

GAMA Special Studies on Nitrate in California Groundwater

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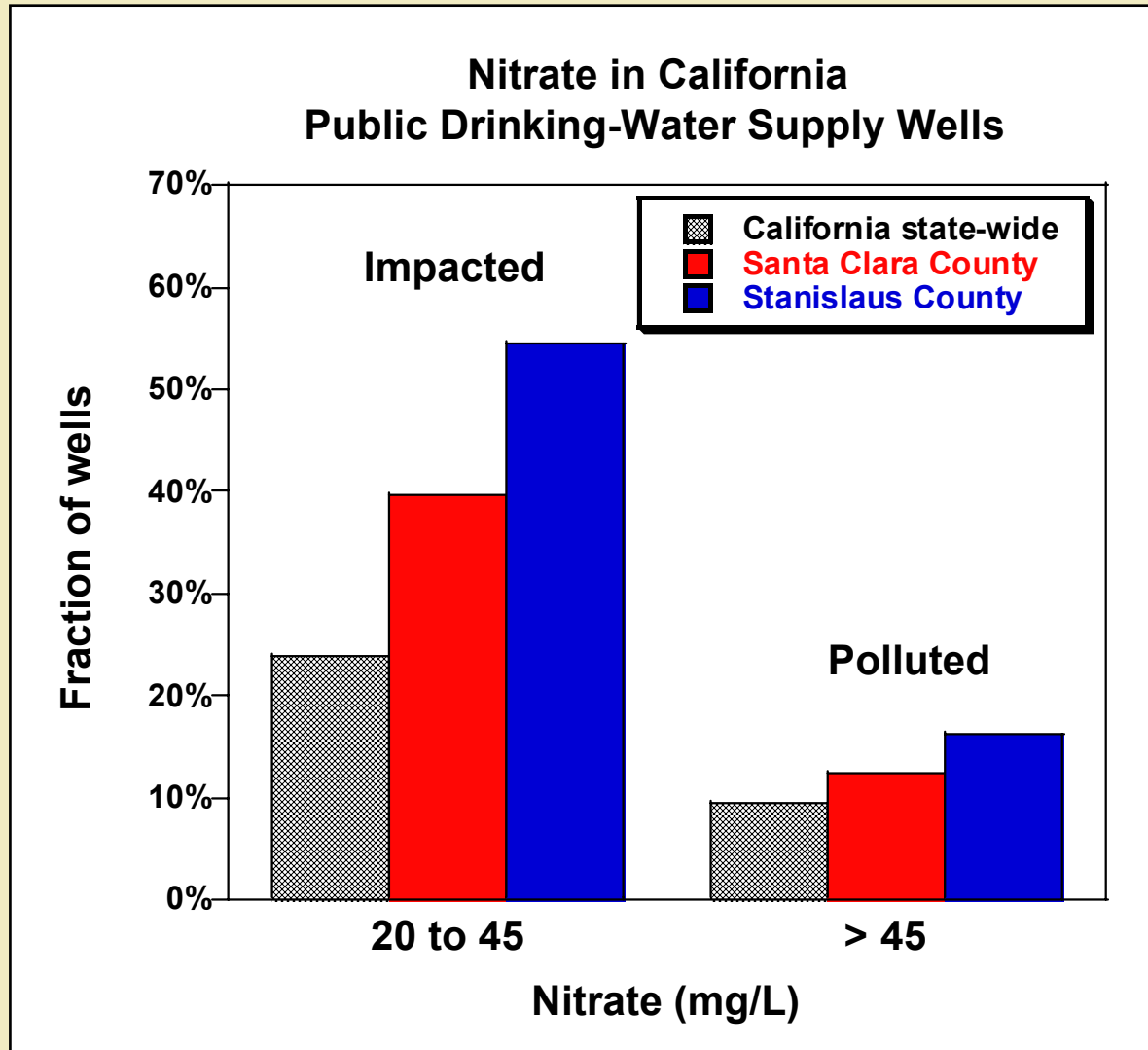
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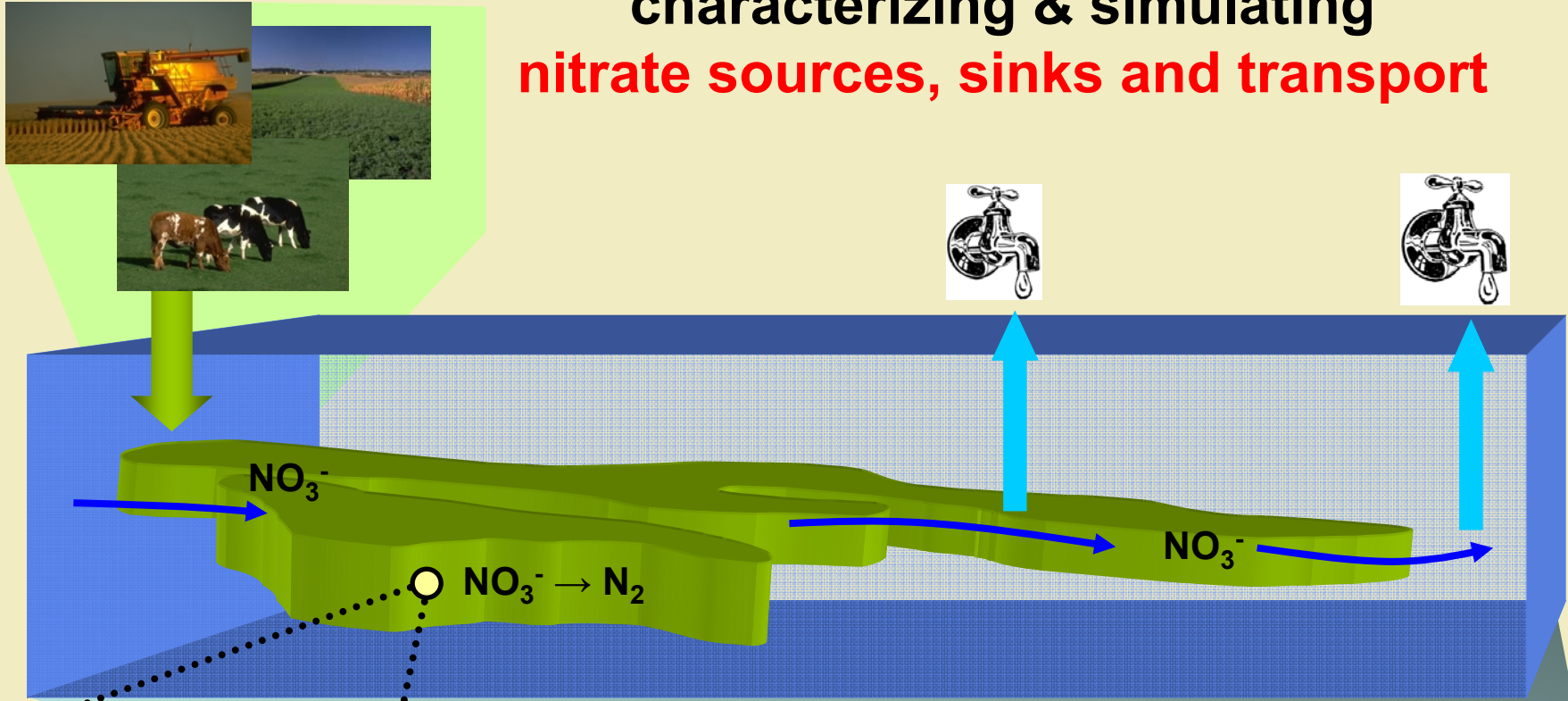
Nitrate is contaminating California's groundwater (which supplies half the drinking water supply)



California DHS data obtained through Geotracker
(geotracker.swrcb.ca.gov), August 2003.

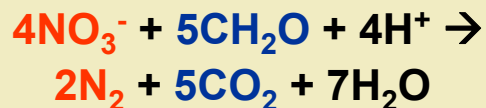


Effective management of subsurface nitrate contamination requires better tools for characterizing & simulating nitrate sources, sinks and transport



