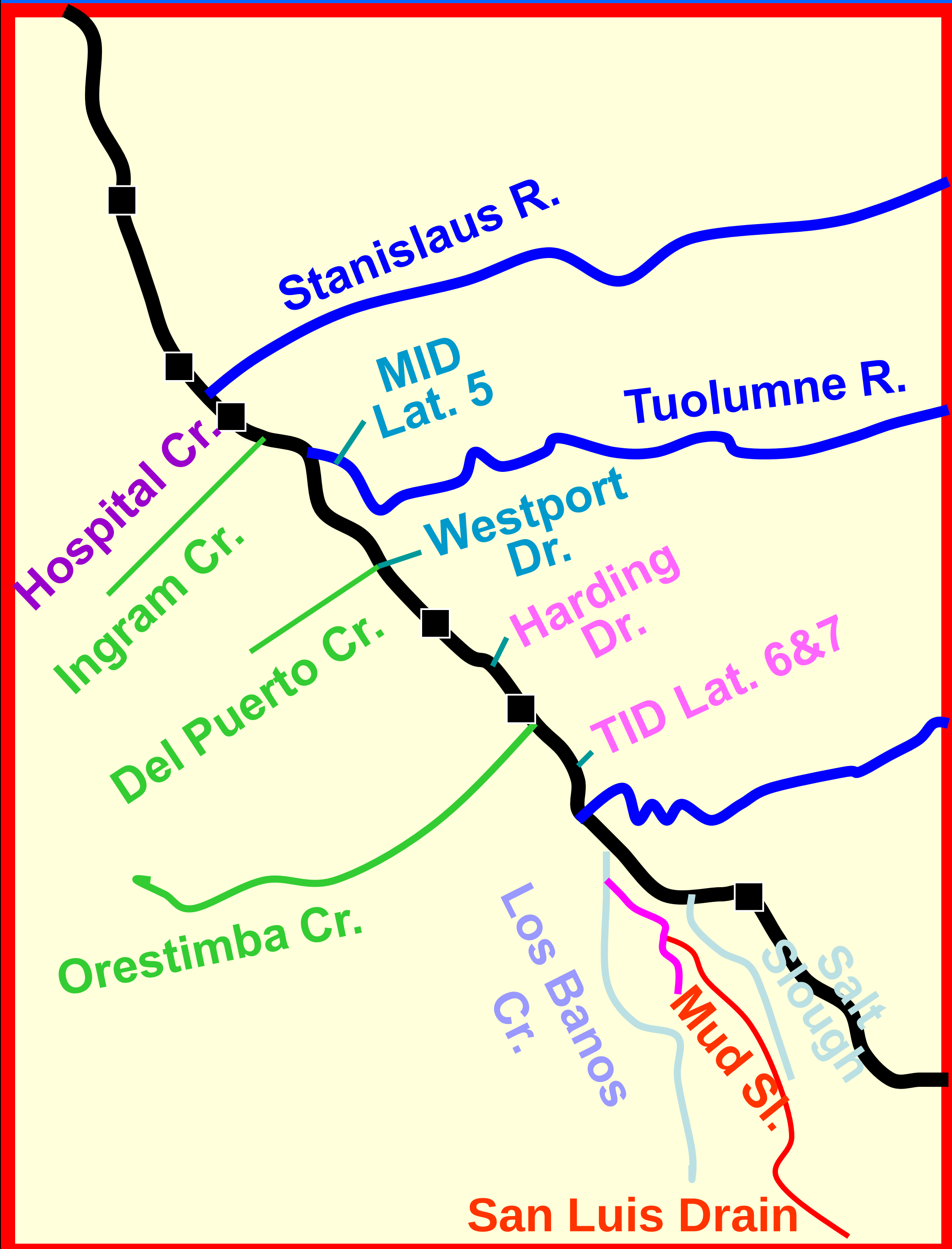
TID 6&7: Agricultural, but always high $\delta^{15}N$-animal source?

Consistently high $\delta^{15}N\text{-}NO_3$ values throughout the year, different from the other eastside tributaries.

3) Eastside Tributaries



Mix of land uses- all show a range of isotope values, with weak positive correlations between $\delta^{18}O$ and $\delta^{15}N$ (except Salt Slough), strong seasonal changes



Summary

1) Westside agricultural drains primarily contain fertilizer- derived nitrate, and possibly soil nitrate

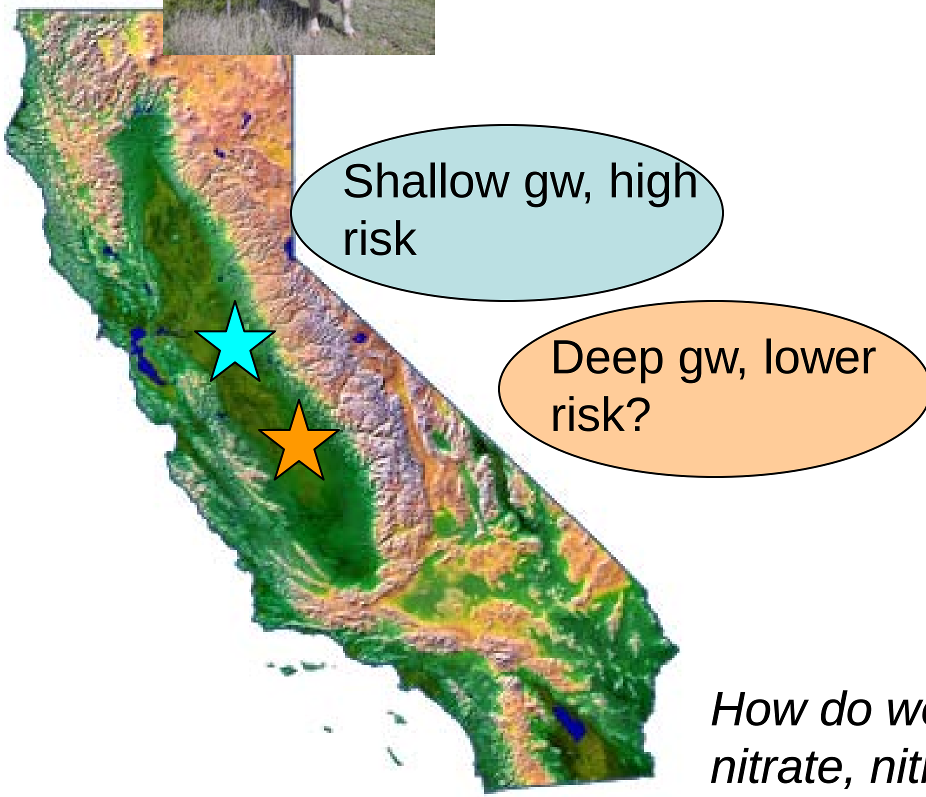
2) Harding Drain and TID Lat 6&7 have consistently high $\delta^{15}N$ year-round: waste source or heavily denitrified, stable source.

3) Other tributaries show complex mixing of different sources, most likely variable inputs of denitrified water, and assimilation during the summer, possible waste inputs.

California Dairy Study

In collaboration with Thomas Harter, UC Davis

Nitrate concentrations above the drinking water limit of 10 mg/L as N are common in domestic wells throughout the Central Valley.



