

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

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Wakulla Springs BMAP meeting

April 18, 2013



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 (NO₃) Isotopes?

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



- The nitrate (**NO₃⁻**) molecule contains nitrogen and oxygen. Nitrogen has 2 stable isotopes (**¹⁵N and ¹⁴N**); oxygen has 3: (**¹⁸O**, ¹⁷O and **¹⁶O**).

¹² O 26.9s 2p	¹³ O 26.9s β ⁺	¹⁴ O 70.6s β ⁺ γ	¹⁵ O 122s β ⁺ ε	¹⁶ O 99.76	¹⁷ O 0.04	¹⁸ O 0.20	¹⁹ O 26.9s β ⁻ γ	²⁰ O 13.5s β ⁻ γ
	¹² N 11ms β ⁺ γ	¹³ N 9.97m β ⁺	¹⁴ N 99.63	¹⁵ N 0.37	¹⁶ N 7.13s β ⁻ γ	¹⁷ N 4.17s β ⁻ γ	¹⁸ N 0.62s β ⁻ γ	¹⁹ N 0.3s β ⁻ γ

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

How are Nitrate Isotope Data Reported?

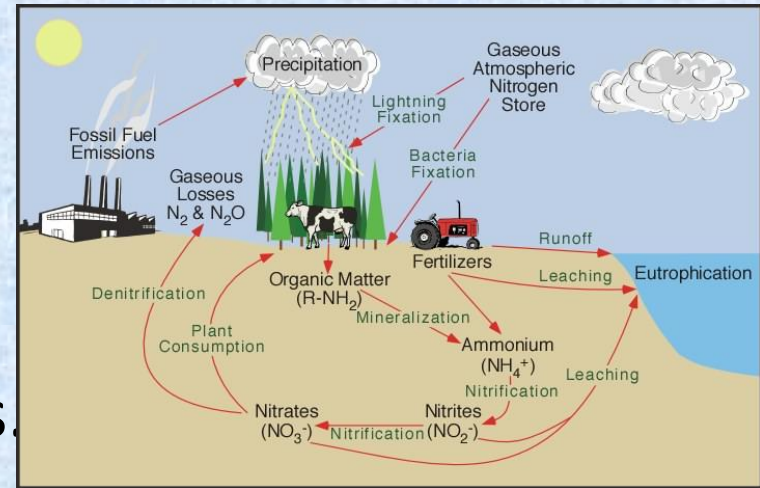
- Changes in the ratio of nitrogen isotopes ($^{15}\text{N}/^{14}\text{N}$) are reported relative to atmospheric nitrogen in parts per thousand (‰).
- If a sample has a value of 0 ‰ then it has the same composition as atmospheric N
- If it has a higher value, it contains more ^{15}N ; a lower value then more ^{14}N .
- $\delta^{15}\text{N} (\text{‰}) = ([^{15}\text{N}/^{14}\text{N}]_{\text{sample}}/[^{15}\text{N}/^{14}\text{N}]_{\text{standard}} - 1) * 1000$

How are Nitrate Isotope Data Reported?

- By convention, changes in the ratio of **oxygen** isotopes ($^{18}\text{O}/^{16}\text{O}$) in nitrate are reported relative to standard mean ocean water (VSMOW) in parts per thousand (‰).
- $$\delta^{18}\text{O} (\text{‰}) = ([^{18}\text{O}/^{16}\text{O}]_{\text{sample}} / [^{18}\text{O}/^{16}\text{O}]_{\text{standard}} - 1) * 1000$$