MICROBIAL control of denitrification

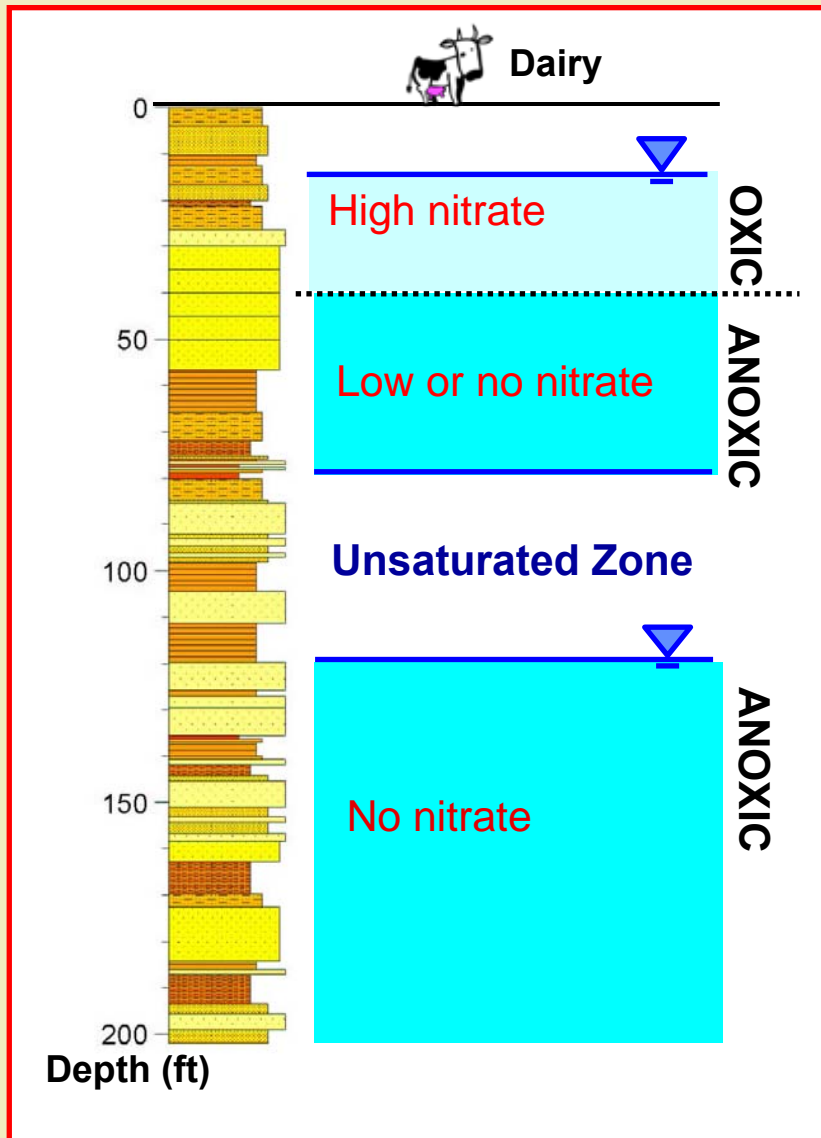
Heterotrophic denitrification



Case Studies

- Dairy farm: subsurface denitrification
- Coastal basins: urbanization
- Central valley basin: septic discharge

Dairy Farm in Kings County, CA



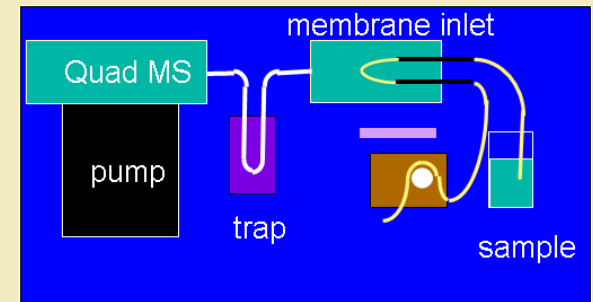
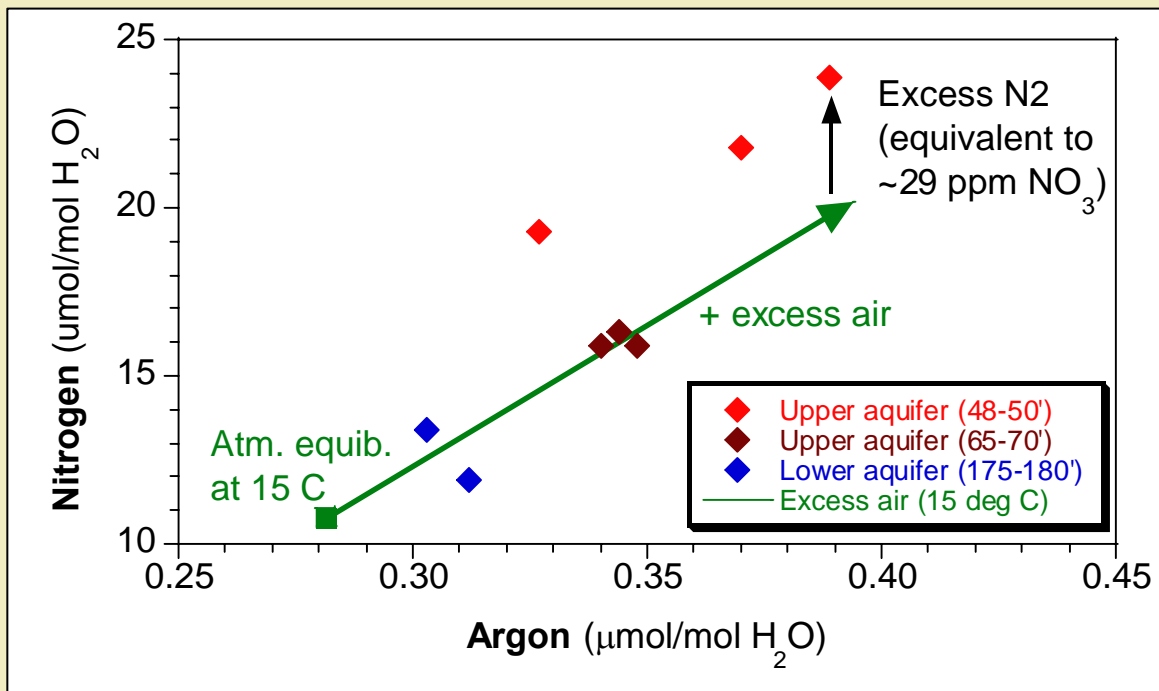
- Why is there no nitrate at depth?
 - Denitrification?
 - Mixing with old water?
- Is dairy nitrate loading being mitigated by natural or induced subsurface processes?
 - Does operation of the dairy create subsurface conditions conducive to denitrification?

We use “excess nitrogen” to distinguish denitrification from dilution

- The end product of denitrification is molecular nitrogen (N_2 , gas)
 - Groundwater contains “excess air” above equilibrium solubility
 - “Excess nitrogen” is the non-air component due to denitrification

- **Excess N_2 allows quantification of degree of denitrification**

$$\text{Degree of denitrification} = \frac{\text{Excess nitrogen}}{(\text{excess nitrogen} + \text{residual nitrate})}$$