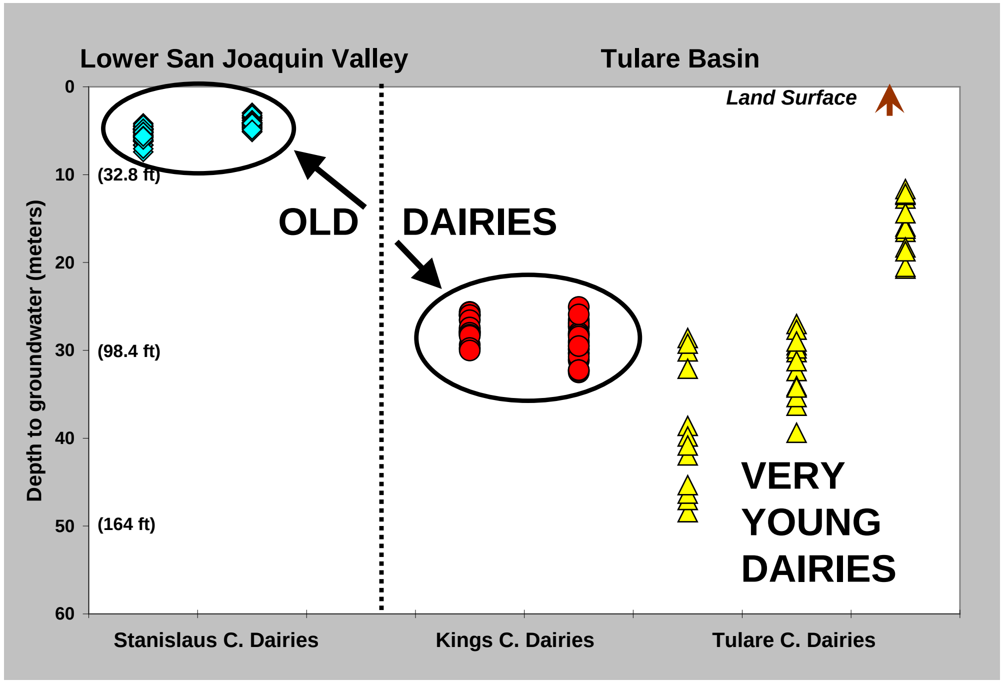
There are around 1500 dairies (managed as confined animal feeding operations) in the Central Valley.

How do we distinguish between dairy-derived nitrate, nitrate from current other agricultural uses, and nitrate from past agricultural uses?

Samples Collected at Seven Dairies

Some direct gw discharges to surface water

Water Depth Measurements



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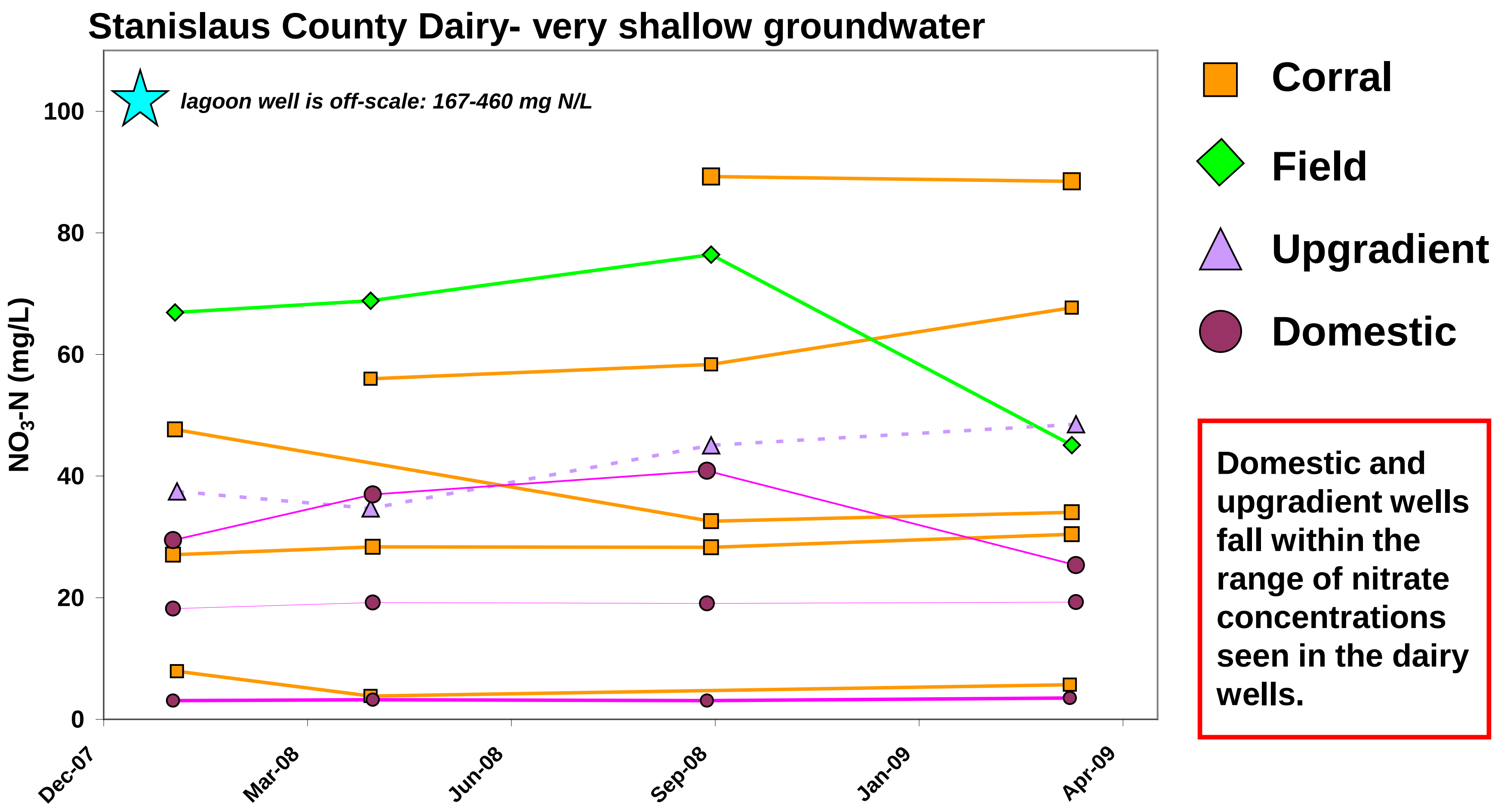
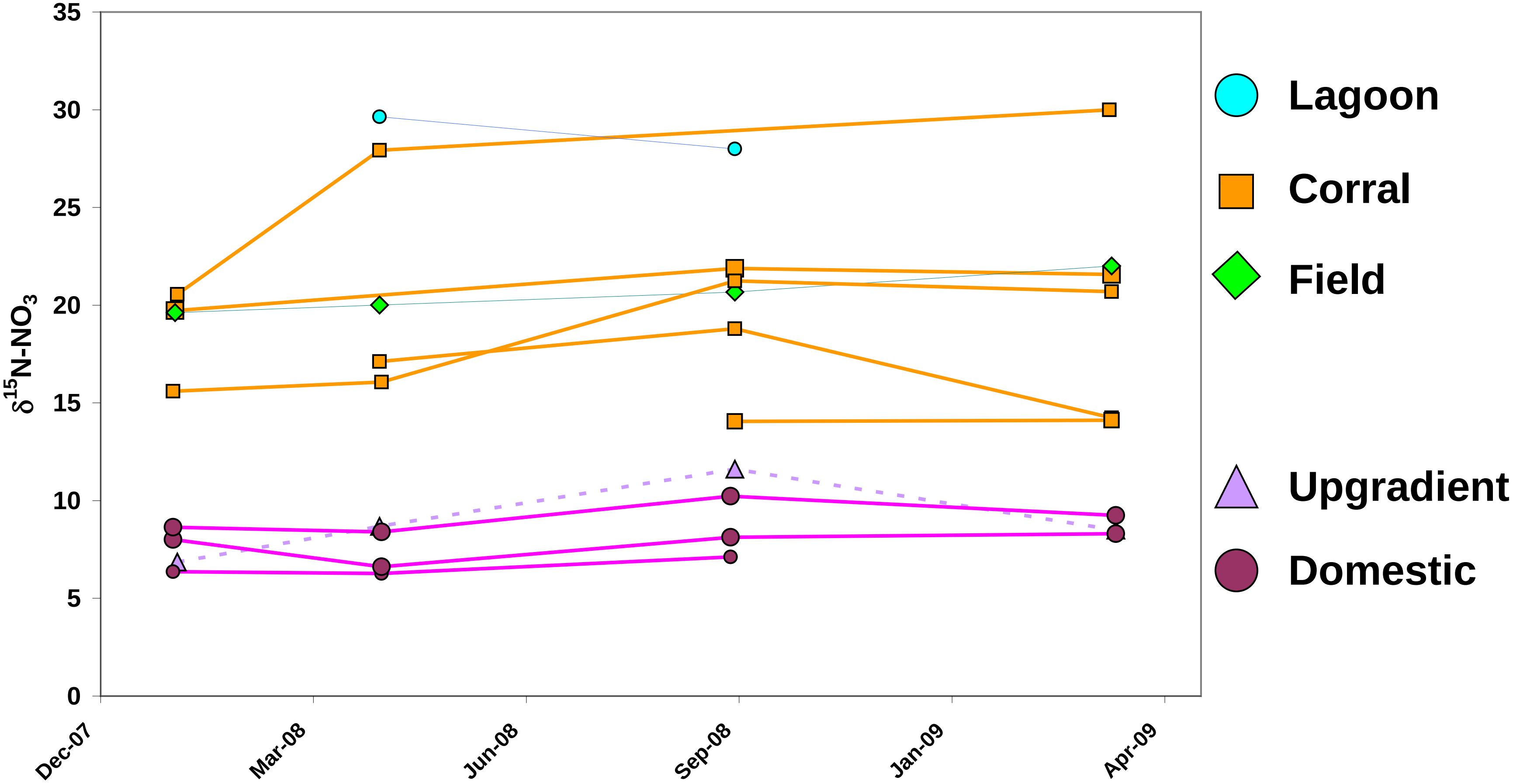
Nitrate in wells within a single dairy