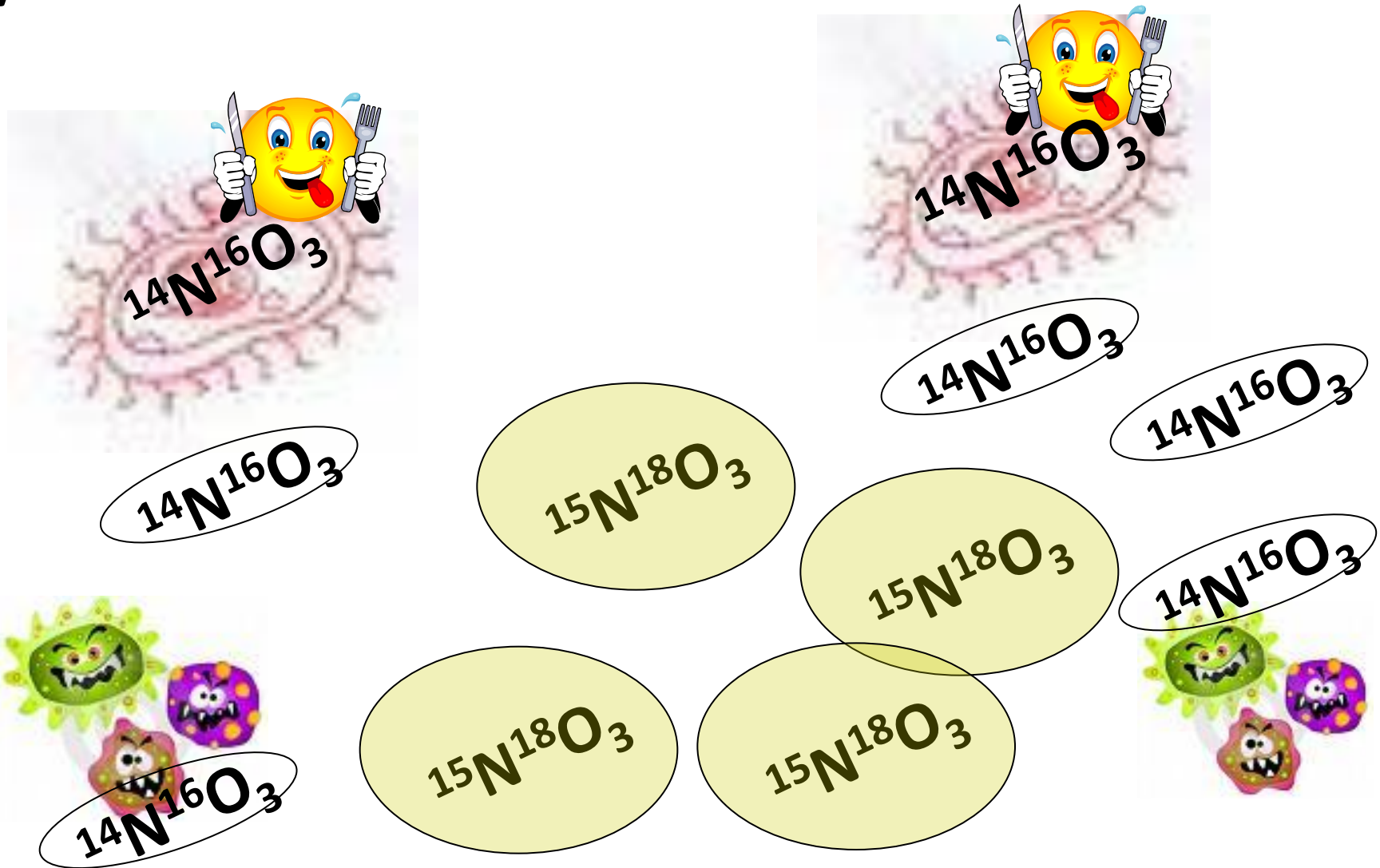
Isotopic Fractionation

➤ 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.