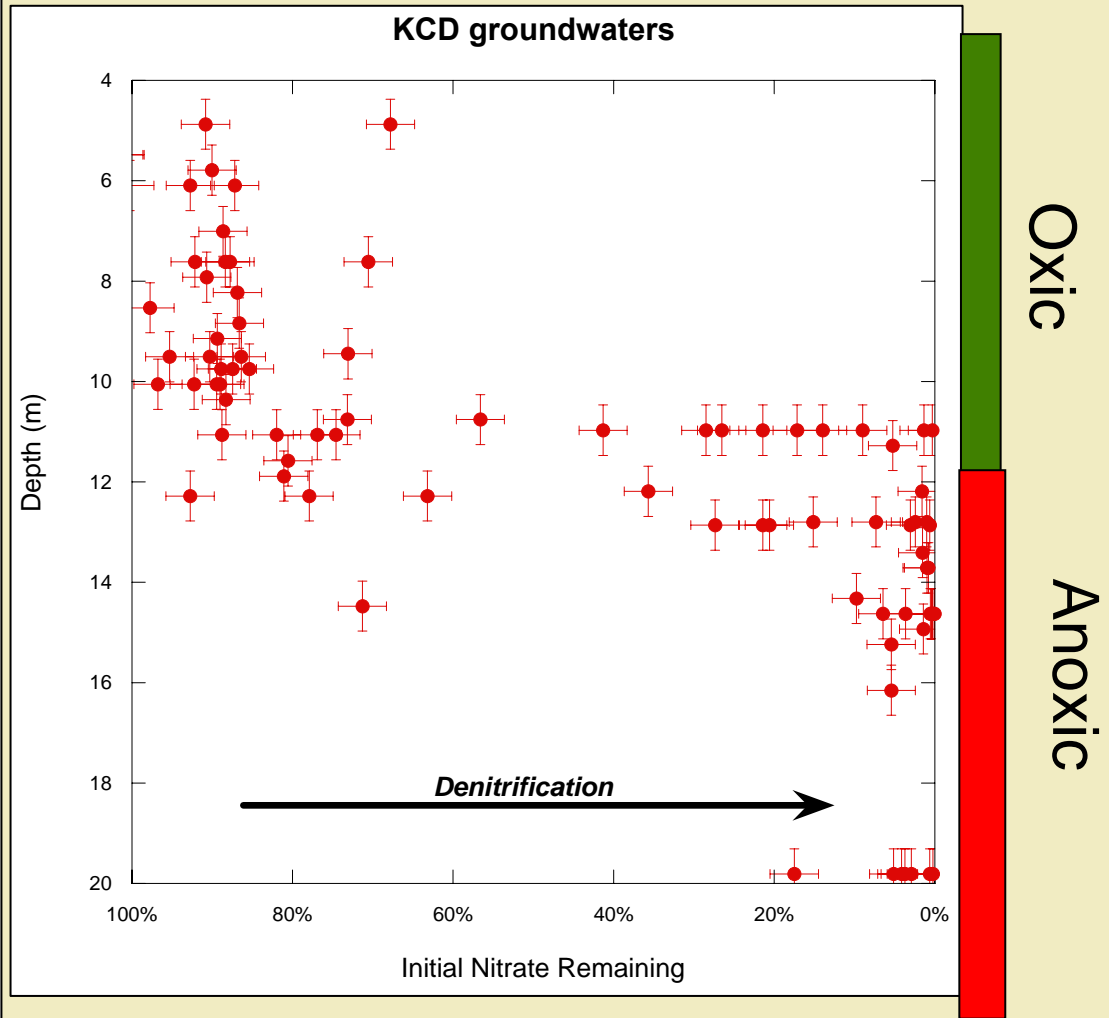
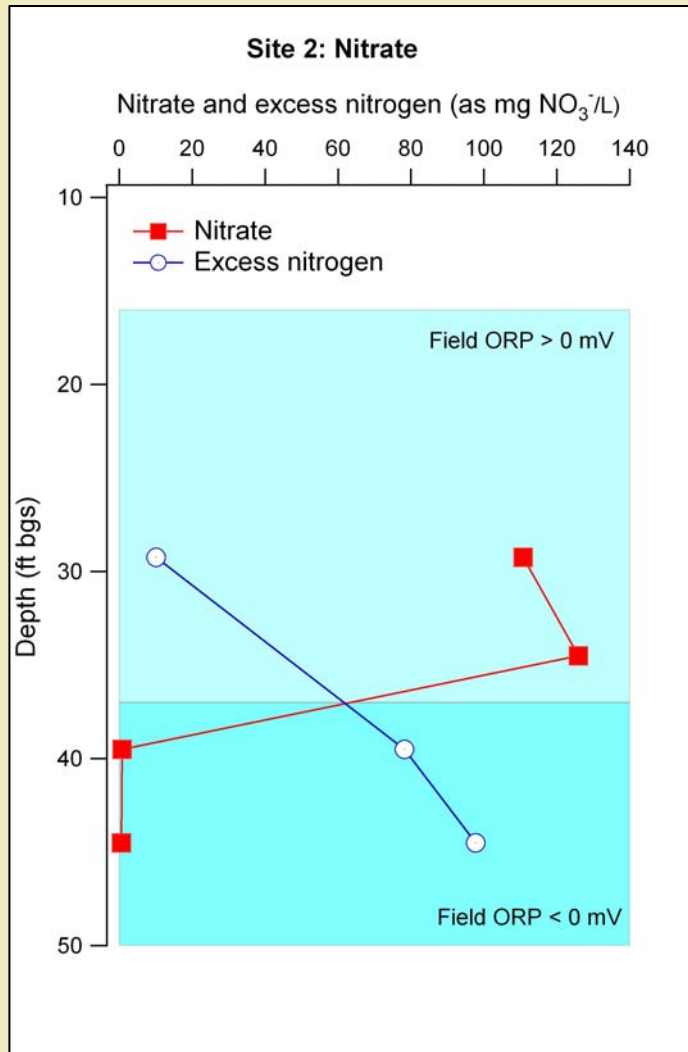


MIMS: Membrane inlet mass spectrometry

- Measures nitrogen, argon, oxygen
- Fast and inexpensive
- Field deployable



Excess nitrogen indicates that denitrification has occurred in deeper waters

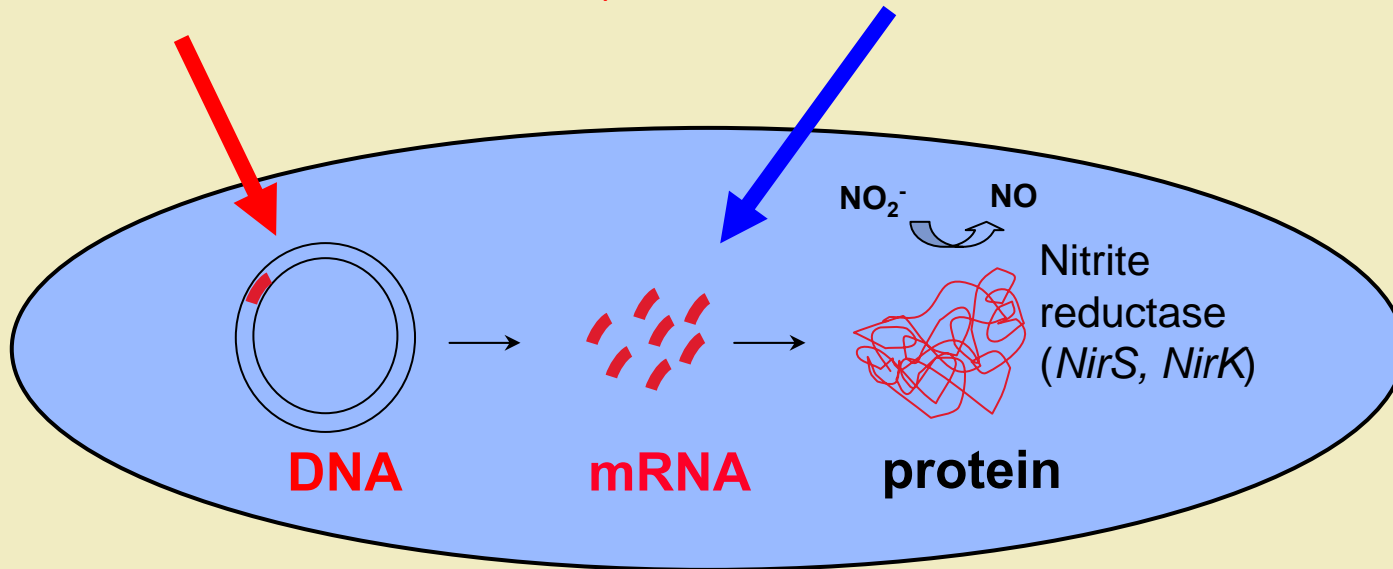


$$f = C_{\text{NO}_3^-} / (C_{\text{NO}_3^-} + C_{\text{excess N}_2})$$

We are using molecular biology to characterize where denitrification occurs

**Bacterial population
capable of denitrification**
(PCR for nitrite reductase DNA)

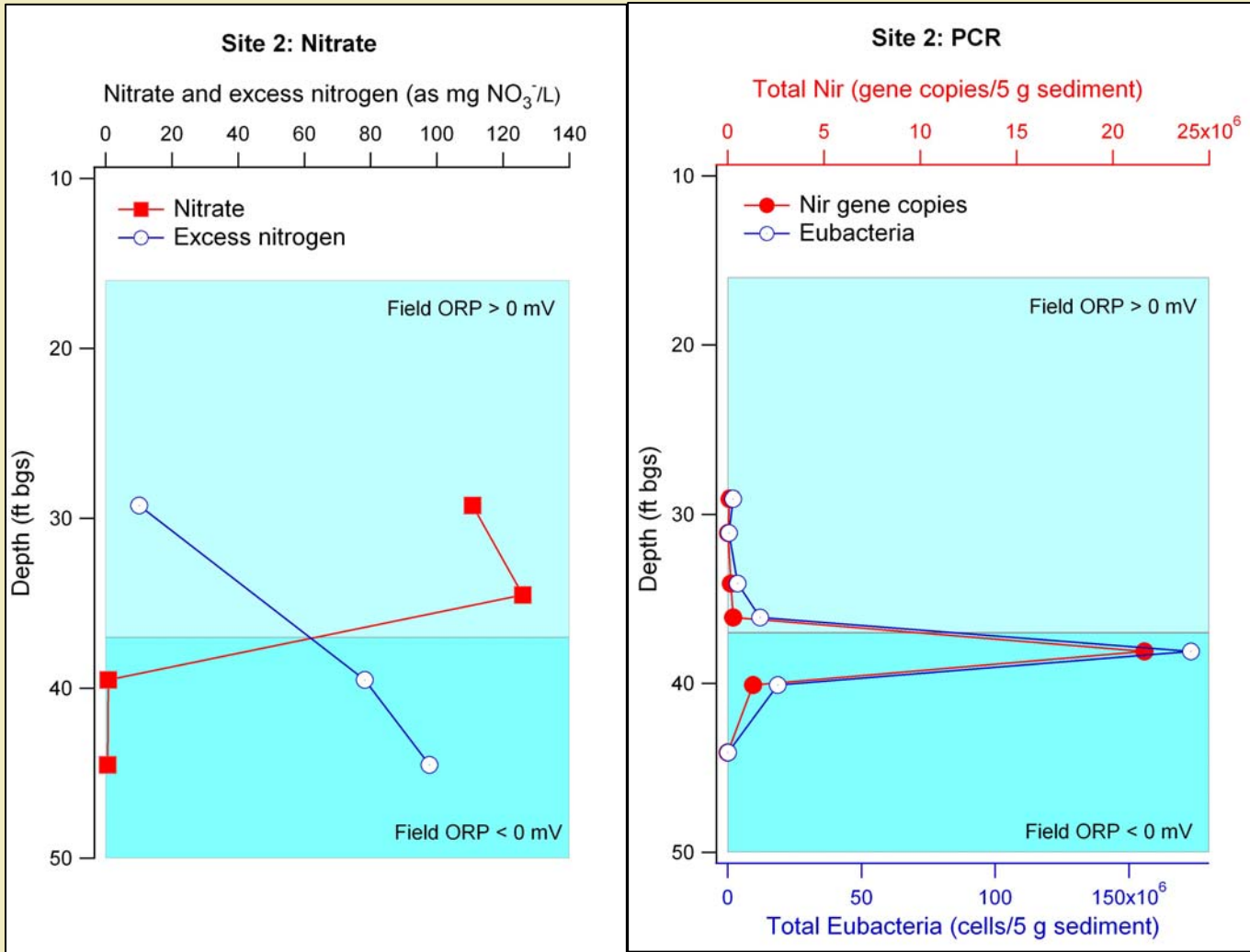
**Bacterial population
actively denitrifying**
(PCR for nitrite reductase RNA)



