# Using Nitrate Isotopes to Identify Sources of Nitrogen in the Wakulla Springs Basin

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# Outline of Presentation

- **Brief background information** on nitrate isotopes* and ranges of nitrate isotope values for various N sources

- **Nitrate isotope data for water samples collected in the Wakulla Springs basin**

*analytical technique has been around for ~ 12 yrs






# What are Nitrate ($NO_3$) Isotopes?

- All elements have more than one isotope, some of which are stable (do not decay) and some are unstable (radioactive).

- The nitrate (**$NO_3^-$**) molecule contains nitrogen and oxygen. Nitrogen has 2 stable isotopes (**$^{15}N$ and $^{14}N$**); oxygen has 3: (**$^{18}O$**, $^{17}O$ and **$^{16}O$**).

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $^{12}O$ 26.9s 2p | $^{13}O$ 26.9s $\beta^+$ | $^{14}O$ 70.6s $\beta^+\gamma$ | $^{15}O$ 122s $\beta^+\varepsilon$ | $^{16}O$ 99.76 | $^{17}O$ 0.04 | $^{18}O$ 0.20 | $^{19}O$ 26.9s $\beta^-\gamma$ | $^{20}O$ 13.5s $\beta^-\gamma$ |
| | $^{12}N$ 11ms $\beta^+\gamma$ | $^{13}N$ 9.97m $\beta^+$ | $^{14}N$ 99.63 | $^{15}N$ 0.37 | $^{16}N$ 7.13s $\beta^-\gamma$ | $^{17}N$ 4.17s $\beta^-\gamma$ | $^{18}N$ 0.62s $\beta^-\gamma$ | $^{19}N$ 0.3s $\beta^-\gamma$ |

- Changes in the ratios of the less abundant isotope ($^{15}N$ relative to $^{14}N$) and ($^{18}O$ relative to $^{16}O$) reflect biological and physical processes and can be used as tracers of these processes.

# How are Nitrate Isotope Data Reported?

- Changes in the ratio of nitrogen isotopes ($^{15}N/^{14}N$) are reported relative to atmospheric nitrogen in parts per thousand (‰).

- If a sample has a value of 0 ‰ then it has the same composition as atmospheric N

- If it has a higher value, it contains more $^{15}N$; a lower value then more $^{14}N$.

- $\delta^{15}N$ (‰) = $([^{15}N/^{14}N]_{sample}/[^{15}N/^{14}N]_{standard}\ -1)*1000$

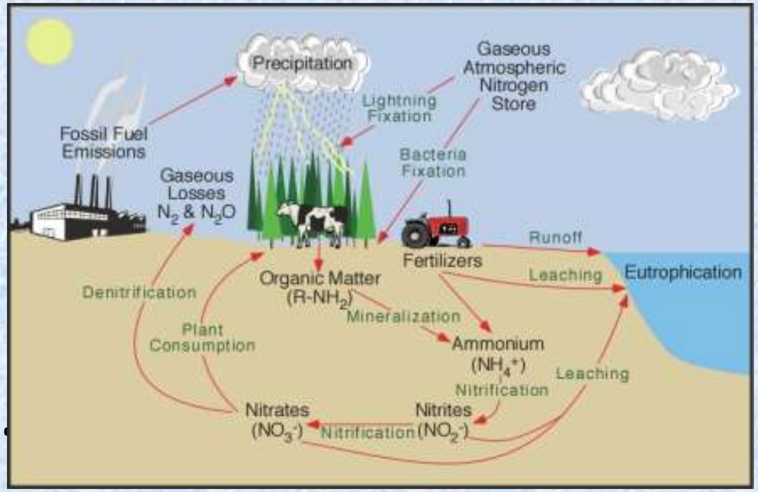
# How are Nitrate Isotope Data Reported?

- By convention, changes in the ratio of oxygen isotopes ($^{18}O/^{16}O$) in nitrate are reported relative to standard mean ocean water (VSMOW) in parts per thousand (‰).

- $\delta^{18}O$ (‰) $=([^{18}O/^{16}O]_{sample}/[^{18}O/^{16}O]_{standard} -1)*1000$