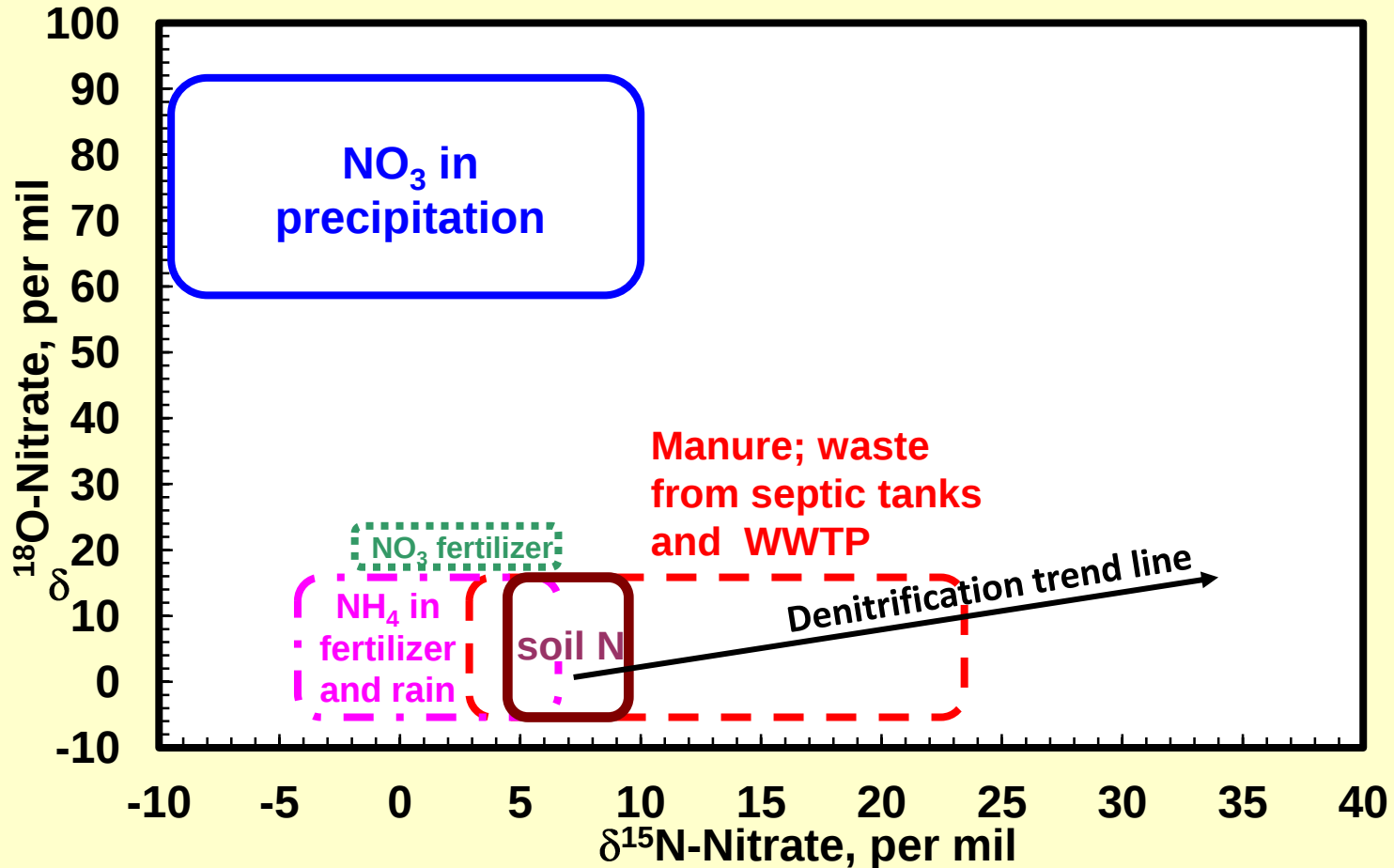


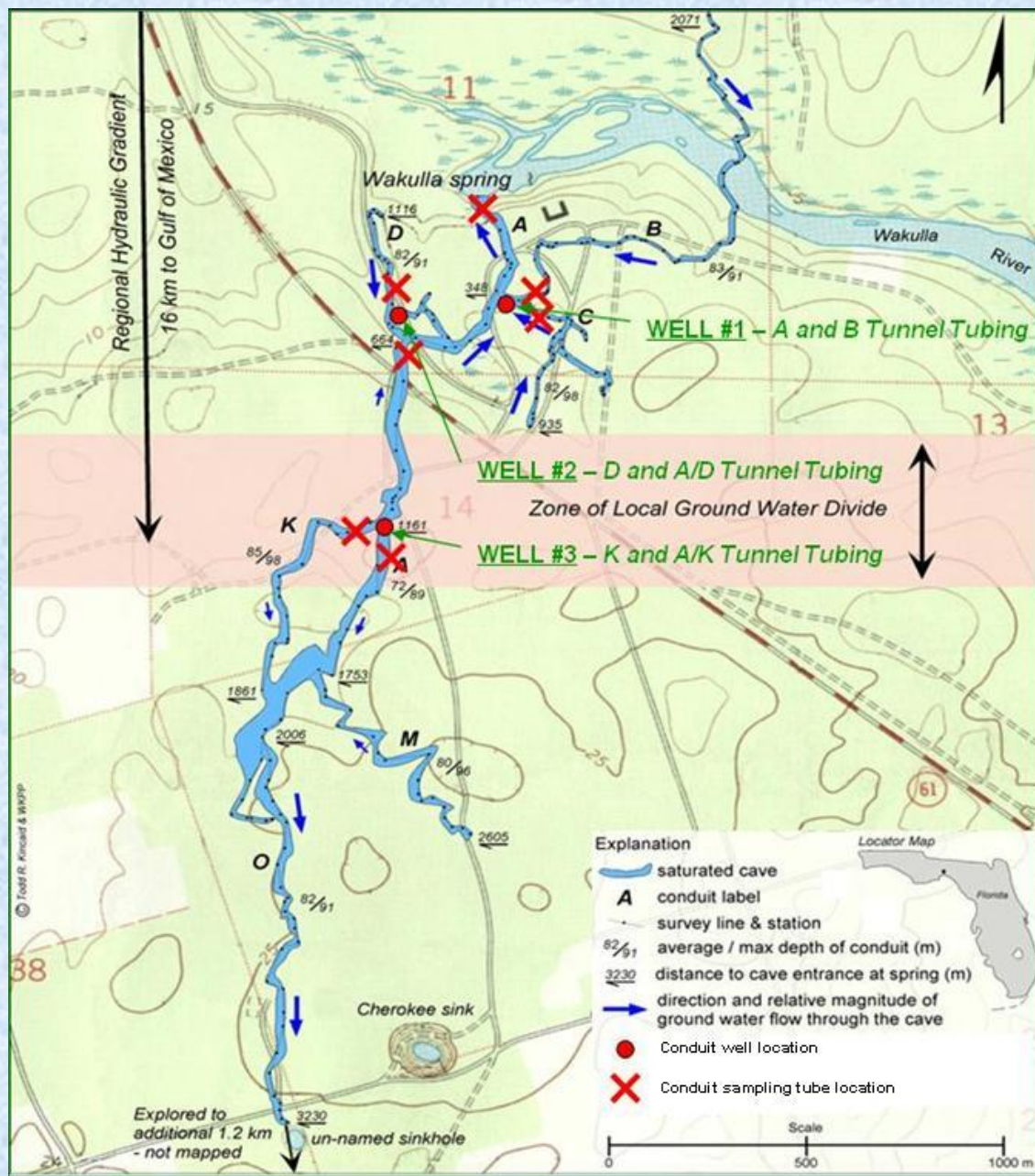
➤ So, during denitrification ($\text{NO}_3^- \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$), the resulting N_2 , N_2O (products) have a lower $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ than the residual NO_3 (reactant), which develops a higher $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$.