Quantitative real-time polymerase chain reaction (PCR)

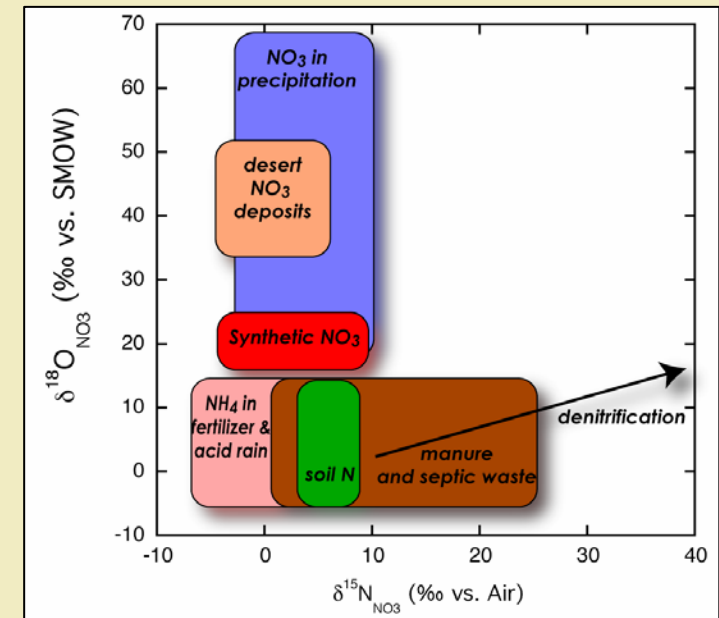
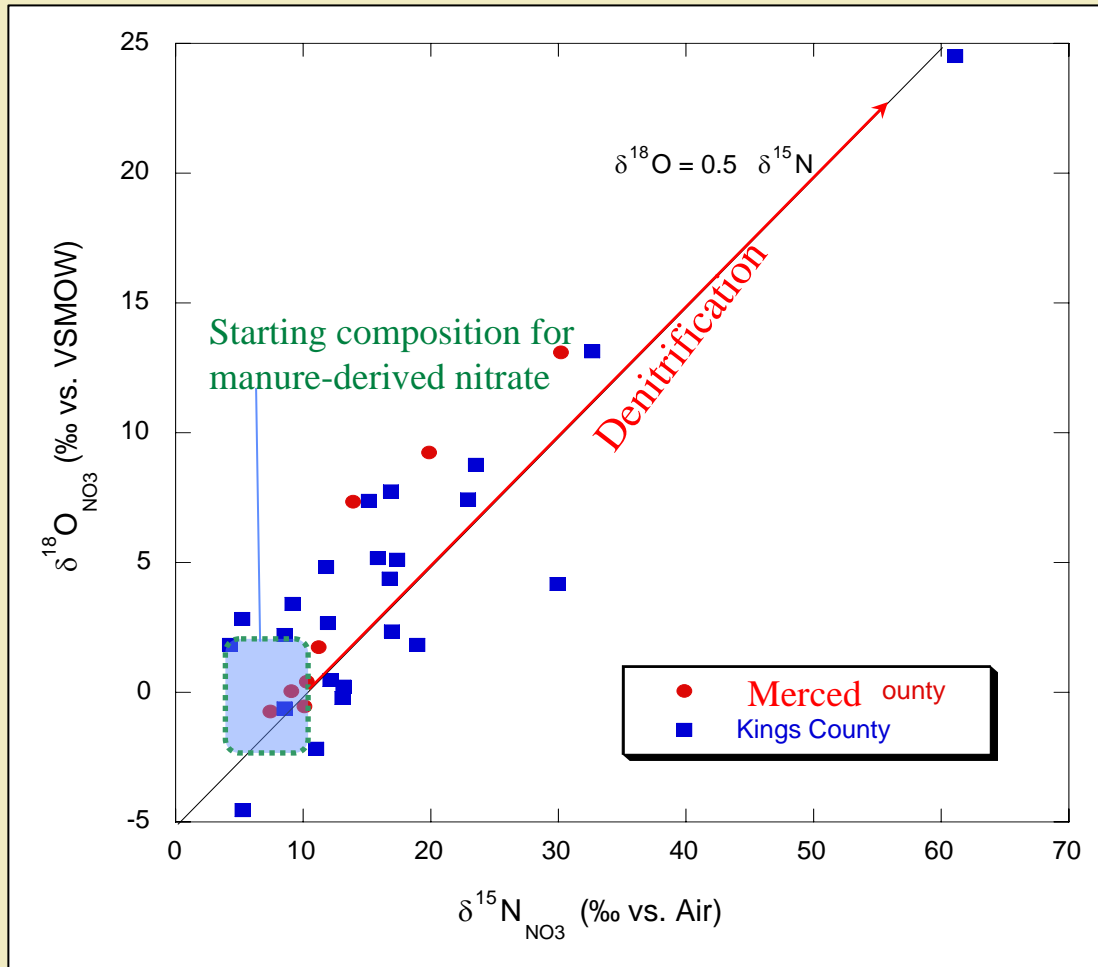
is a rapid, sensitive, and highly specific method that can be used to quantify denitrifying bacterial populations based on a diagnostic, **functional** gene.

Real-time qPCR of denitrifier bacterial populations show that denitrification occurs at the oxic-anoxic interface



Stable isotopic composition of nitrate indicates denitrification of a manure nitrogen source

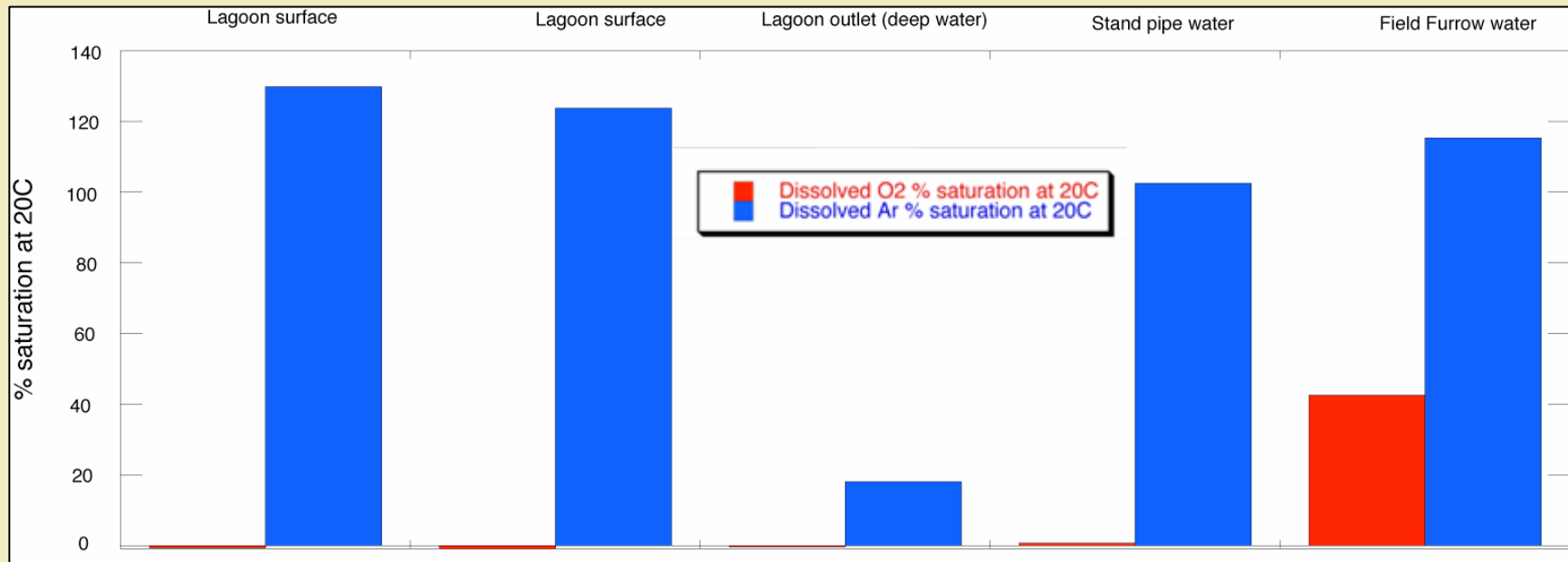
Dairy farm



Ranges based on compilation of data in Kendall, 1998.

