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Springs Protection Assessment Using Nitrate Isotope Analysis

FSA Winter Conference
December 2021

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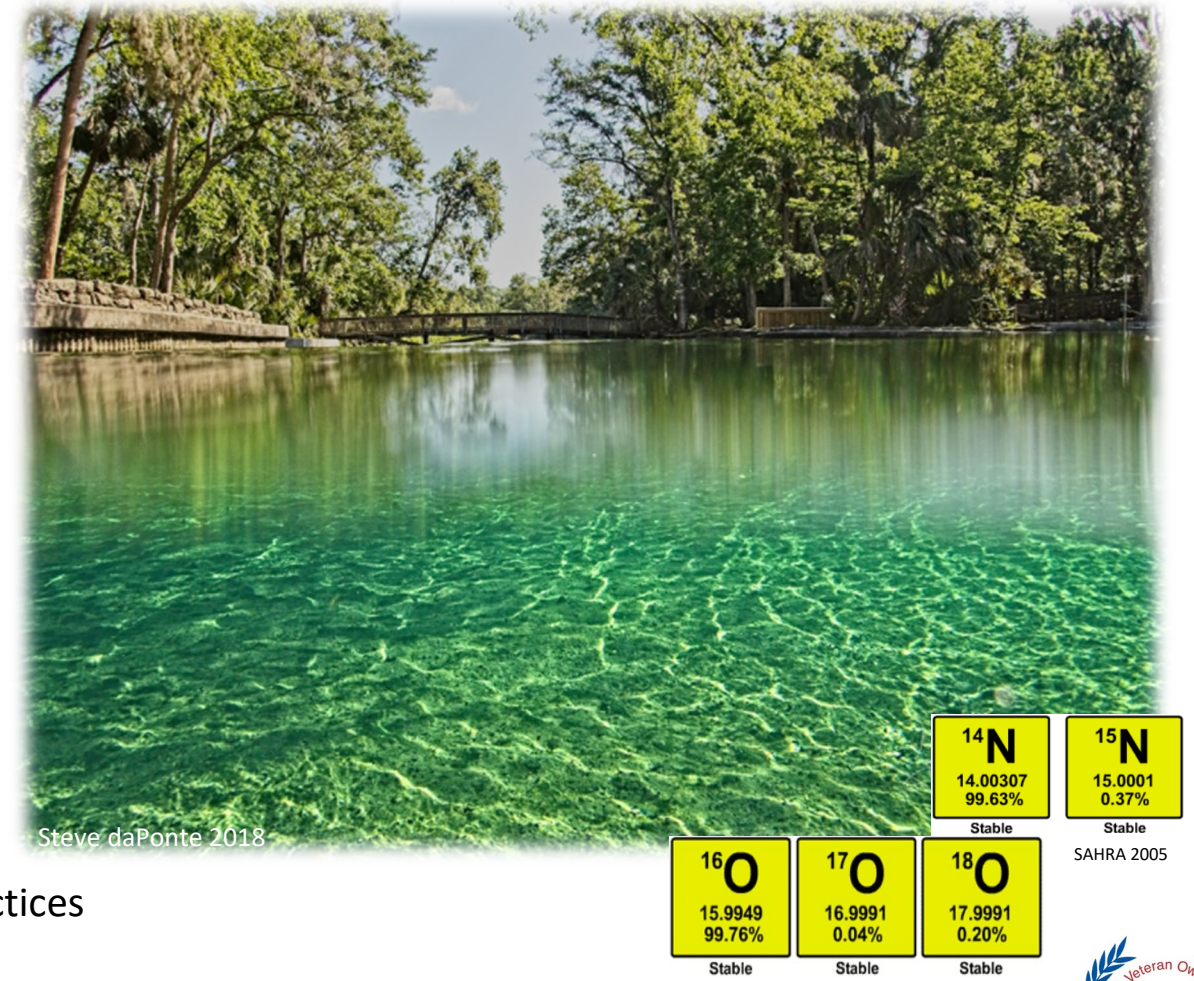
Springs Protection Assessment Using Nitrate Isotope Analysis

OUTLINE

- **Why is nitrogen so important?**
  - Nitrogen and the Springs and Aquifer Protection Act
  - Nitrogen Sources
- Dual Nitrate Isotopes
  - What they are
  - How they work
  - Data Limitations
  - Practical guidelines for sampling
- Case Study: Nitrate sources to Wekiwa spring
  - Sources of nitrate to spring
  - Mixing models
  - Outcomes: Identification of hotspots, Management Practices



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WHY IS NITROGEN SO IMPORTANT?