Domestic and upgradient wells fall within the range of nitrate concentrations seen in the dairy wells.

Each line represents nitrate concentrations in a single well over four quarterly sampling trips.

$\delta^{15}N\text{-}NO_3$ composition within a single dairy



The $\delta^{15}N\text{-}NO_3$ values suggest that the nitrate in the domestic wells on this dairy ***IS NOT*** *primarily from animal waste.*

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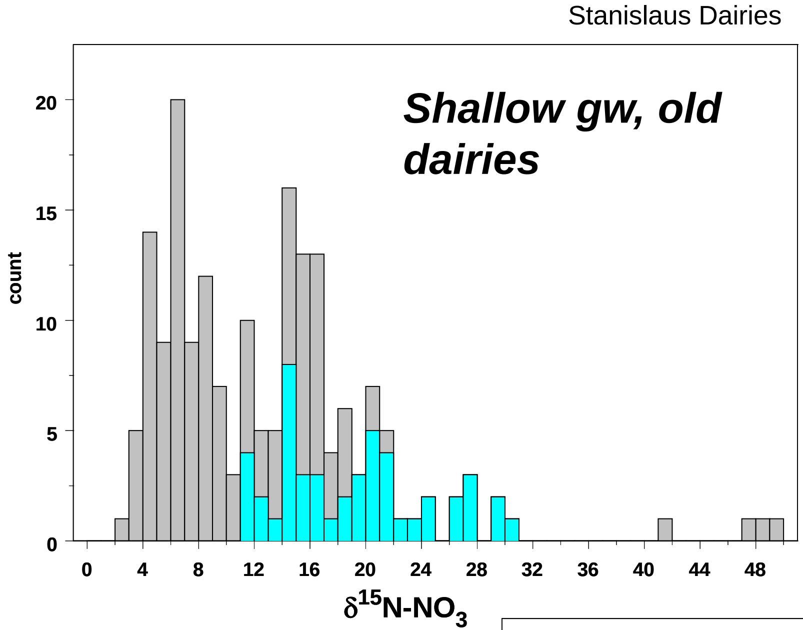
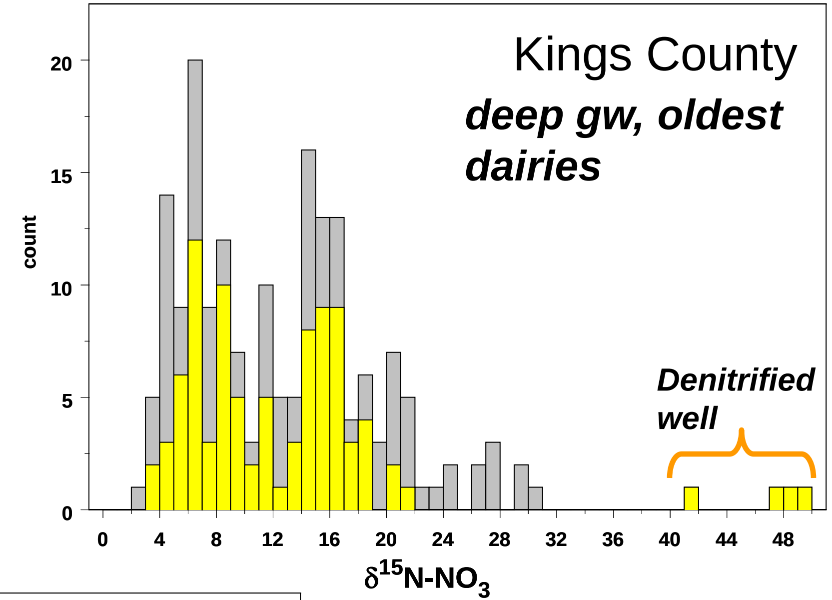
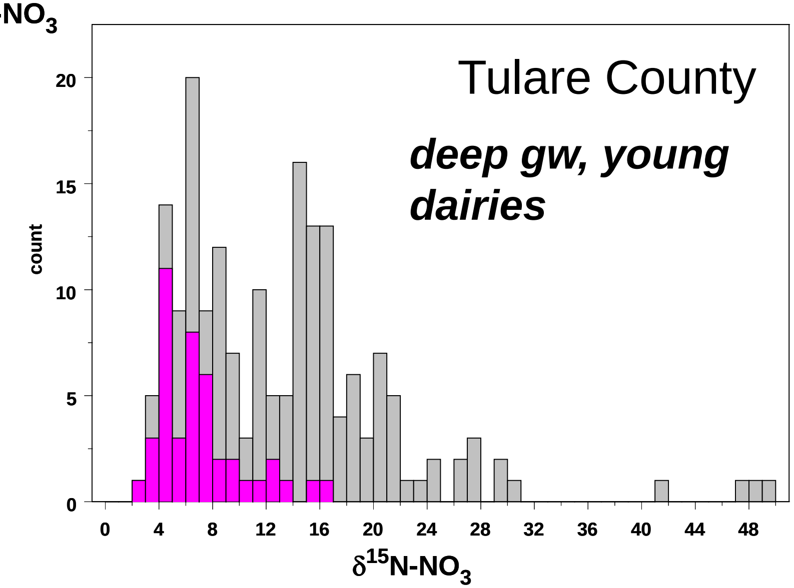
Nitrate Isotope Comparison By Locations







Shallower groundwater and longer use as a dairy results in shifts towards higher δ^{15}N-NO_3 values.