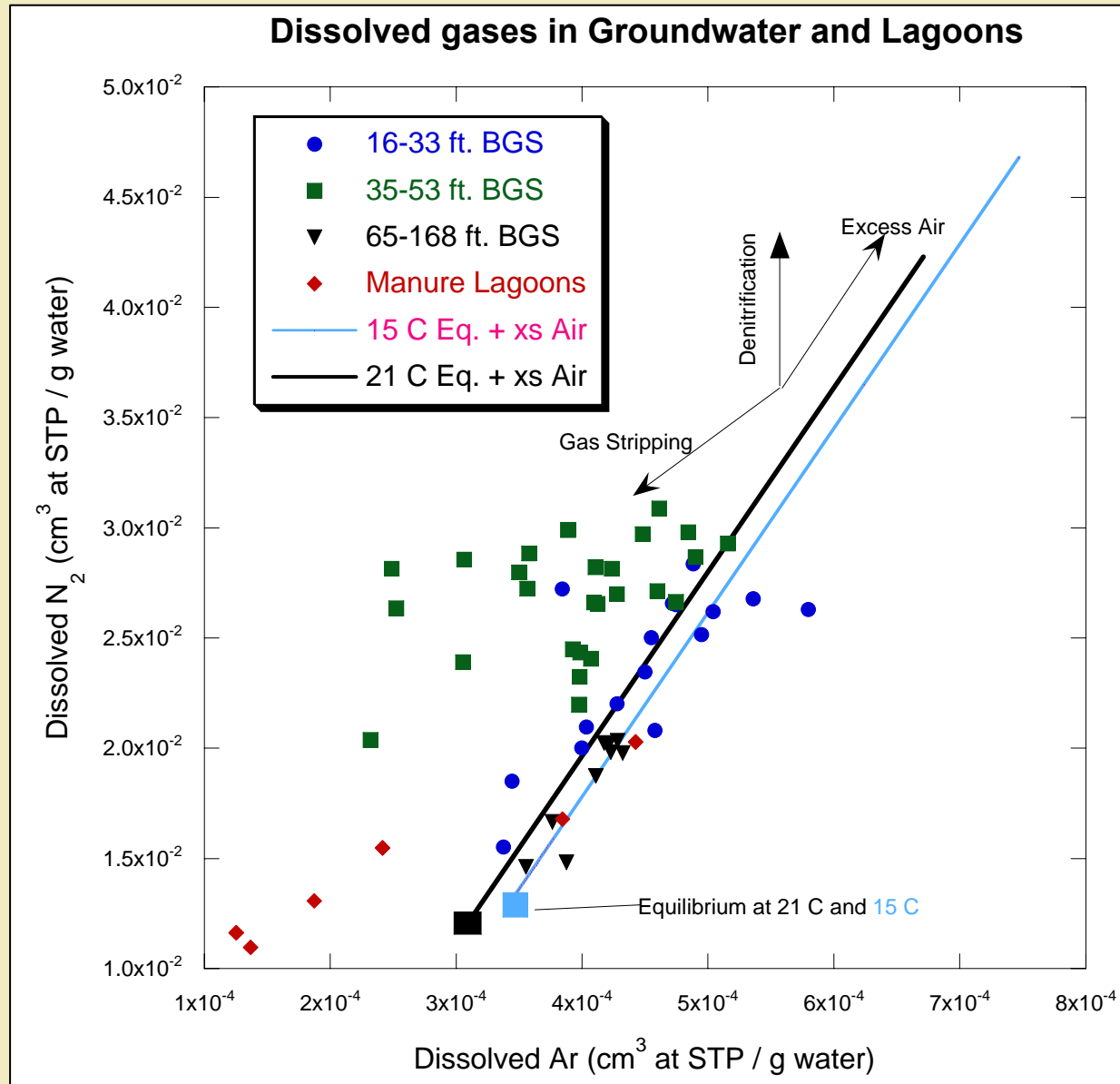
We can use dissolved gases to distinguish between lagoon seepage and field-applied wastewater

Production of methane and carbon dioxide in manure lagoons appears to “strip” atmospheric gases from lagoon waters