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Nitrogen Paradox: One of the 5 elements necessary for life, BUT more than 99% occurs as triple bonded N_2, which cannot be used by organisms.

Breaking the bond requires lots of energy

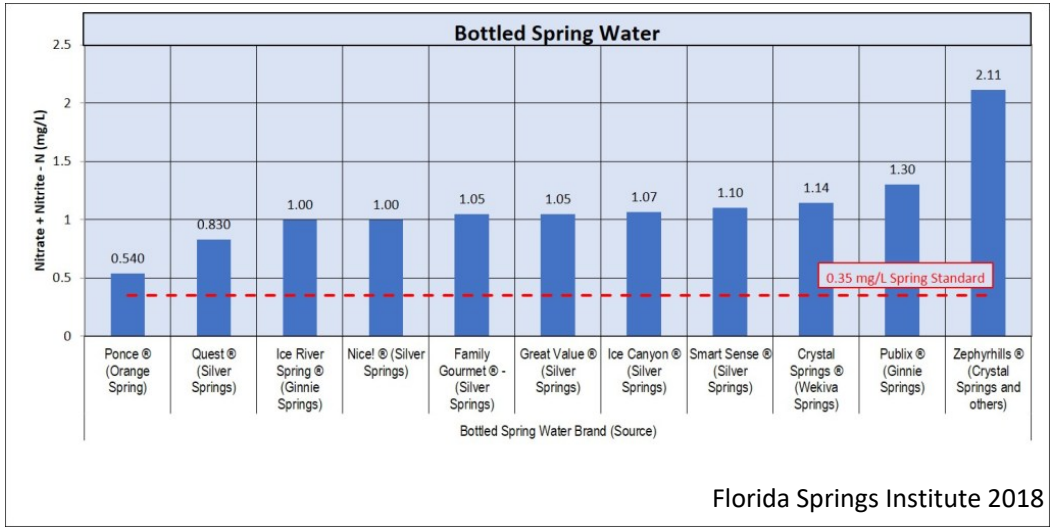
- High temperature processes (lightning)
- Nitrogen-fixing microbes

Anthropogenic inputs have caused concentrations to rise to harmful levels

- High nitrate can cause eutrophication
- In Florida, eutrophication → impaired springs

- 90% Florida's drinking water from GW
  - Springs 'window' into health of GW
  - Threaten recreational /economic value of springs

FDEP 2018



Florida Springs Institute 2018

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SPRINGS AND AQUIFER PROTECTION ACT 2016