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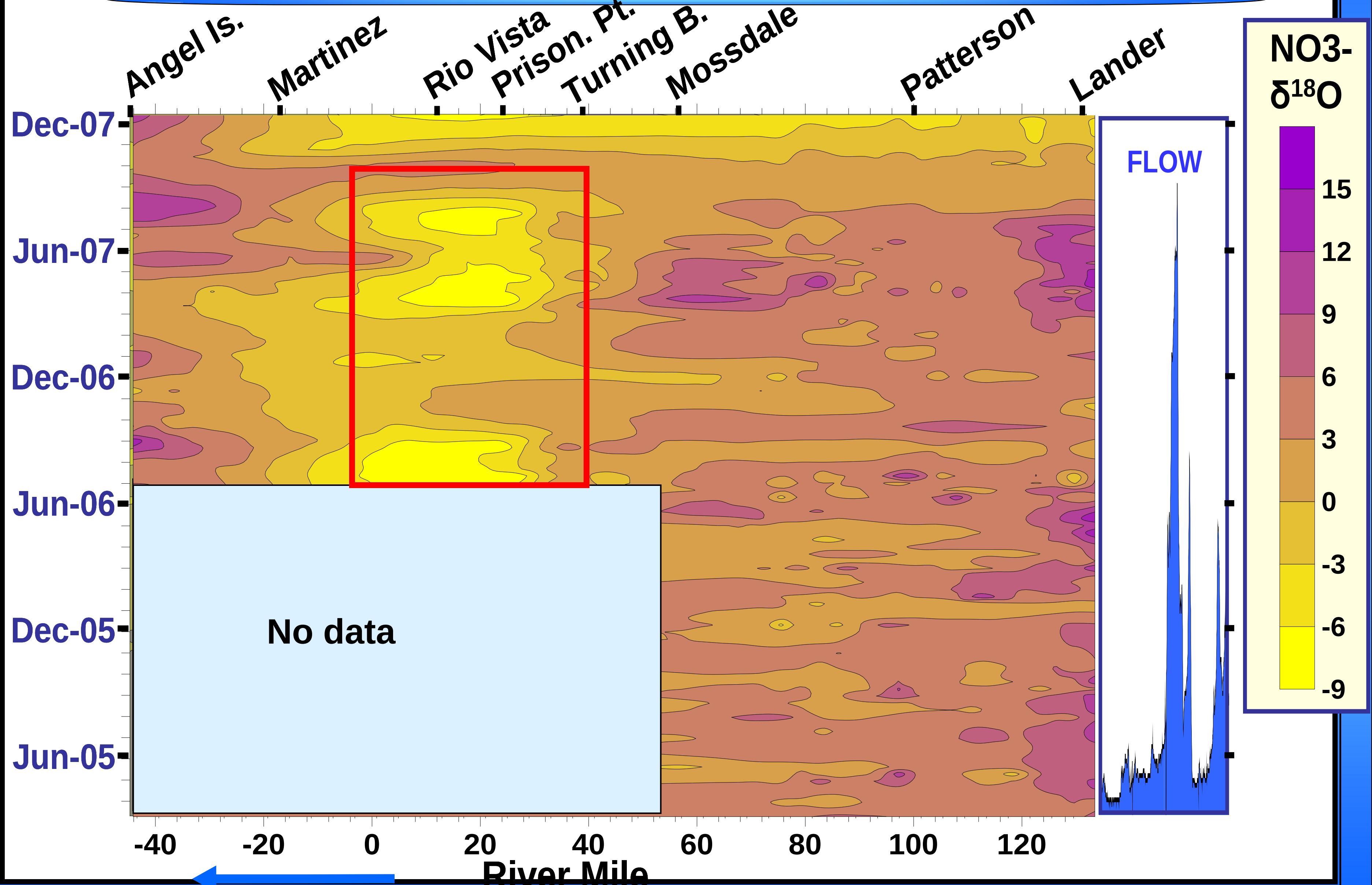
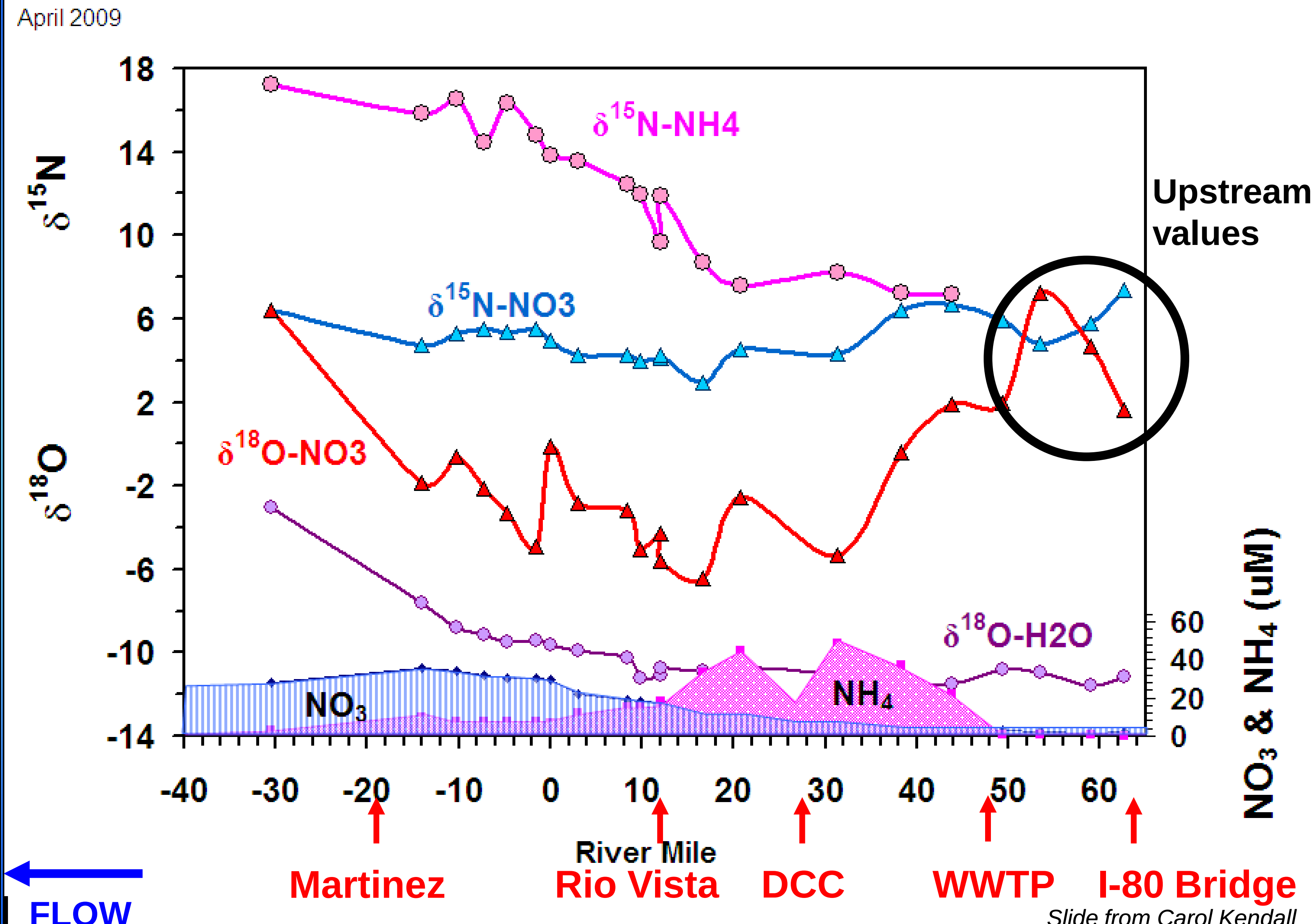
Low $\delta^{18}O$-NO_3, evidence of nitrification?