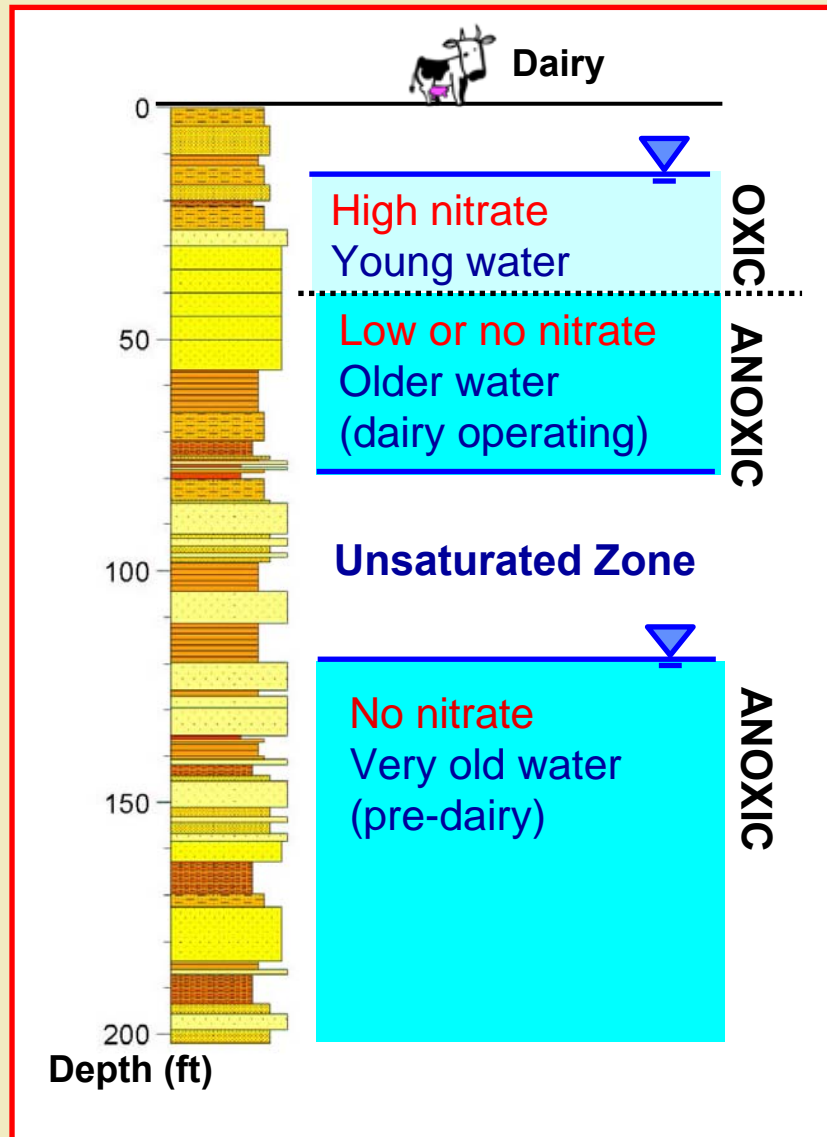


Manure lagoon seepage appears to be associated with denitrification

Dairy farm



Two aquifers with low nitrate – two different mechanisms mitigating impact



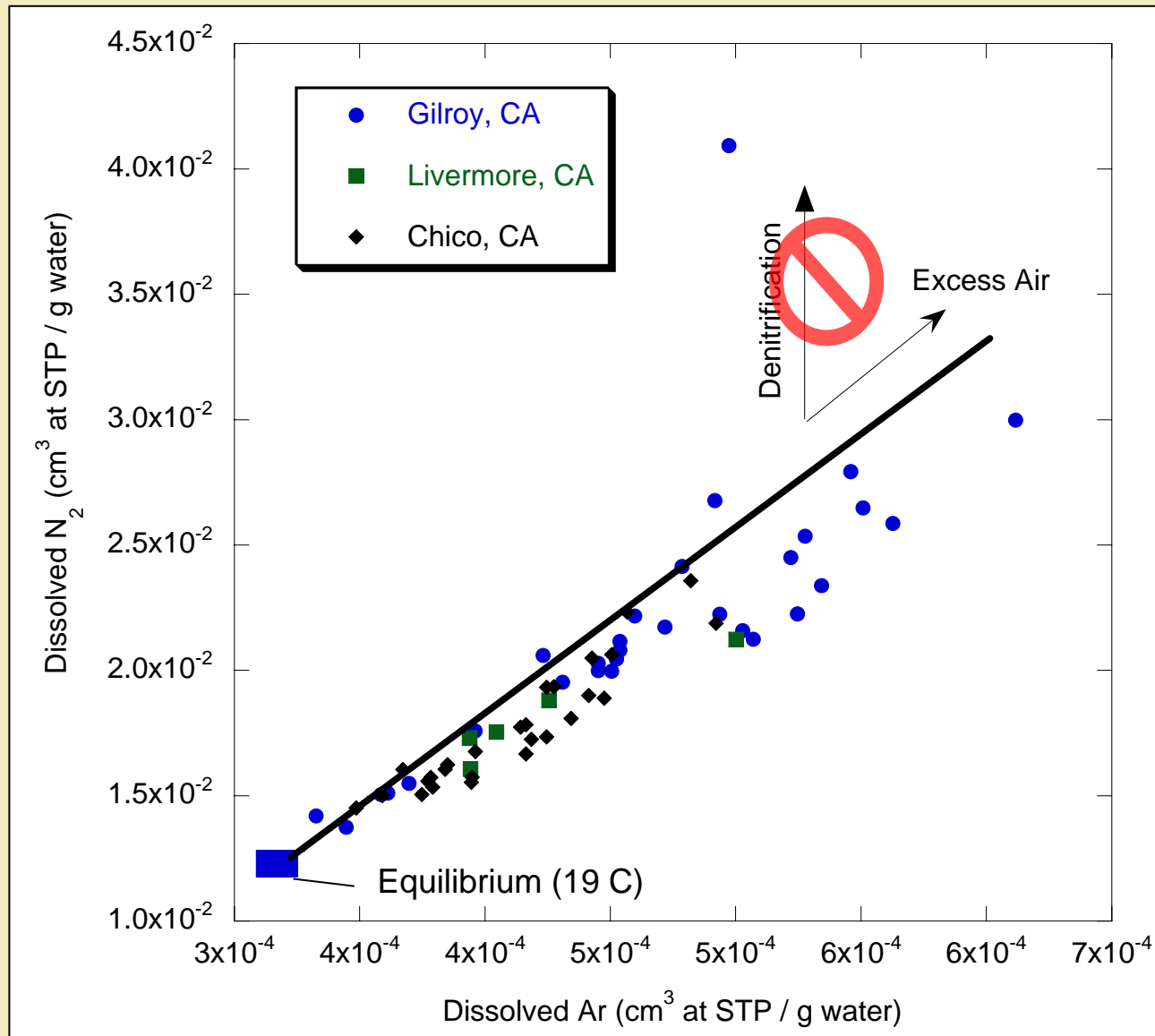
UPPER LOCAL AQUIFER

- Chemical mitigation: **degradation**
- Active **denitrification** mitigates impact of high-nitrate recharge
- **Denitrification** may be driven by dairy operations

LOWER REGIONAL AQUIFER

- Physical mitigation: **transport**
- Confining layer prevents recharge of high-nitrate irrigation water

Denitrification may not be common in drinking water basins in California



Moore et al (2006) Appl. Geochem.

Livermore-Amador Basin: Multiple nitrate sources

Groundwater nitrate issues

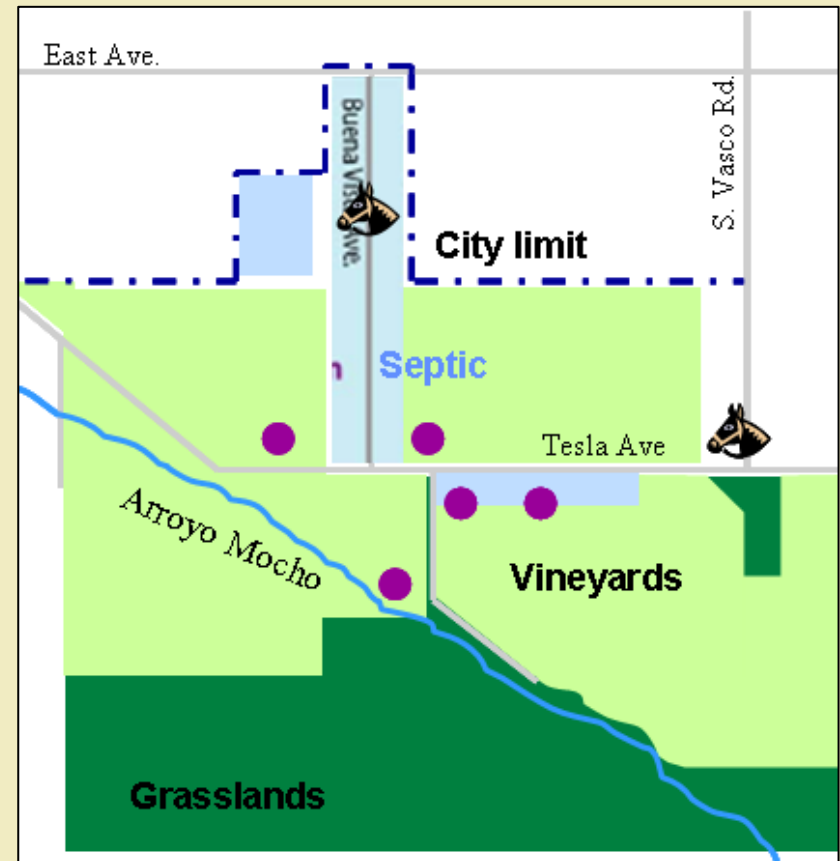
- City & private wells contaminated
- Significant land use changes
- To manage or not to manage!
 - Convert septic to sewage?
 - Regulate animal waste?
 - Educate growers?

Potential nitrogen sources

- **NW:** Wastewater treatment
- **W:** Historic?
- **SE:** Septic, animals, vineyards

LLNL multi-tracer approach

- **Stable nitrate isotopes** - source
- **Excess nitrogen** – denitrification
- **Stable water isotopes** – recharge, flow
- **GW age** – recharge, flow. natural nitrate



SE Livermore source area

A multi-tracer approach for a complex source term

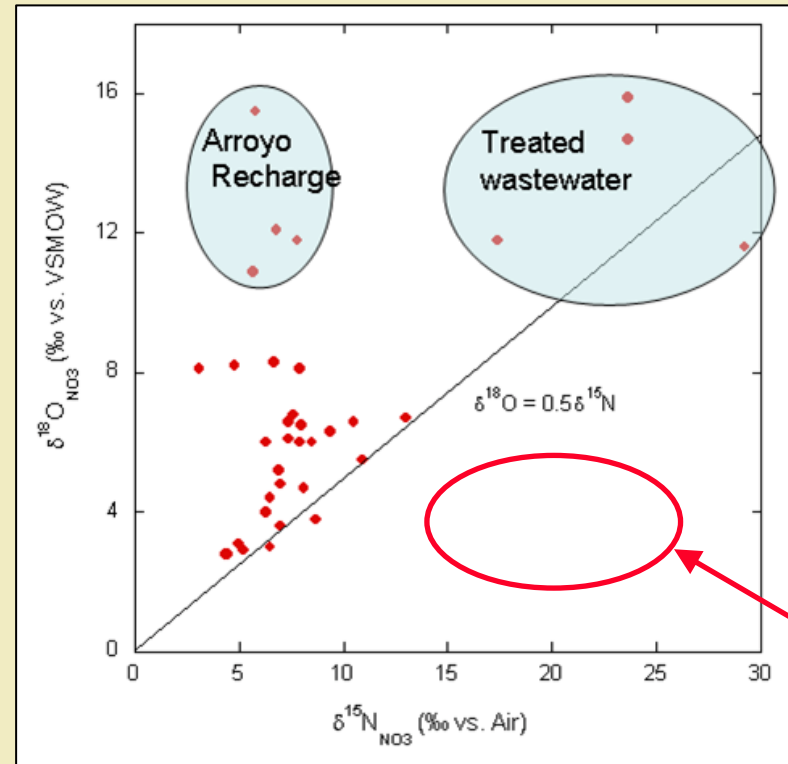
- Groundwater H^3/He ages delineate flow and ambient conditions.

- Old groundwater has 10-20 mg/L NO_3 with soil N isotopics.
- Artificial recharge on Arroyo Mocho
 - Mobilizes nitrate in source areas.
 - Dilutes nitrate near supply wells.

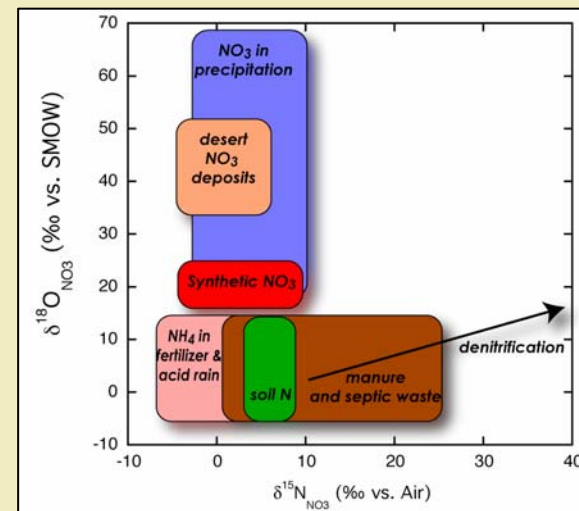
- Multiple sources of nitrate exist.

- NW: wastewater, decreasing.
- W: livestock, decreasing.
- SE: fertilizer and soil N.