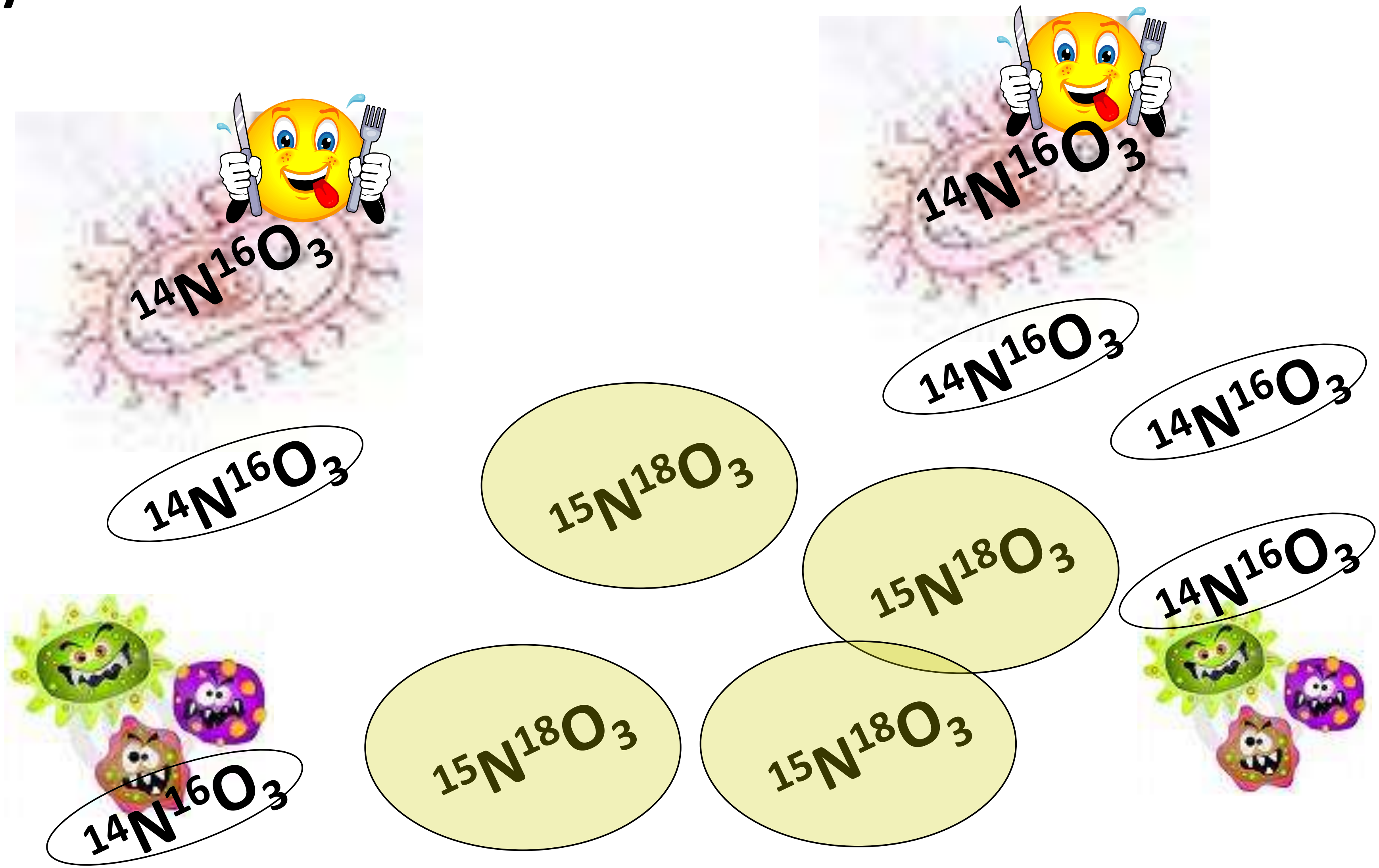
# Isotopic Fractionation

- During biological processes (e.g. nitrification, denitrification), the lighter isotope ($^{14}N$, $^{16}O$) ends up being concentrated in the products while the heavier isotope ends up being concentrated in the reactants.