Nitrification- $\delta^{15}N-NH_4$ becomes distinct



Slide from Carol Kendall

Next Steps

- Trace WWTP NH_4 through north San Francisco Bay
- Combine stable isotope measurements and hydrologic modeling to estimate nitrification rates
- Examine seasonal changes in NH_4 sources, cycling and relationship to NO_3 dynamics.

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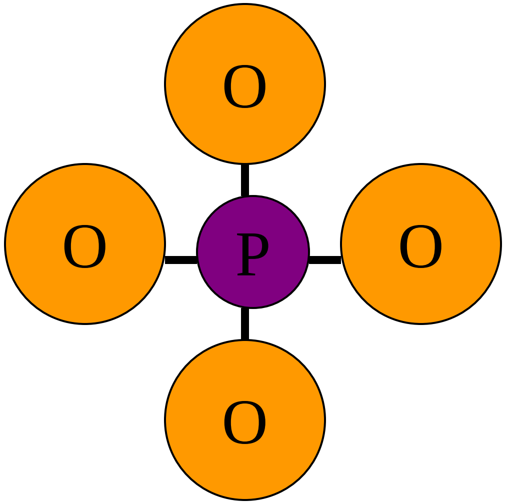
Stable Isotopes & Phosphate



Primary collaborators: Adina Paytan (UC Santa Cruz), Carol Kendall (USGS), Karen McLaughlin (SCCWRP), Katy Elsbury (Stanford University/ UC Santa Cruz)

Phosphorus

Essential macronutrient nutrient for life

Can be limiting or co-limiting in many aquatic ecosystems

Excess P has lead to eutrophication in many locations

Altering N:P ratios may change community composition.

Photo from: McGrath & Quinn, www.qub.ac.uk

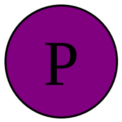
Phosphate Sources

- Amount of P that can impact aquatic ecosystems is tiny compared to what is needed in terrestrial ecosystems

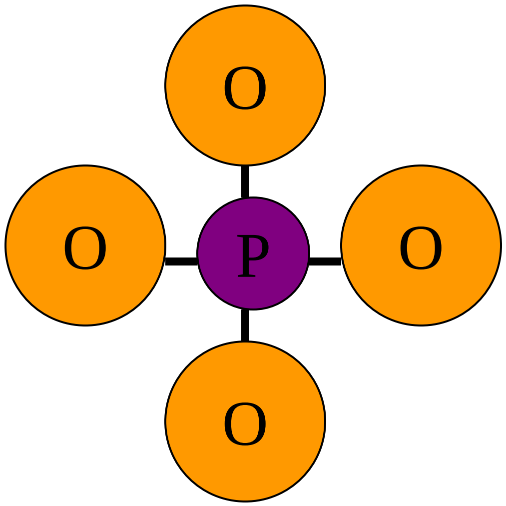
- Tracing and quantifying non-point sources is particularly difficult

Stable Isotopes & Phosphate

Phosphorus only has one stable isotope

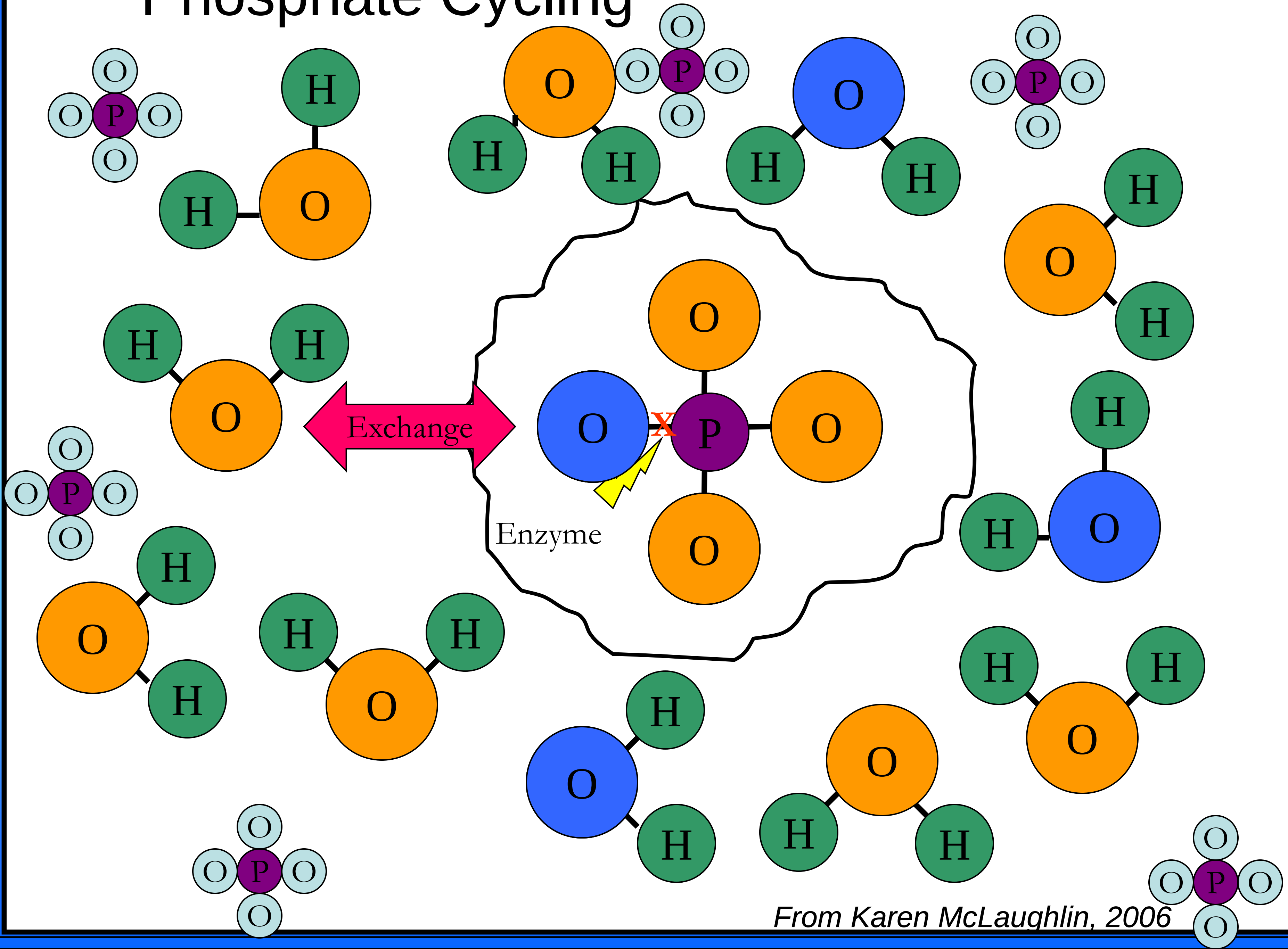


Phosphate has four oxygen atoms, and oxygen has three stable isotopes



Ratio of ^{18}O to ^{16}O relative to a standard

Phosphate Cycling



From Karen McLaughlin, 2006

History of Phosphate Isotopic Analysis

❖Methods for solid phosphate material (rock, bones, teeth) available since 1960.