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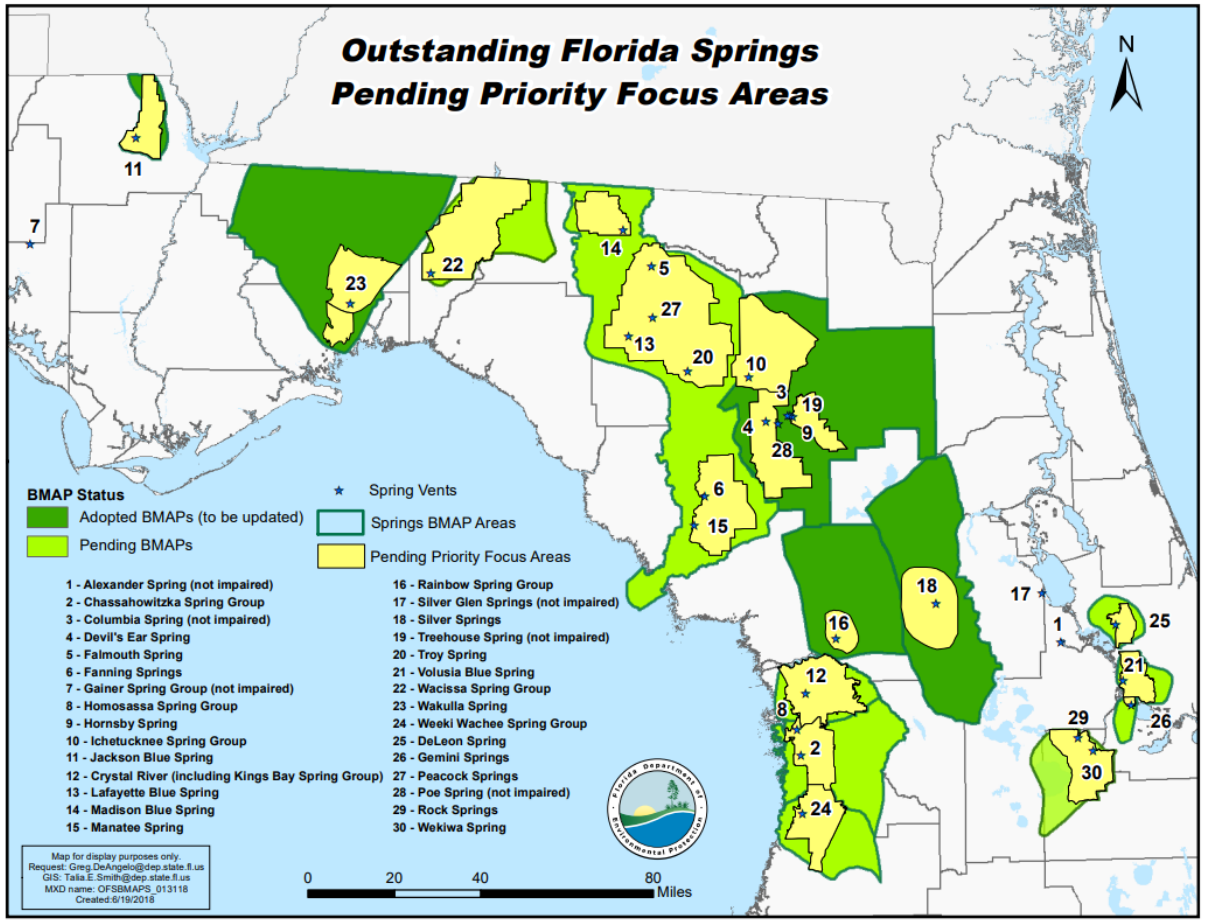
FDEP adopted 13 restoration plans in 2018 to address 24 Nitrogen impaired Outstanding Florida Springs.

- Delineate priority focus areas;
- Prioritize lists of restoration projects which include estimates of **nutrient** load reduction;
- Project milestones to achieve water quality restoration targets in 20 years;
- **Estimated nutrient pollutant loads, allocated to each source or category of sources; and**
- Completed remediation plans for onsite sewage treatment and disposal systems (OSTDS) **where septic loading accounts for at least 20 percent of the estimated nutrient input.**



http://www.floridahealth.gov/environmental-health/onsite-sewage/research/_documents/ofs_bmaps_and_pfas.pdf

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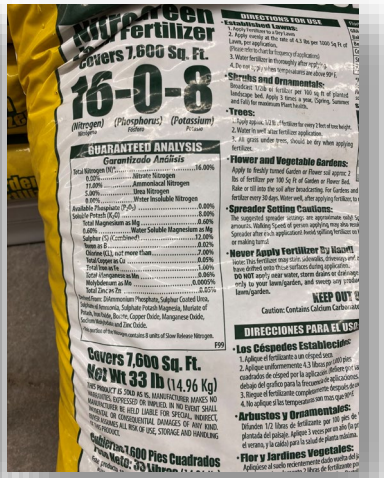
COMMON NITRATE SOURCES

Fertilizers contain varying proportions of nitrogen, nitrogen species, and degrees of slow-release nitrogen.