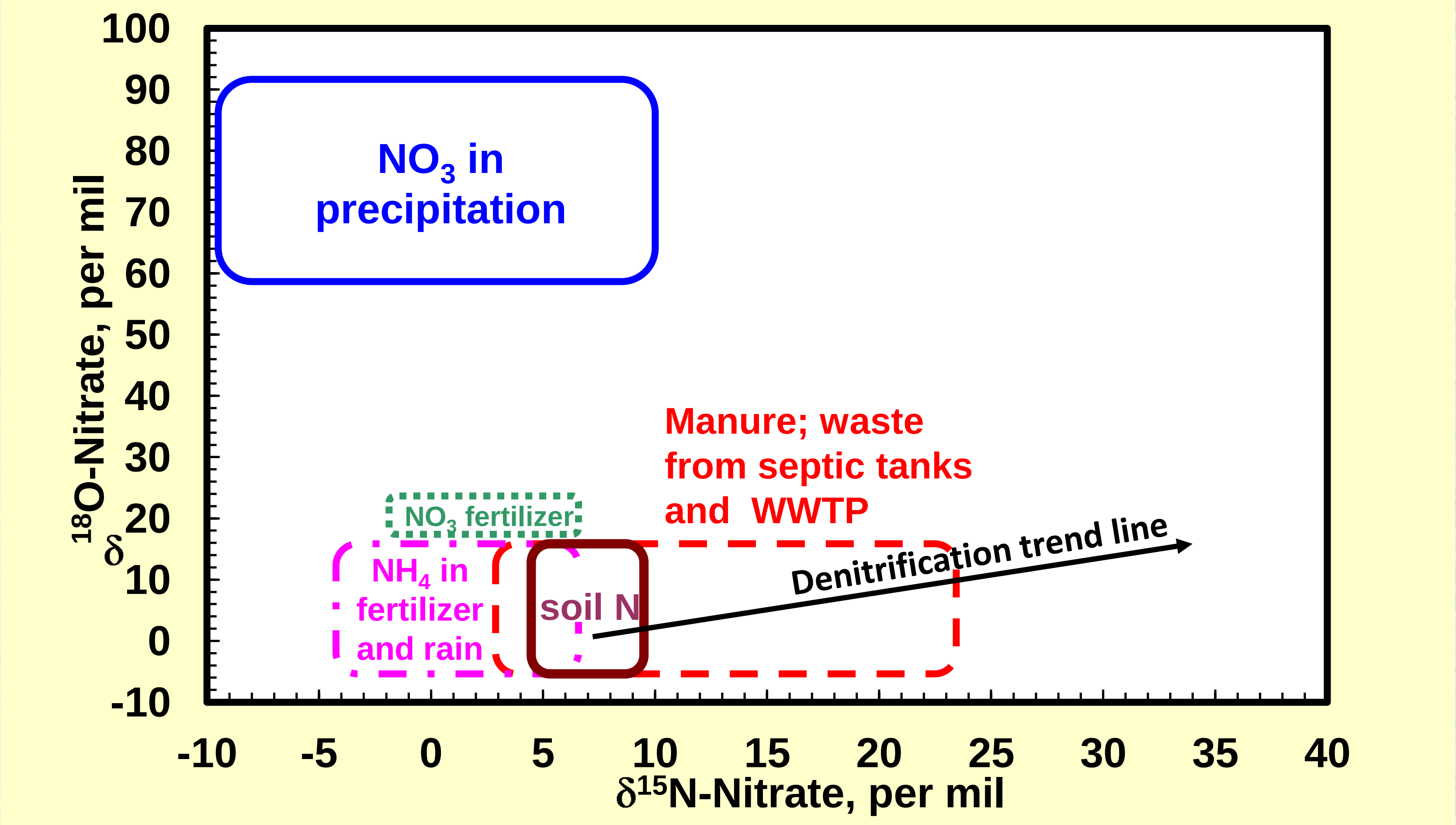


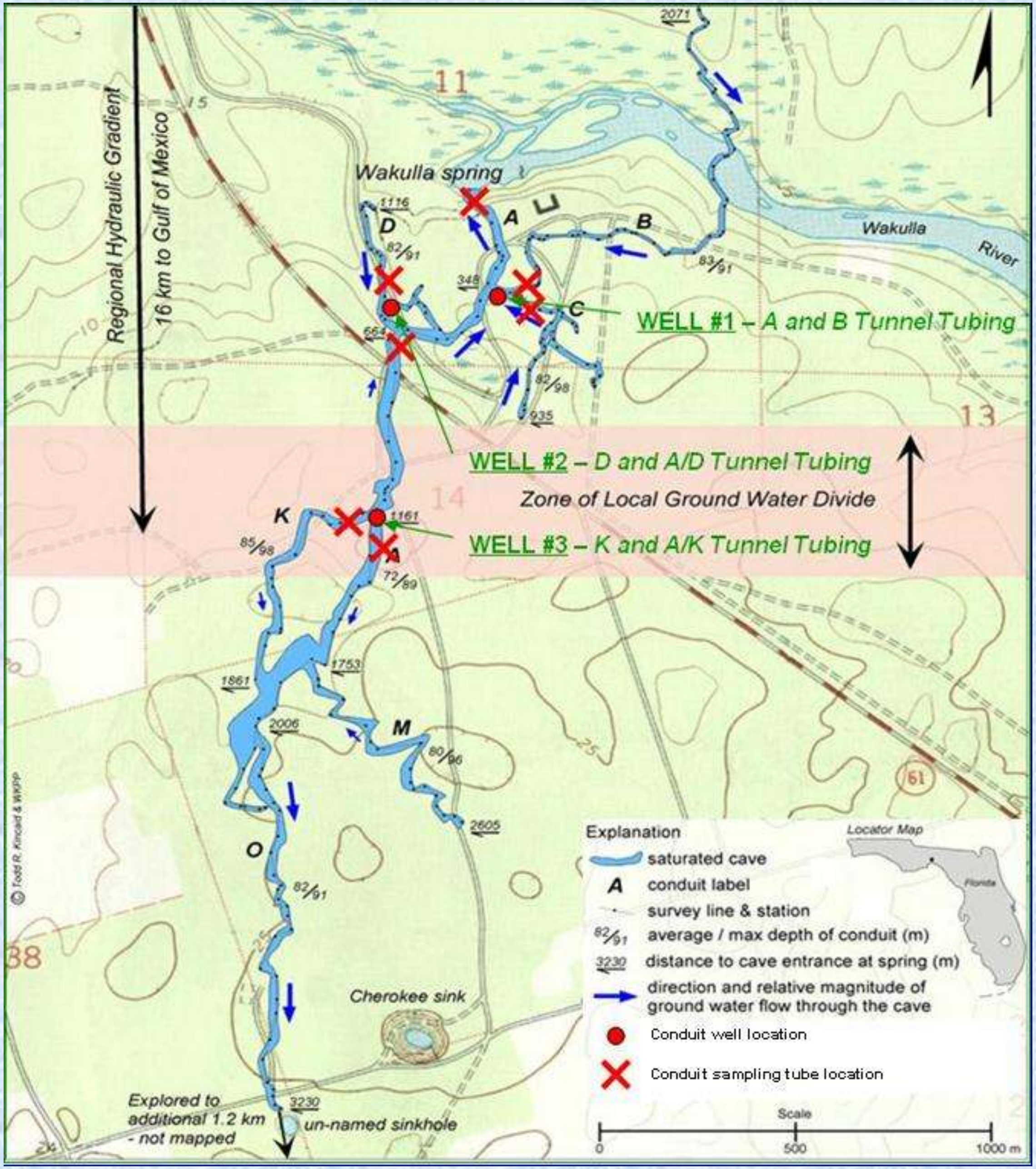

- So, during denitrification ($NO_3^- \rightarrow N_2O \rightarrow N_2$), the resulting $N_2$, $N_2O$ (products) have a lower $\delta^{15}N$ and $\delta^{18}O$ than the residual $NO_3$ (reactant), which develops a higher $\delta^{15}N$ and $\delta^{18}O$.