❖Longinelli (1965) and Longinelli and Nuti (1968, 1973) developed a paleo temperature equation for phosphate precipitation.

❖Early attempts at oxygen isotope analysis in dissolved phosphate required extremely large amounts of water and used BrF_5 for fluorination .

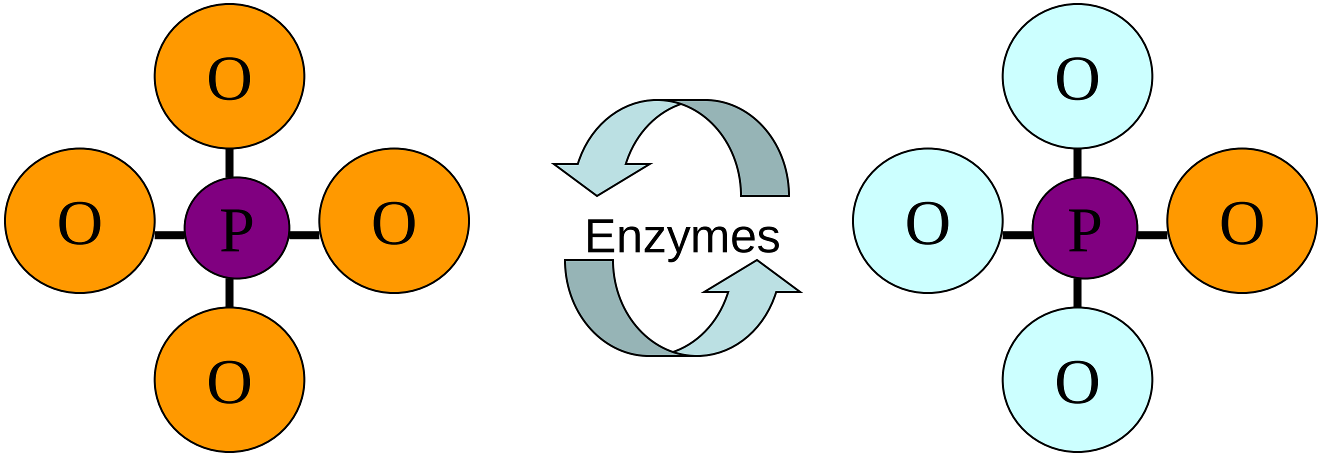
❖Late 1990s- early 2000: Research groups at Stanford/USGS and Yale developed new techniques for the safe chemical precipitation of small amounts of dissolved phosphate .

Two primary questions

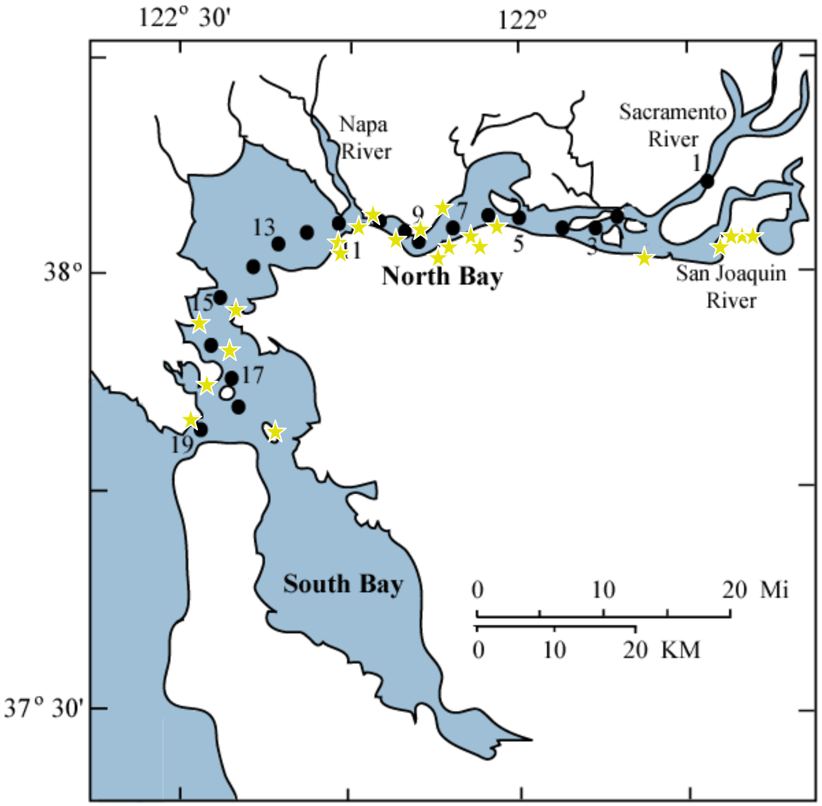
1) Do different sources have different $\delta^{18}O\text{-}PO_4$ values?

Young et al., 2009, ES&T

2) Does biological cycling erase the source value too quickly to be traced in aquatic systems?