- Septic sources are *minor*



No
Septic



Ranges based on compilation of data in Kendall, 1998.

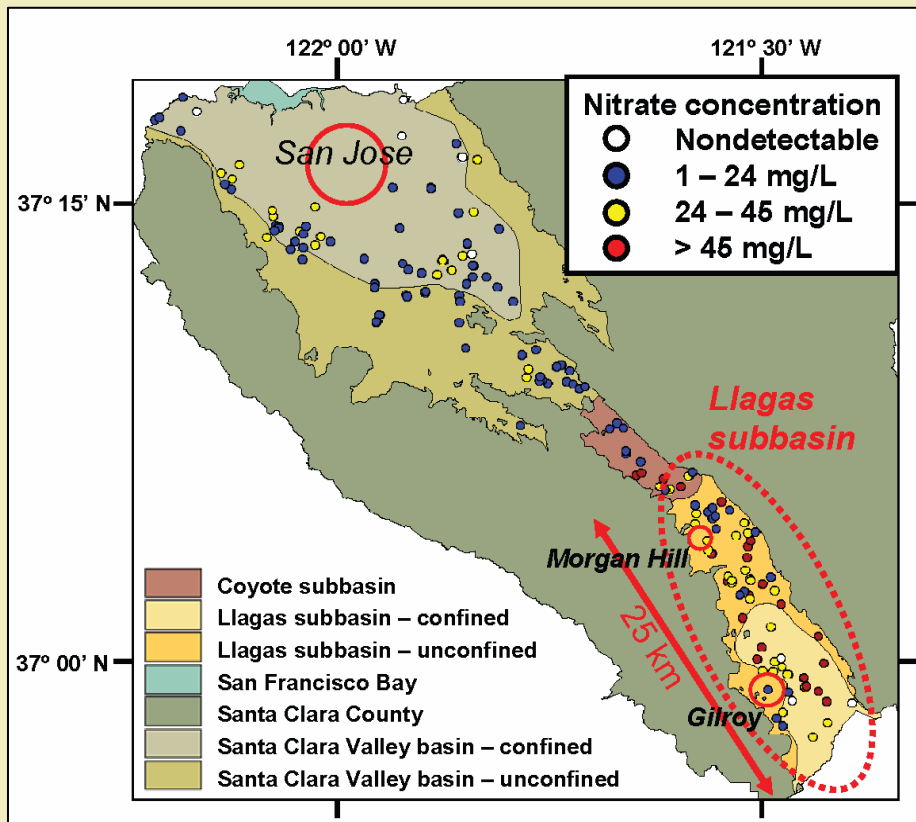
Llagas Basin, Santa Clara County: Vulnerability

Nitrate contamination

- Pervasive shallow (“domestic”)
- None deep (“municipal”)

Important groundwater basin

- Not managed; sole source
- Rural to suburban transition



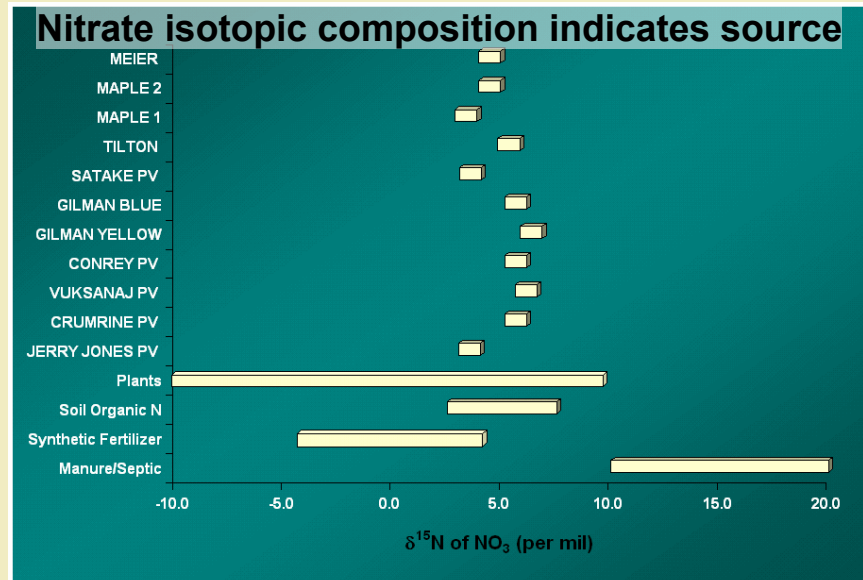
Modified from SCVWD (2002)

Questions about groundwater nitrate

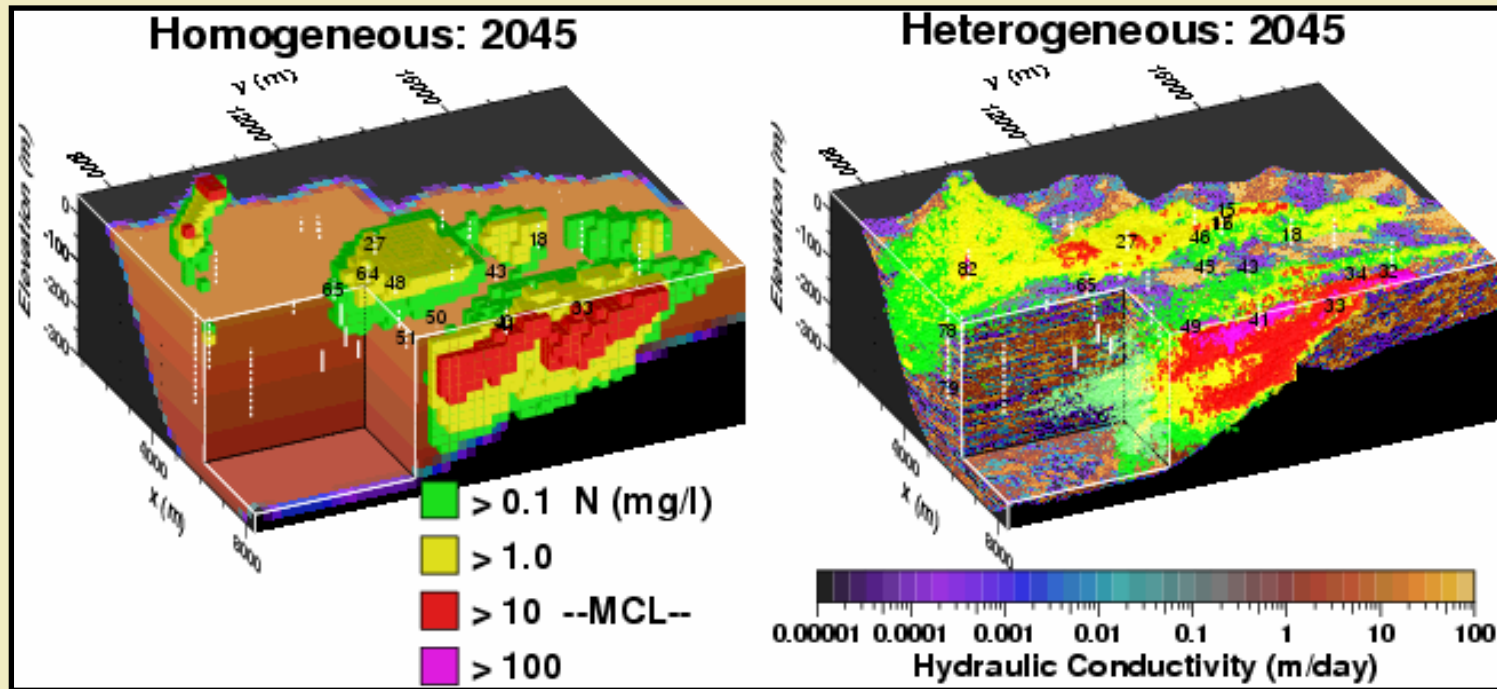
- **Source:** animal vs septic vs fertilizer?
- **Timing:** historic or current?
- **Distribution:** why no nitrate at depth?