# Denitrification– conversion of nitrate to nitrogen gas ($N_2$) by bacteria



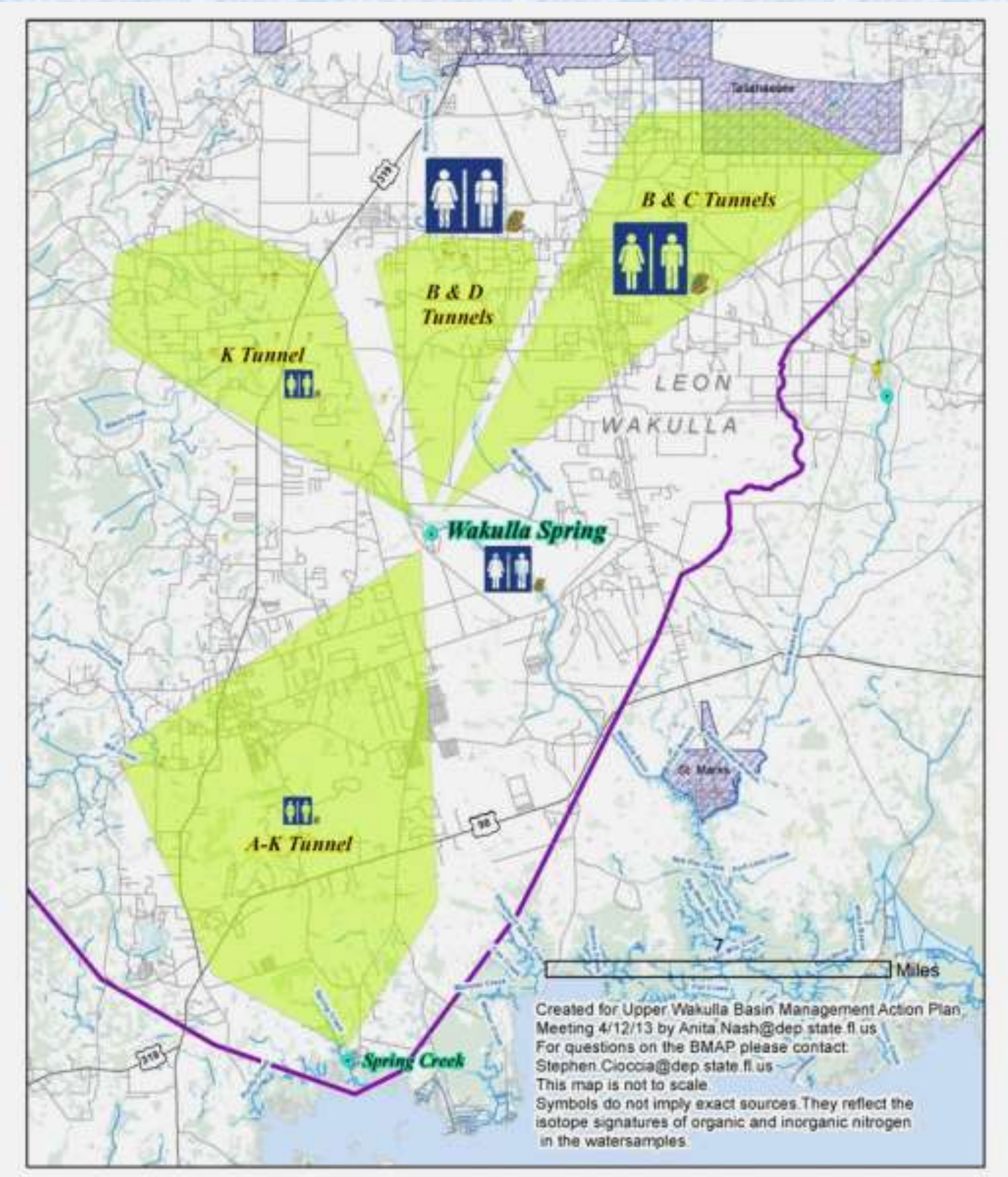
# Ranges of δ$^{15}$N and δ$^{18}$O of nitrate from different sources– and from transformation processes