San Francisco Bay



WWTP locations from Hetzel 2001

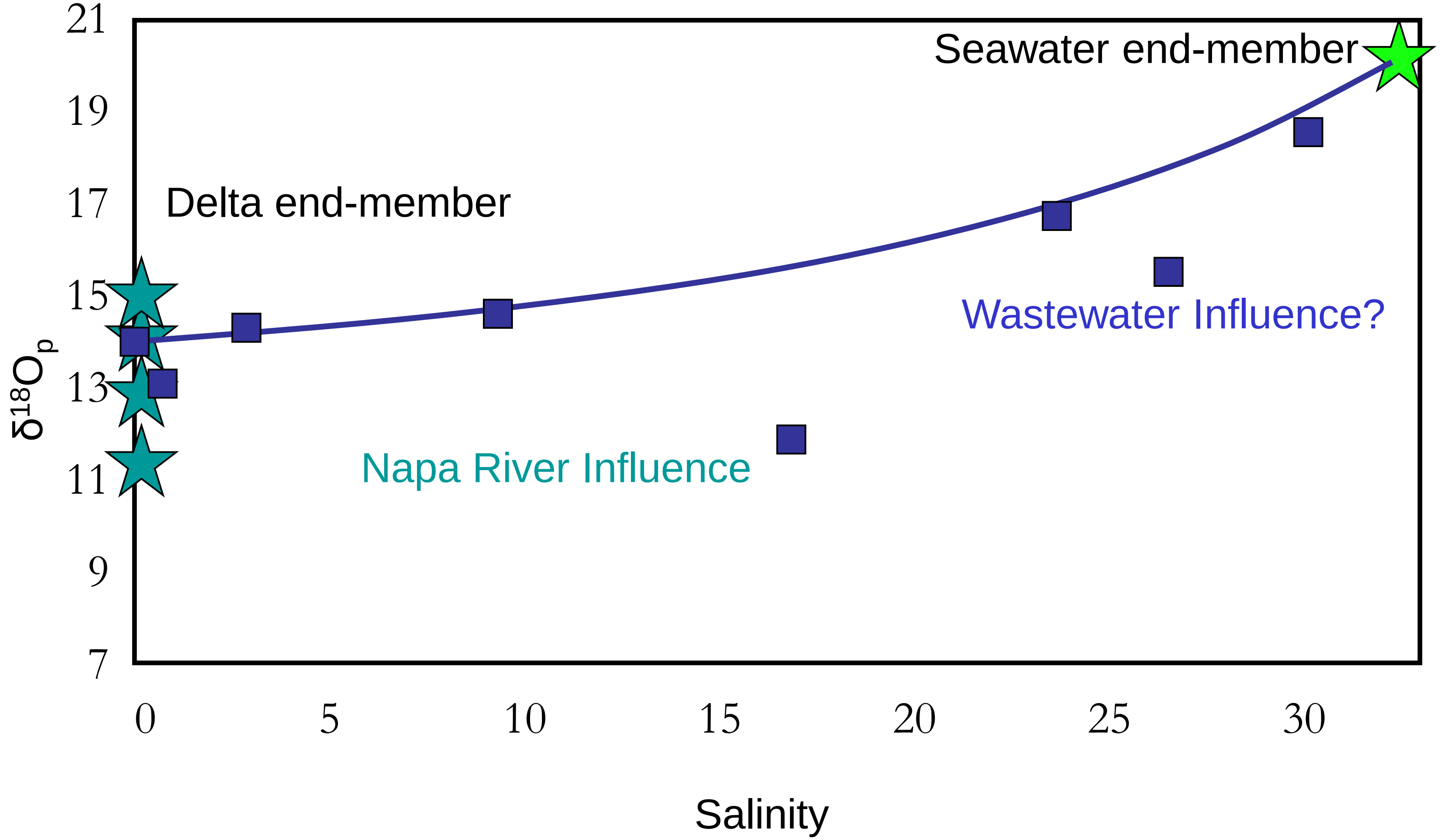
McLaughlin et al., 2006c

Light-limited, not phosphate limited

Many different potential phosphate inputs, including agricultural drainage and WWTPs

Source Signatures in the North Bay & Delta

Did not follow expected equilibrium, some did not follow conservative mixing



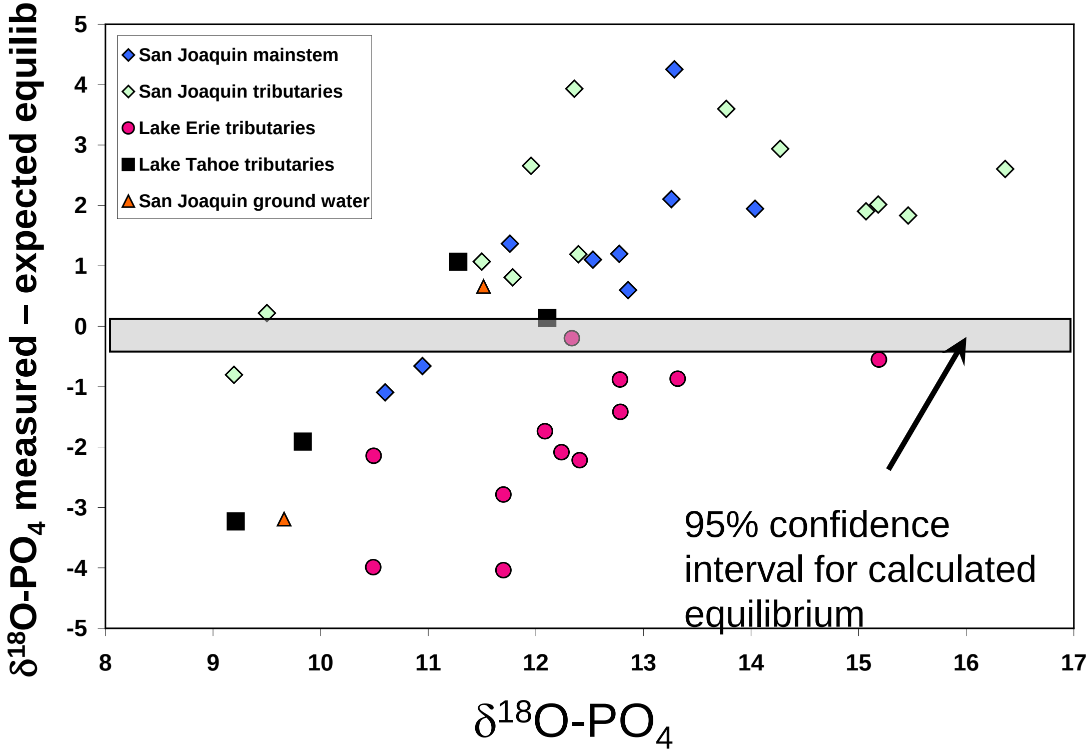
Data from McLaughlin et al., 2006c

Does biological cycling overprint the source value?

Laboratory studies (microcosm & mesocosm) suggest that biological cycling rapidly overprints the source value *(Blake et al., 2001, 2005, Paytan et al., 2002)*

Does not appear to be true for freshwater systems

McLaughlin et al., 2006a,c; Elsbury et al., 2009, Young et al., 2009)



- Elkhorn Slough, CA
  McLaughlin et al., 2006a
- San Joaquin River, CA
- Lake Tahoe, CA
- Lake Erie, MI
  Elsbury et al., 2009
- Boise River, ID