- Lawn or crop-applied
- UF/IFAS estimates **1-55%** of fertilizer nitrogen applied on Florida lawns leaches to groundwater (Shaddox and Unruh 2018)

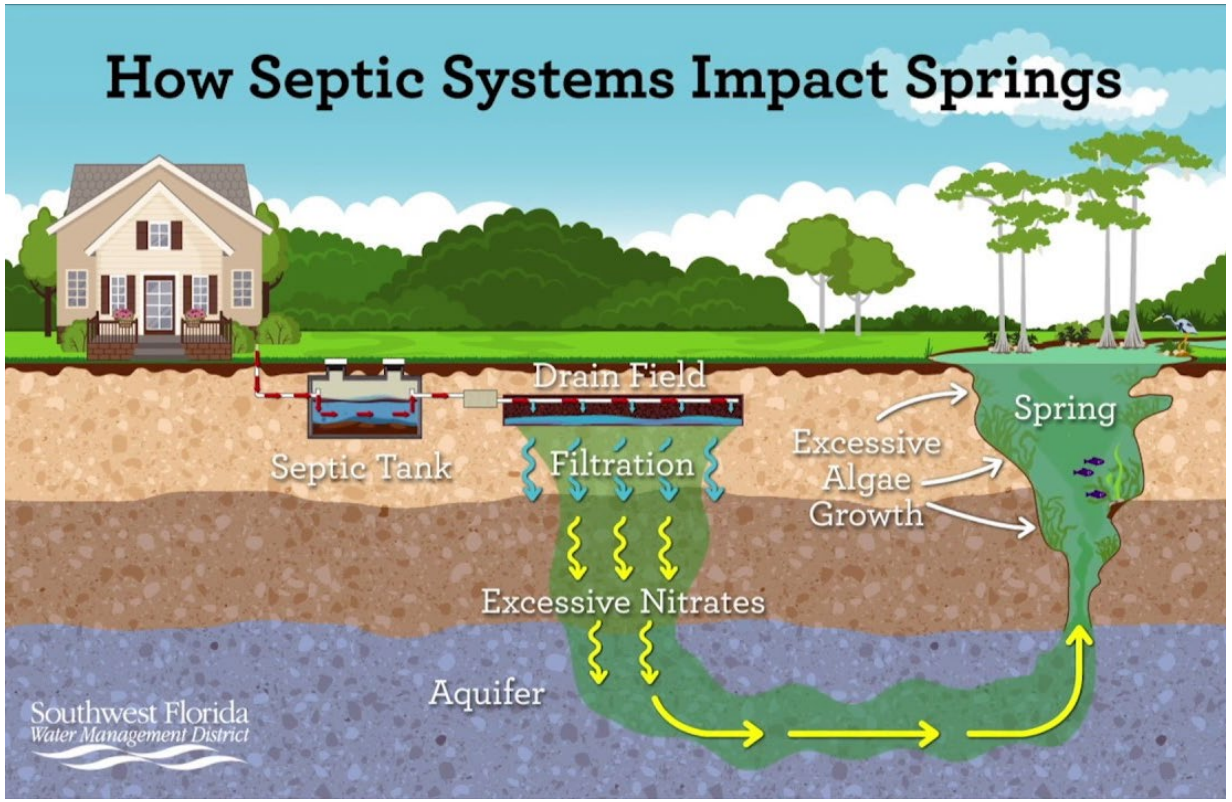
-Adobe Stock Image



COMMON NITRATE SOURCES

Human (Wastewater / Septic Leachate) and Animal Wastes contain fixed nitrogen that can reach springs.

- Urine is mineralized to ammonia, then oxidized to nitrate.
- Nitrate is very soluble; when it enters the aquifer, it moves with water.