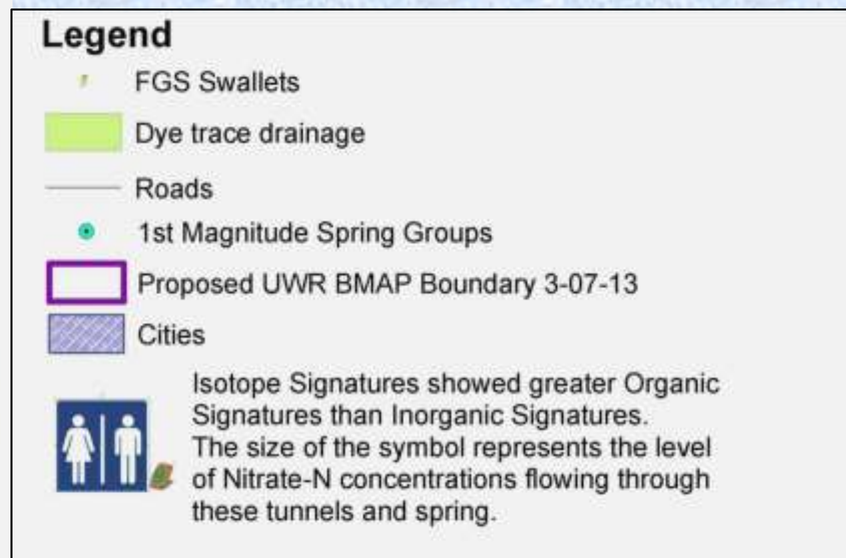




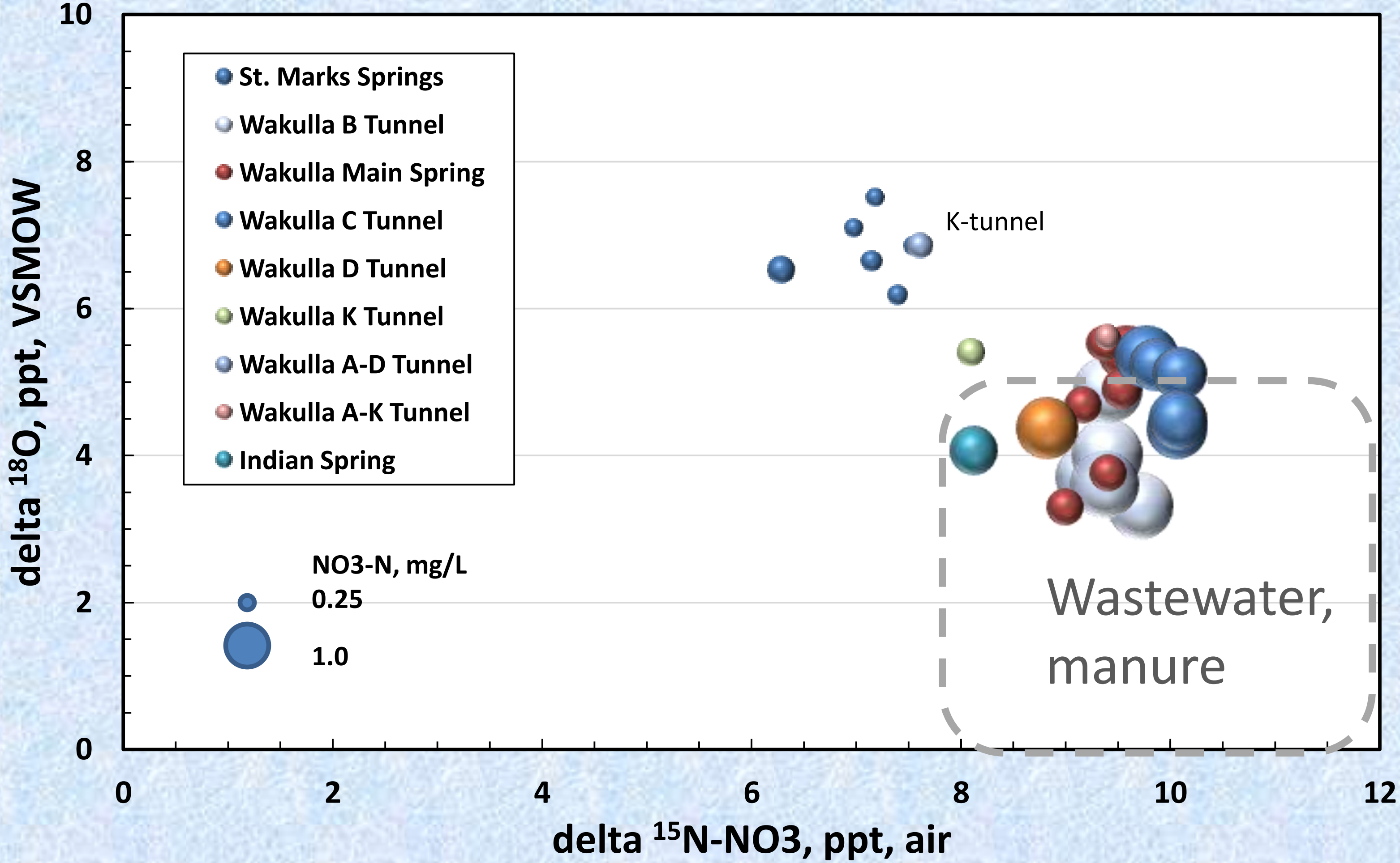

# Wakulla Springs Cave System—water samples collected during March-December 2011 for nitrate isotopes and other chemical indicators.

# Sources of nitrate and direction of groundwater flow based on dye trace studies for Wakulla Springs and associated tunnels.



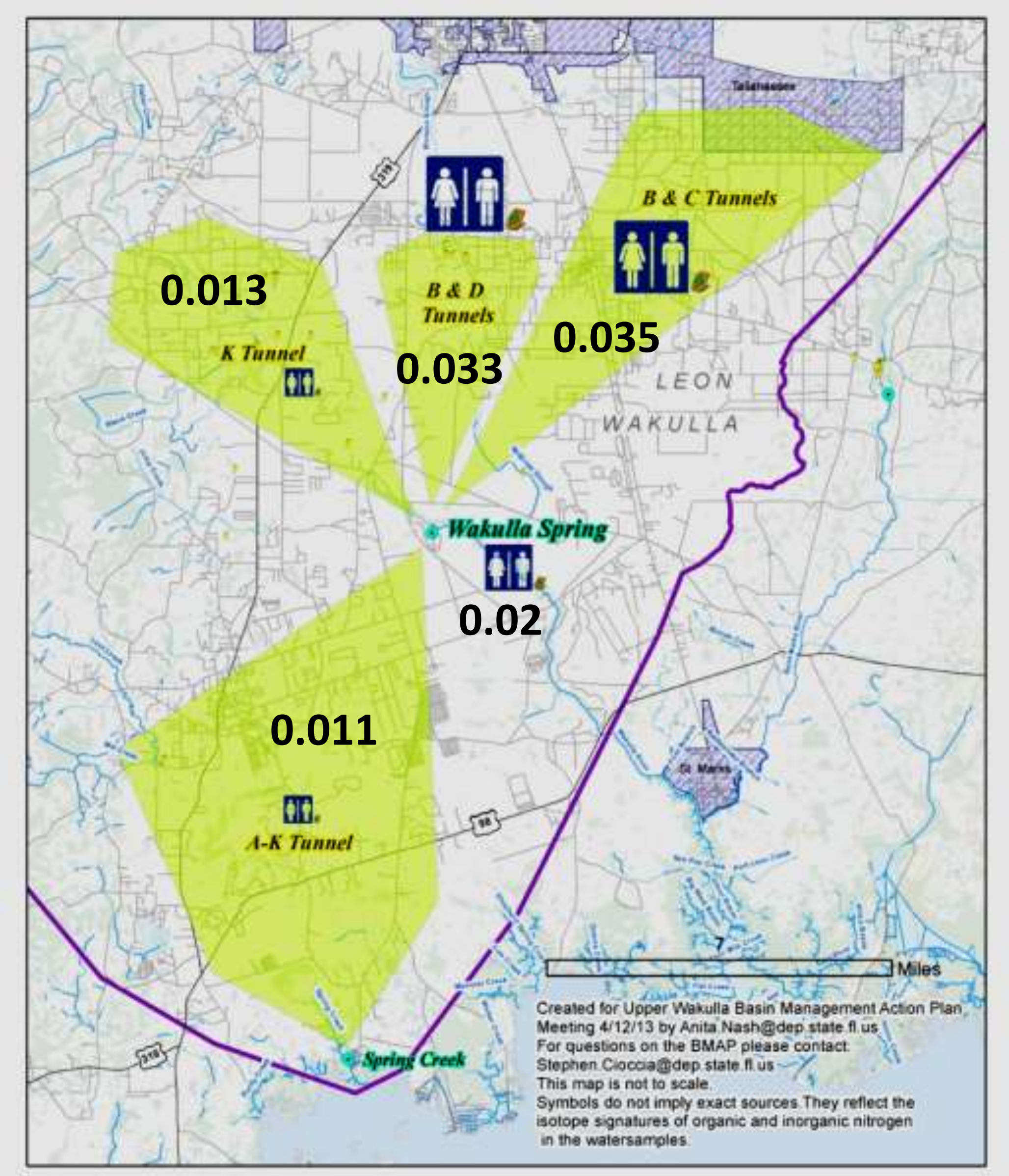
# Nitrate isotope data– water samples collected by FDEP (March-Dec 2011)