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



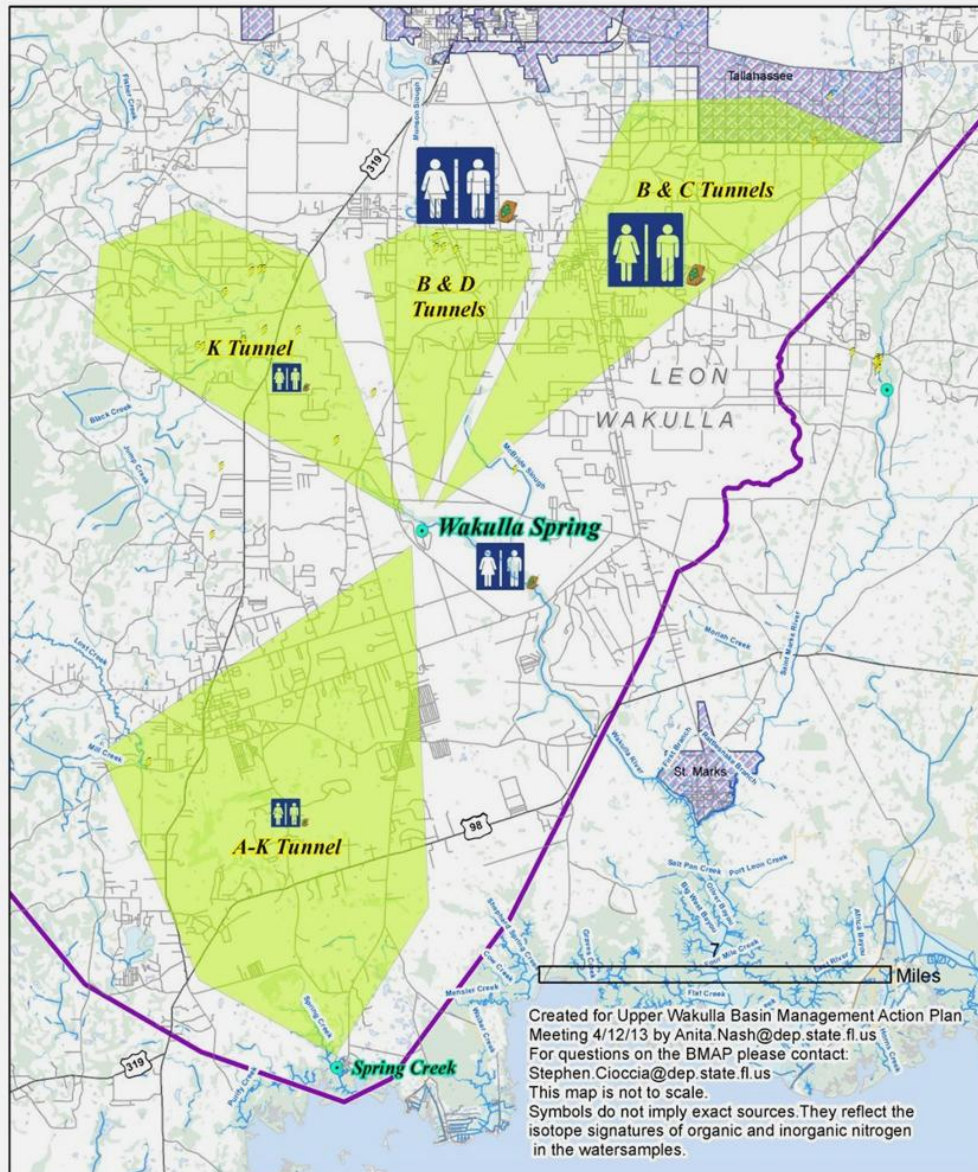
Ranges of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate from different sources— and from transformation processes





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.