Findings

- Synthetic fertilizer source
- Oxidic shallow; anoxic at depth
- No denitrification shallow or deep
- Distribution controlled by transport



The effect of heterogeneity on nitrate transport



Carle et al (2006) Geosphere

- If sources **stabilized**, shallow gw concentrations will level off this century.
- If sources **eliminated**, shallow gw impacts may linger for 40-100+ years.
- Including heterogeneity into transport modeling results in:
 - More wells impacted.
 - More dispersion than a homogenous model with high (10m) dispersivity.
 - Rising nitrate concentrations in deep wells this century

Chico & Butte County: Conversion from septic to sewer

Chico

■ Groundwater quality issues

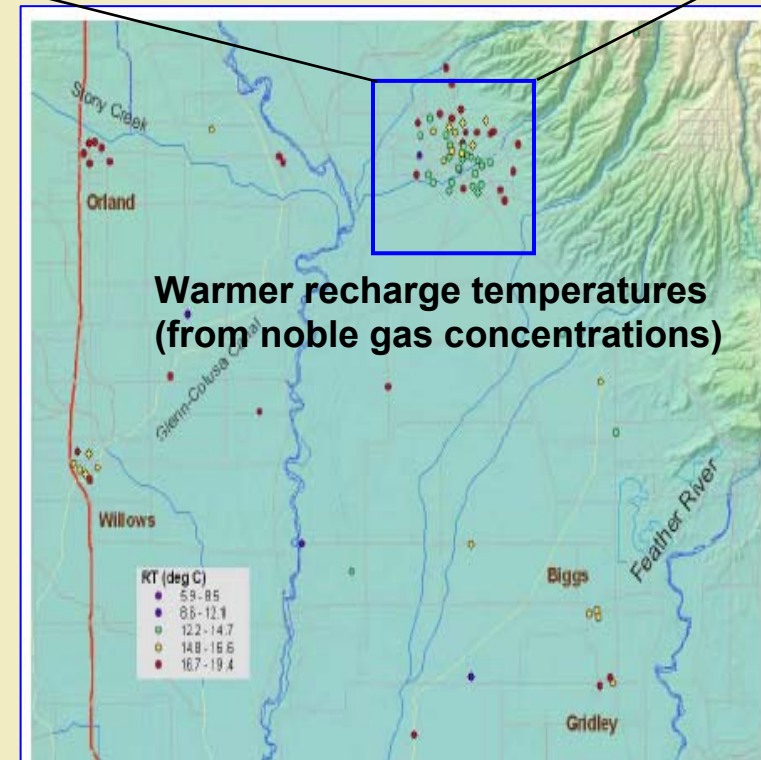
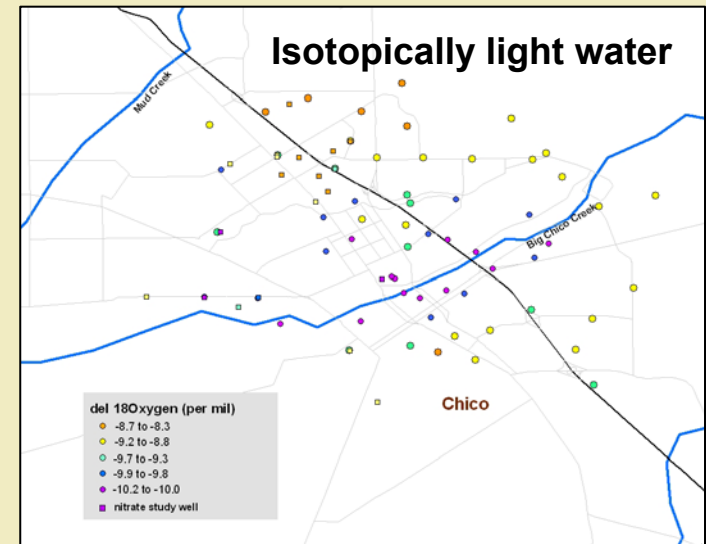
- Reliant on groundwater
- High nitrate since 1980's
- Management plan in effect

■ LLNL Study

- **Goal:** Improve understanding of nitrate fate and transport
- **Multi-tracer approach:**
 - Stable isotopes, excess N_2
 - 3H - 3He age, recharge T
 - Trace organics

■ Early findings

- **No** denitrification
- Trace organics associated with septic (caffeine & nonylphenol) detected
- Recent recharge in Chico low in NO_3



Looking to the future: GAMA Special Studies

■ Septic systems

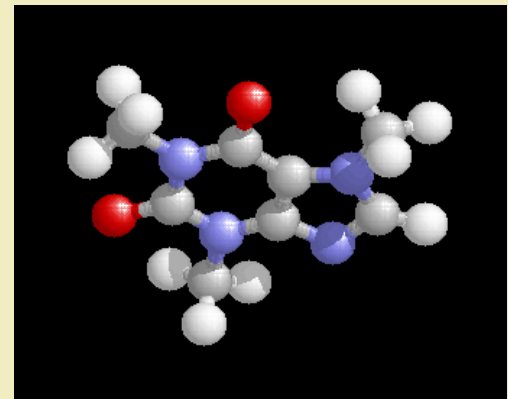
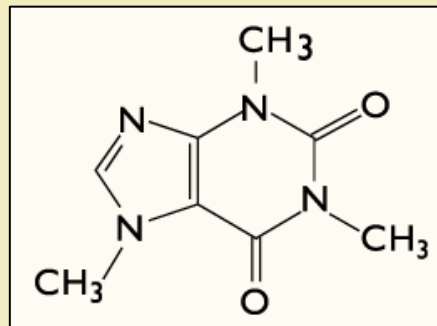
- Field-based Studies of Water Quality Impacts of Septic Systems to Groundwater Basins



■ Emerging contaminants

- Development of standard methods for wastewater indicator compounds and emerging contaminants for technology transfer

Caffeine



Acknowledgements

■ SWRCB Funding

- Groundwater Ambient Monitoring & Assessment (GAMA) Program in collaboration with the USGS

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- Central Valley Regional Water Quality Control Board

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- G. Bryant Hudson
- Steve Carle
- Harry Beller
- Walt McNab
- Staci Kane
- Michael Singleton
- Tracy LeTain
- Cheryl Moody-Bartel
- Roald Leif
- Will McConihe

Contact Information and Publications

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■ Publications

- **Llagas Basin Study:** Carle S. F., Esser B. K., and Moran J. E. (2006) High-resolution simulation of basin scale nitrate transport considering aquifer system heterogeneity. *Geosphere (Special Issue: Modeling Flow and Transport in Physically and Chemically Heterogeneous Media)*, In Press.
- **Livermore-Amador Basin Study:** Moore K., Ekwurzel B. E., Esser B. K., Hudson G. B., and Moran J. E. (2006) Sources of groundwater nitrate revealed using residence time and isotope methods. *Applied Geochemistry*, In Press.

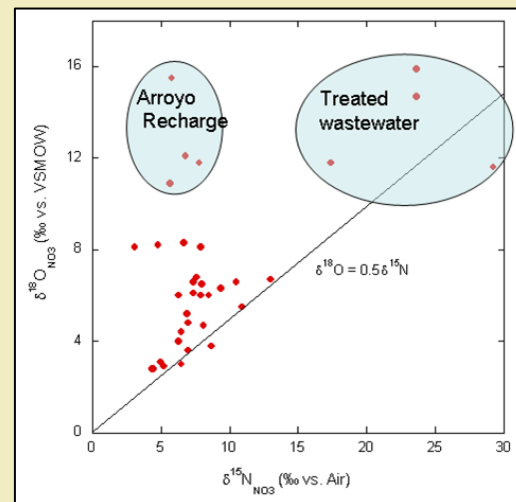
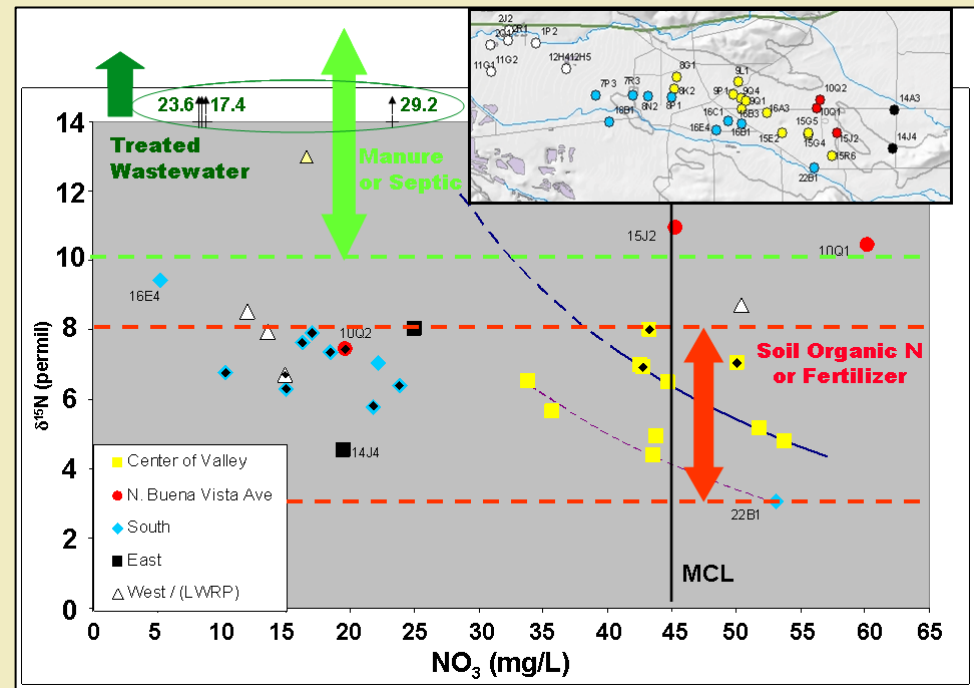
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 - Dilutes nitrate near supply wells.

Multiple sources of nitrate exist.

- **N** source is of historical livestock origin and is decreasing.
- **SE** source is a combination of fertilizer and soil N.
- **NE** source is treated wastewater.
- **Septic** sources, if present, are a *minor* contribution.



Nitrate-N isotopic composition

Nitrate-N & -O isotopic composition