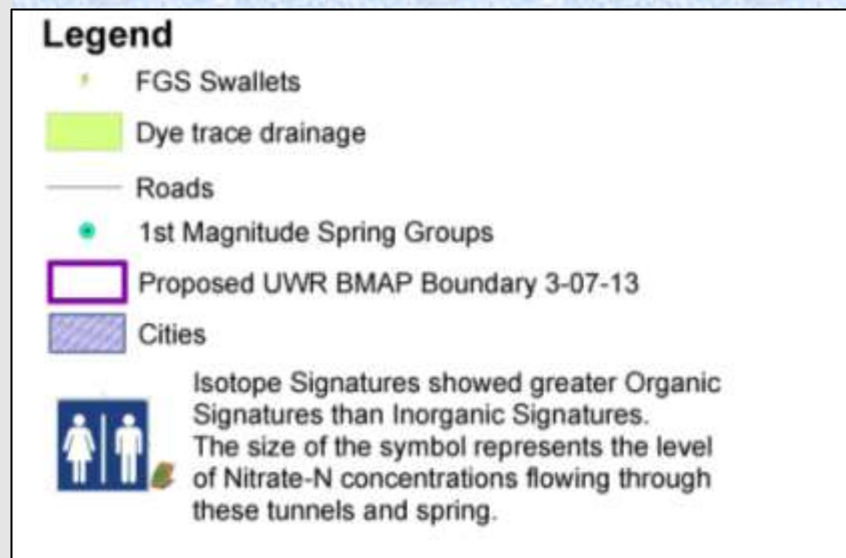


# Sucralose as a Tracer of Wastewater

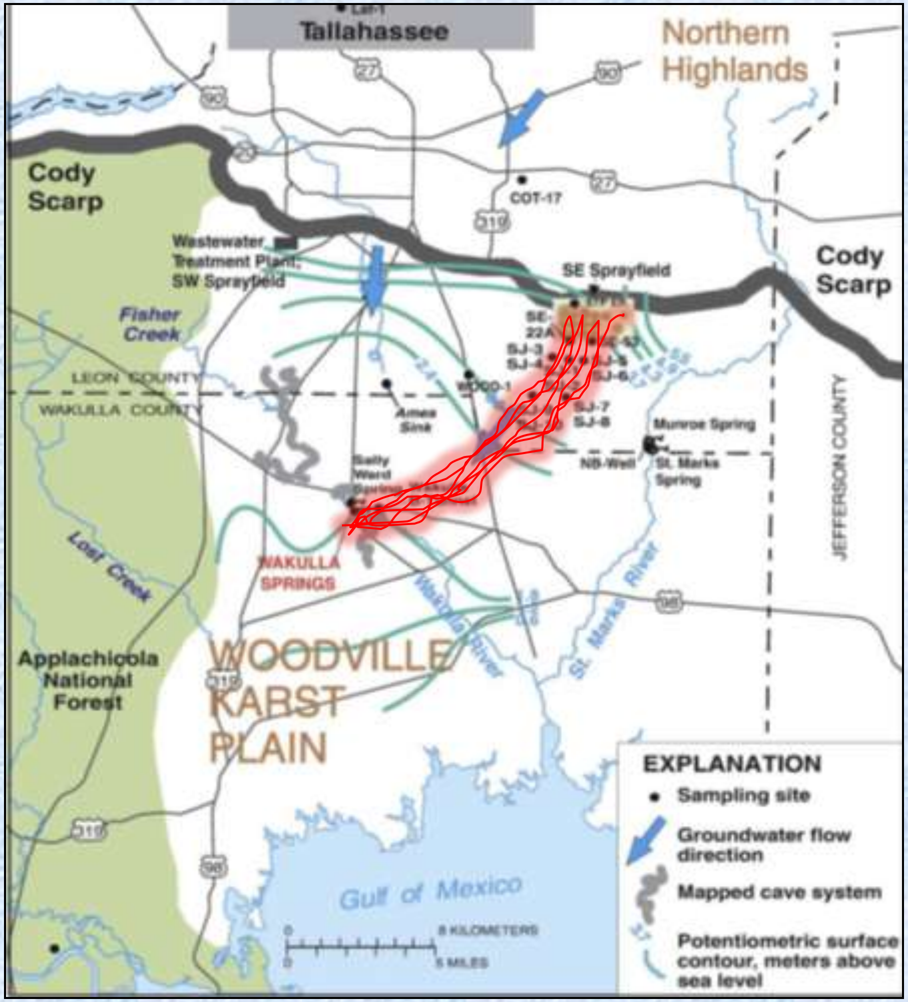
- **Studies around the world have detected sucralose in groundwaters with wastewater influence.**
- **The vast majority of sucralose passes through wastewater and water treatment systems into the final effluent.**
- **It is not affected by chlorination treatment and even survives tertiary-grade wastewater treatment.**