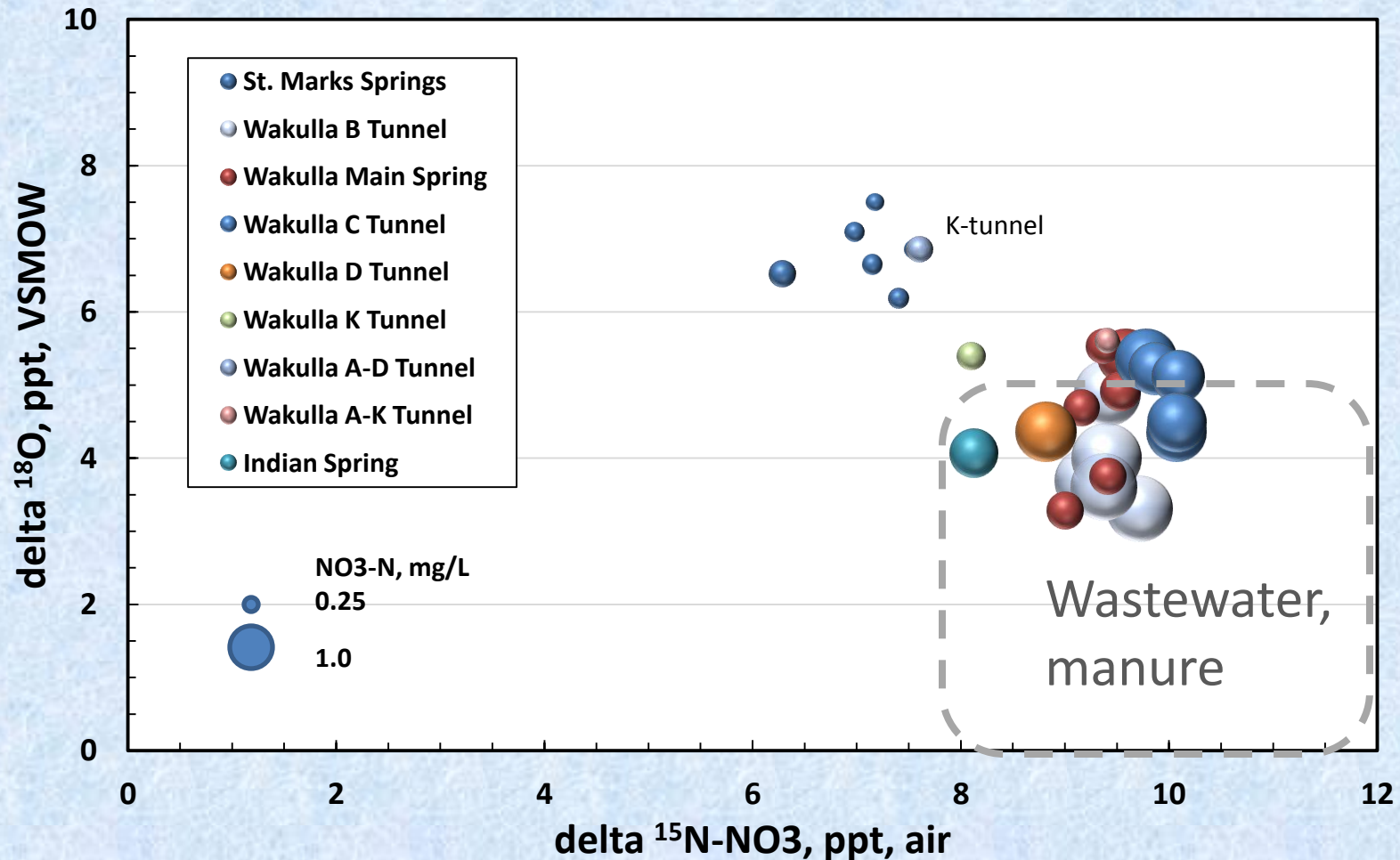
Legend

- FGS Swallets
- Dye trace drainage
- Roads
- 1st Magnitude Spring Groups
- Proposed UWR BMAP Boundary 3-07-13
- Cities



Isotope Signatures showed greater Organic Signatures than Inorganic Signatures. The size of the symbol represents the level of Nitrate-N concentrations flowing through these tunnels and spring.