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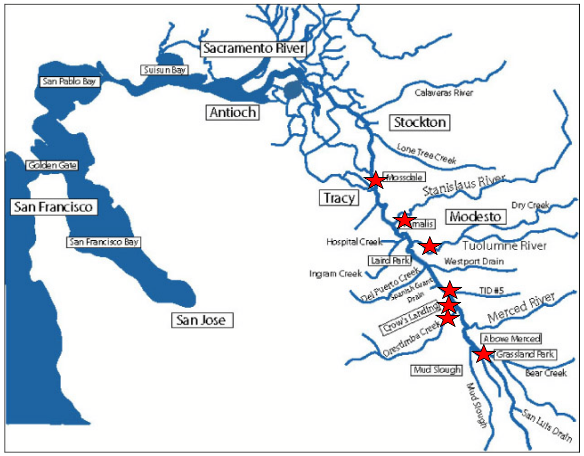
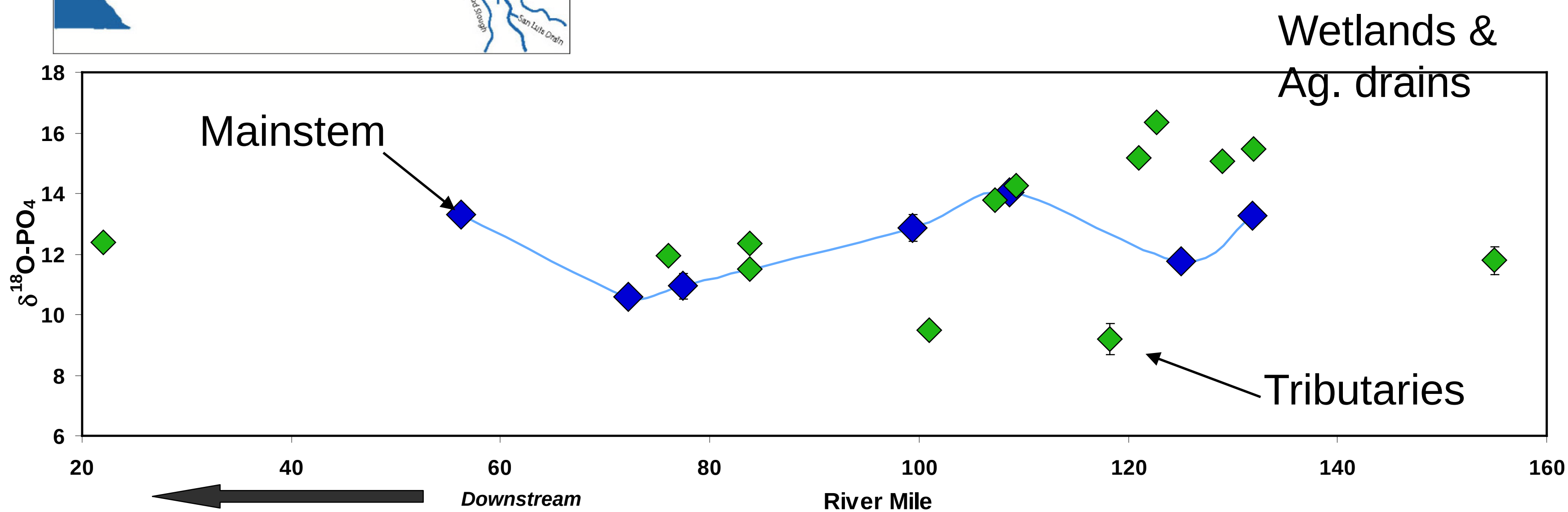
Fig. from Young et al., 2009

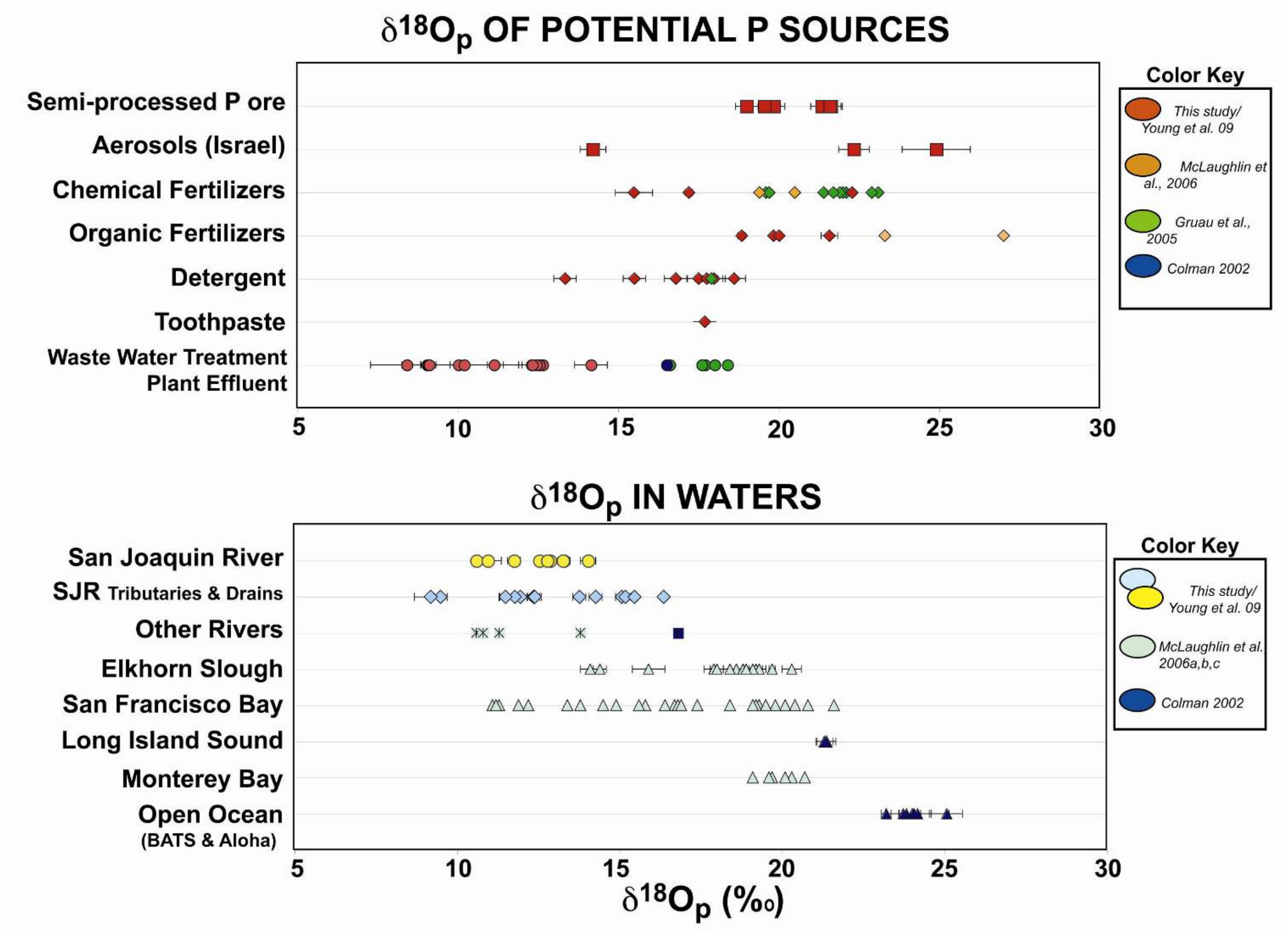
San Joaquin & Tributaries



Some tributaries had very different $\delta^{18}O\text{-}PO_4$ values than the mainstem- more detailed sampling could trace mixing.



Source Values



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Future Directions

- **Expand the range of $\delta^{18}O\text{-}PO_4$ measurements for various phosphate sources**
- **Better understand factors controlling WWTP effluent $\delta^{18}O\text{-}PO_4$**
- **Examine phosphate cycling in soil porewater and shallow groundwater using $\delta^{18}O\text{-}PO_4$** *(Zohar et al, 2010)*
- **Apply technique in other geographical areas**

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Closing thoughts on using stable isotopes: Challenges

- Sources and processes can have overlapping isotope signatures

Isotope analyses may yield fantastic results in one location, and totally inconclusive results in another.

- Cost and time: everyone has tight budgets and busy schedules

Pilot studies are a good idea!

Various Approaches

- Start with small pilot studies, then build to larger studies based on promising results *(match cost and effort to usefulness of results)*
- Ask very specific questions *(is denitrification taking place in this stretch of streambed?)*
- Test several hypotheses (*identify potential nutrient and organic matter sources to large rivers, then see which ones are validated by isotopes*)
- Piggyback on existing projects to allow for more analyses *(have existing monitoring programs collect samples)*

Questions?

Citations

Water quality of San Francisco Bay: http://sfbay.wr.usgs.gov/access/wqdata

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