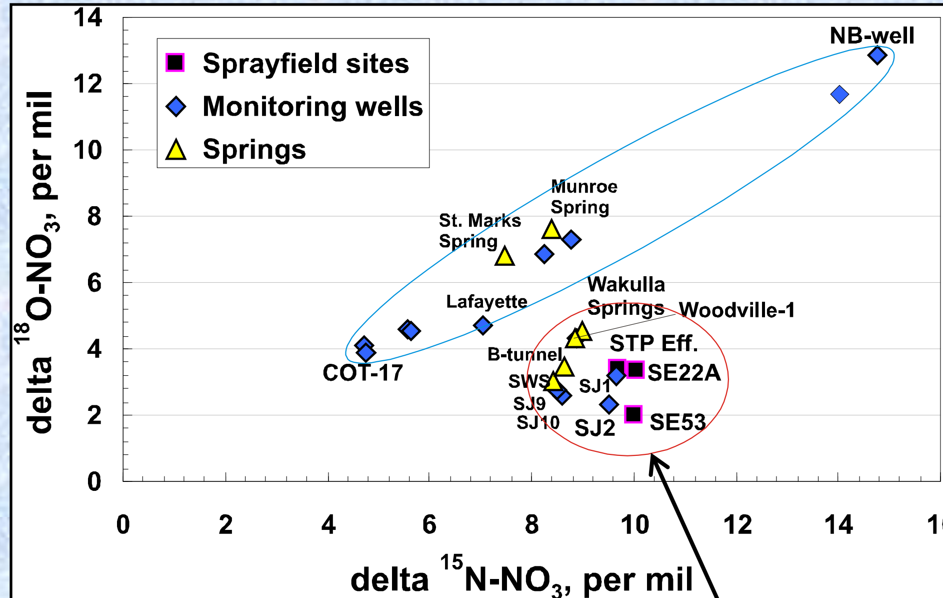
# Median Sucralose concentrations (ppb) in Wakulla Springs and associated tunnels (2011-2012)



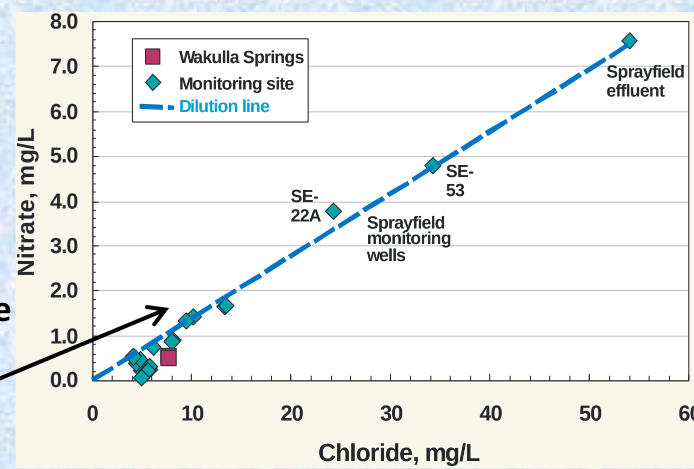



# Tallahassee Sprayfield Study



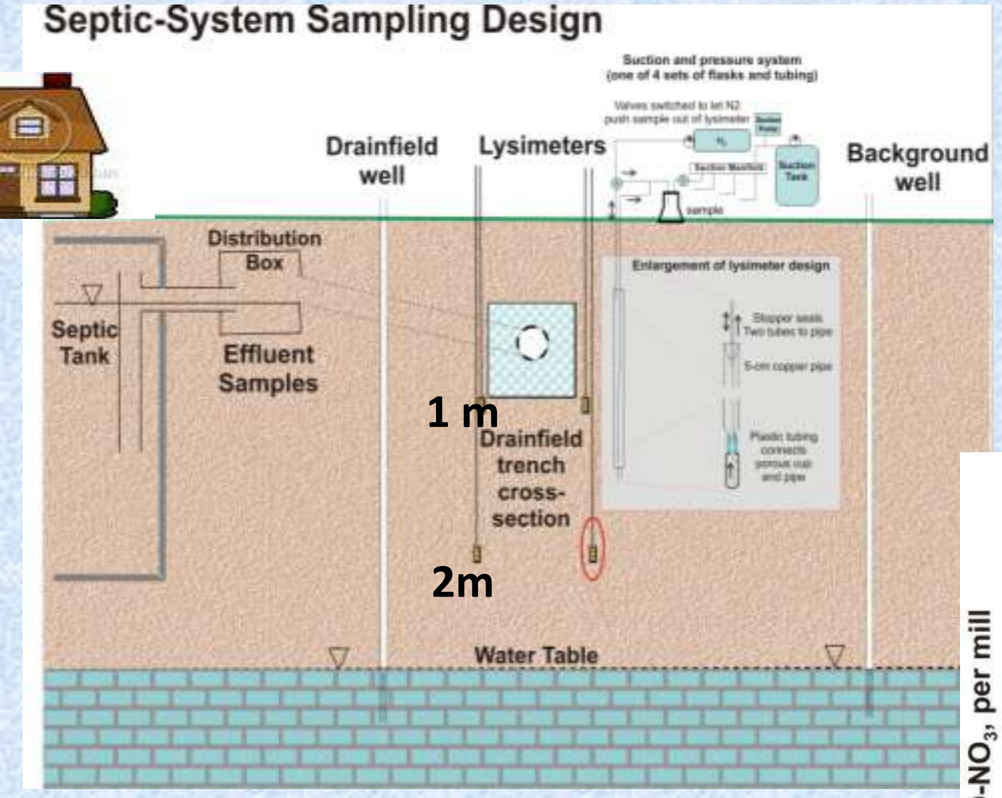




*****Distinct N and O isotopic signature for nitrate was found for downgradient waters affected by sprayfield effluent–***