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

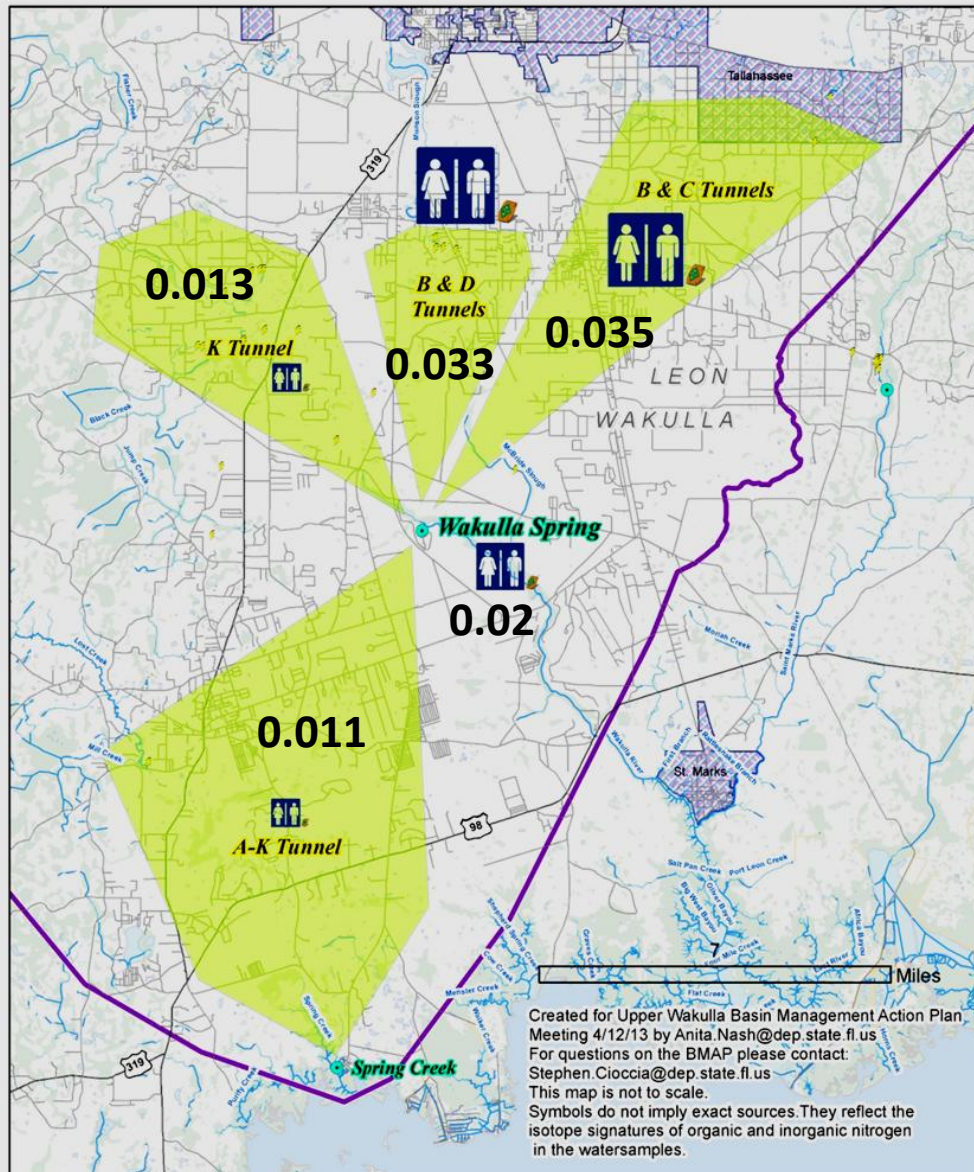


Sucralose as a Tracer of Wastewater

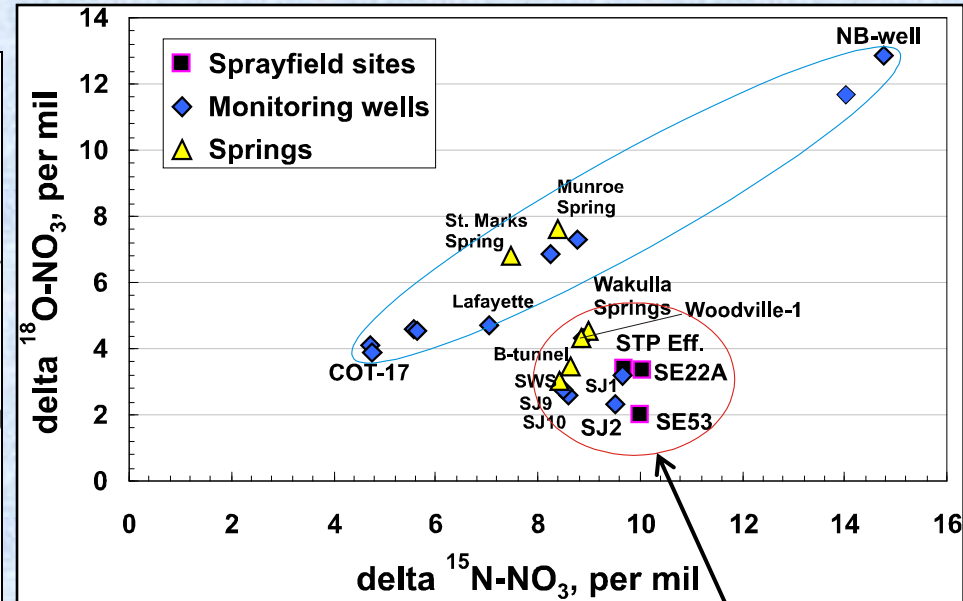
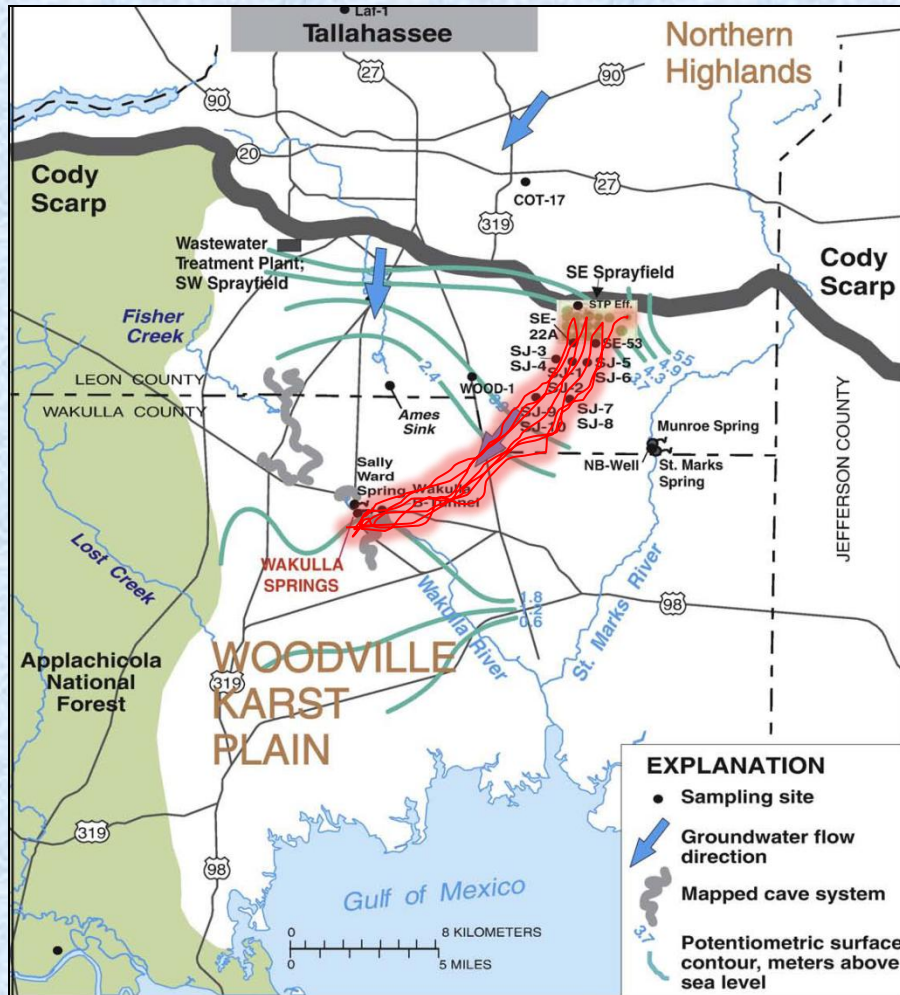


- **Studies around the world have detected sucralose in groundwaters with wastewater influence.**
- **The vast majority of sucralose passes through wastewater and water treatment systems into the final effluent.**
- **It is not affected by chlorination treatment and even survives tertiary-grade wastewater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

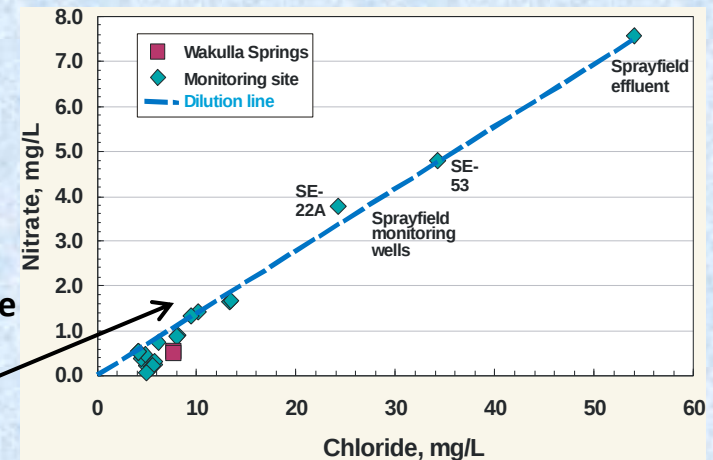
Median Sucralose concentrations (ppb) in Wakulla Springs and associated tunnels (2011-2012)



Tallahassee Sprayfield Study



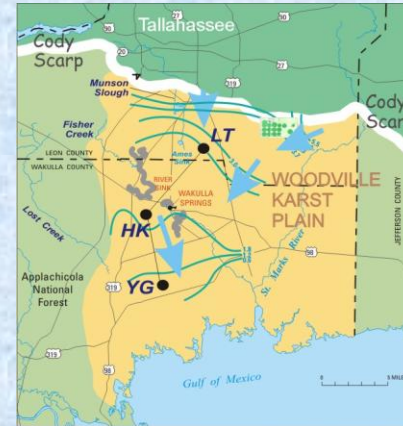
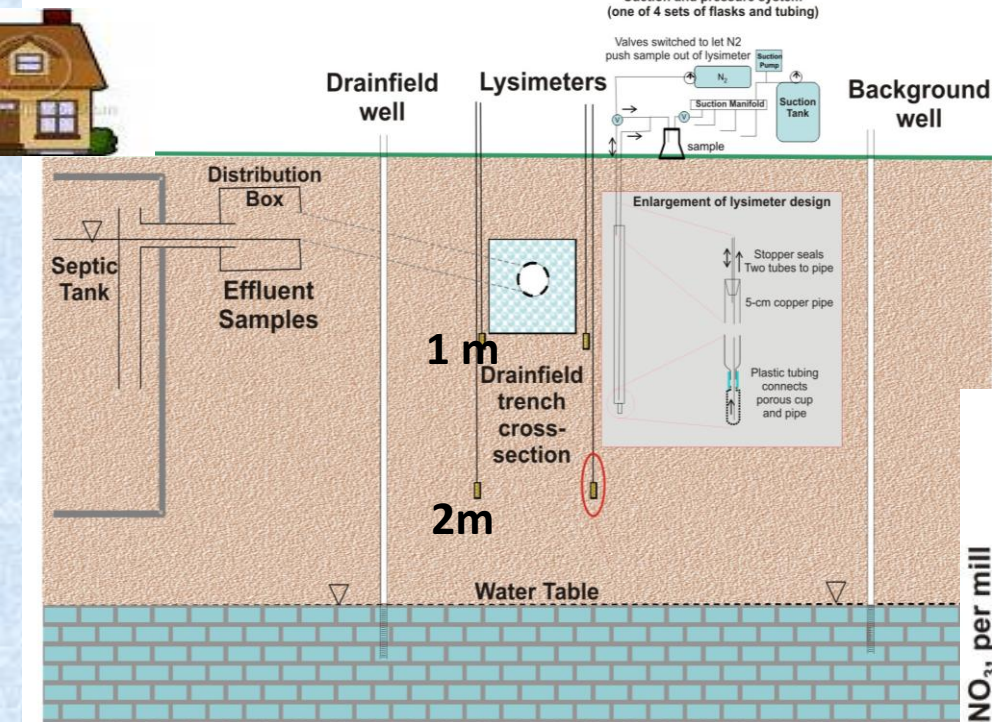
*****Distinct N and O isotopic signature for nitrate was found for downgradient waters affected by sprayfield effluent—***