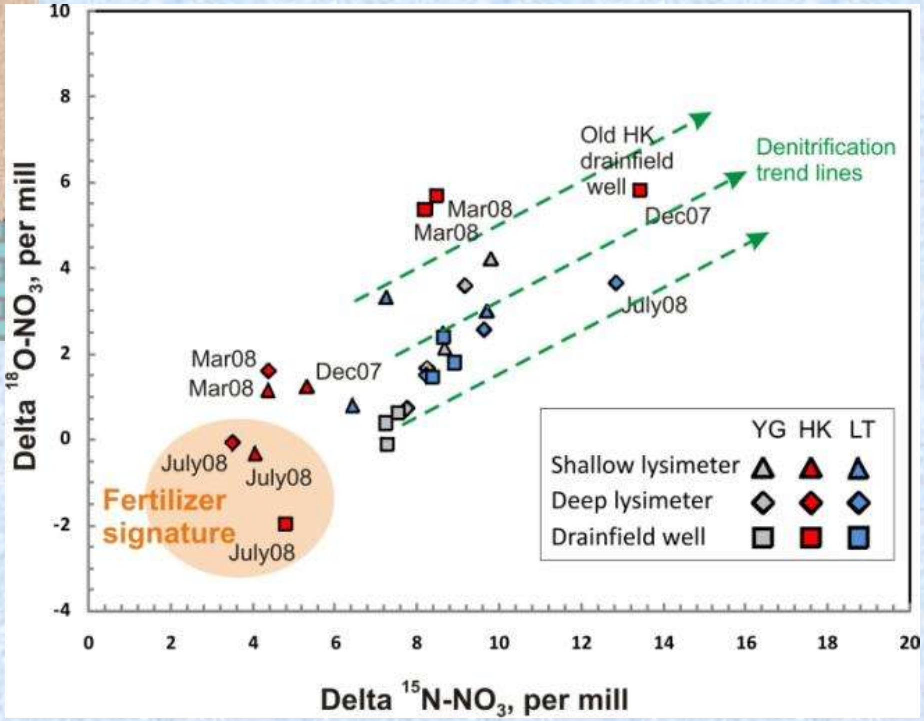



**Nitrate moves with chloride and plots along a dilution line from the sprayfield effluent.**

# Septic Tank Study—Woodville Karst Plain





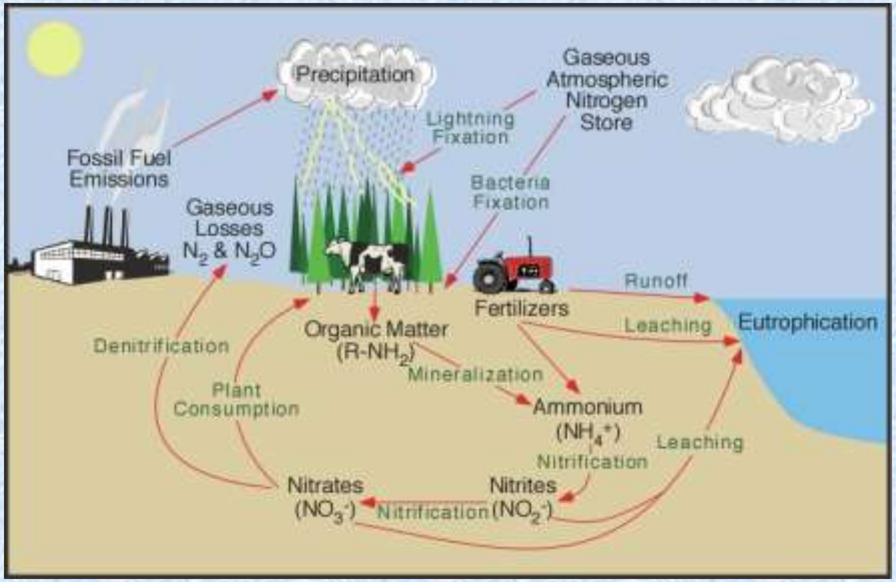



**Evidence for some denitrification in shallow lysimeters;**

**Information about fertilizer application is consistent with the lower $^{15}$N signal.**

# Summary

- Nitrate isotopes ($^{15}N/^{14}N$ and $^{18}O/^{16}O$ of $NO_3$) can provide important information about contaminant sources and nitrogen transformation processes.




- Nitrate isotopes are one tool in the toolbox– other information needed on the land use, hydrology and other chemical indicators to understand sources and processes.

# Questions ??

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# Determining $\delta^{15}N$ and $\delta^{18}O$ of nitrate in water (Revesz and Casciotti, 2007)

• A culture of denitrifying bacteria (Pseudomonas chlororaphis and P. aureofaciens) is used to convert nitrate ($NO_3$) to nitrous oxide ($N_2O$), which is analyzed by mass spectrometry


• The denitrifying bacteria are used in the enzymatic conversion of $NO_3$ to $N_2O$

$NO_3 - \rightarrow NO_2 - \rightarrow NO \rightarrow 1/2\ N_2O$