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

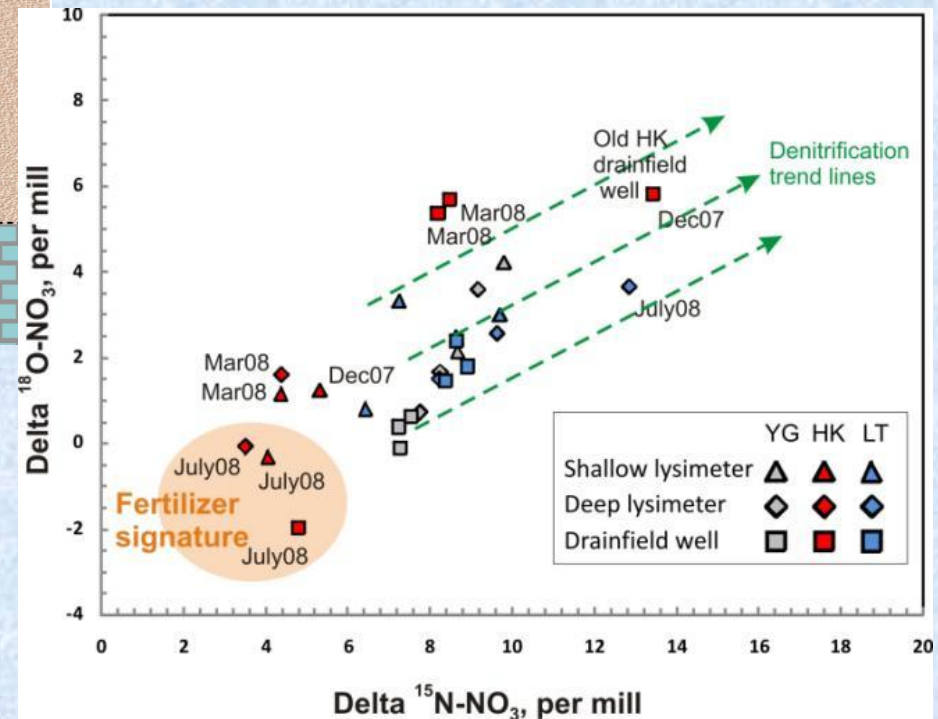
Septic Tank Study—Woodville Karst Plain

Septic-System Sampling Design



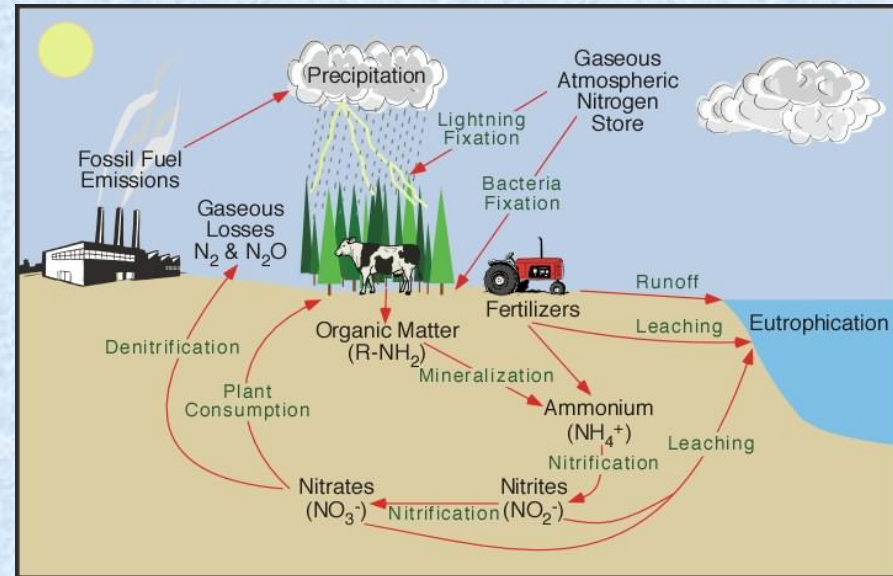
Evidence for some denitrification in shallow lysimeters;

Information about fertilizer application is consistent with the lower ¹⁵N signal.



Summary

➤ Nitrate isotopes ($^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ 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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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
 $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow 1/2 \text{N}_2\text{O}$