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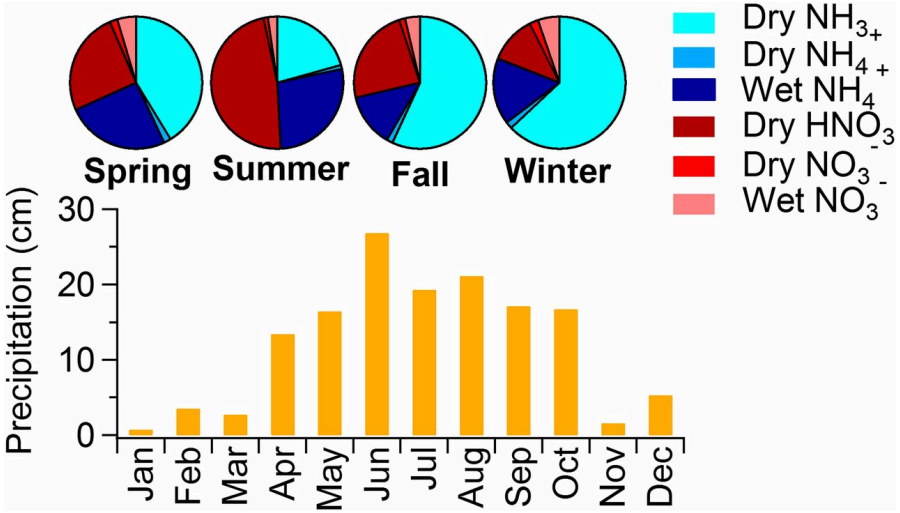
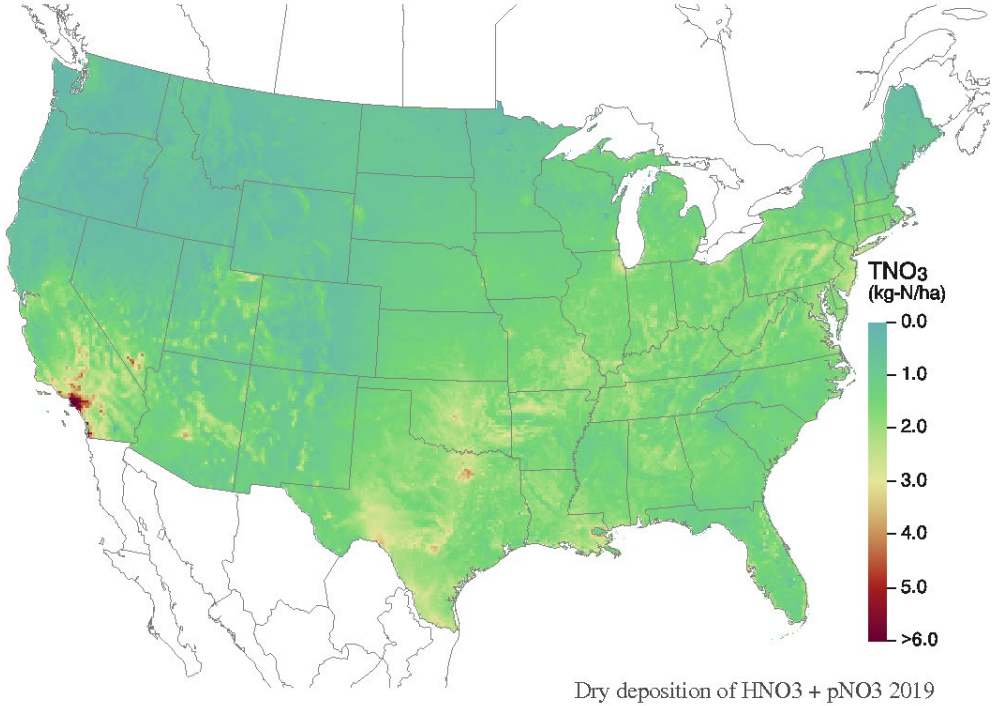
Atmospheric Nitrogen accumulates in the atmosphere from powerplants, vehicles, and industrial emissions.

- Nitrogen is deposited **through wet and dry deposition.**



Pie charts of seasonal N deposition species pathways (Upper) and total monthly measured precipitation (Lower) in Florida area (Li et al. 2016)



Dry deposition of HNO3 + pNO3 2019
USEPA 11/19/20

Source: CASTNET/CMAQ/NADP

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COMMON NITRATE SOURCES

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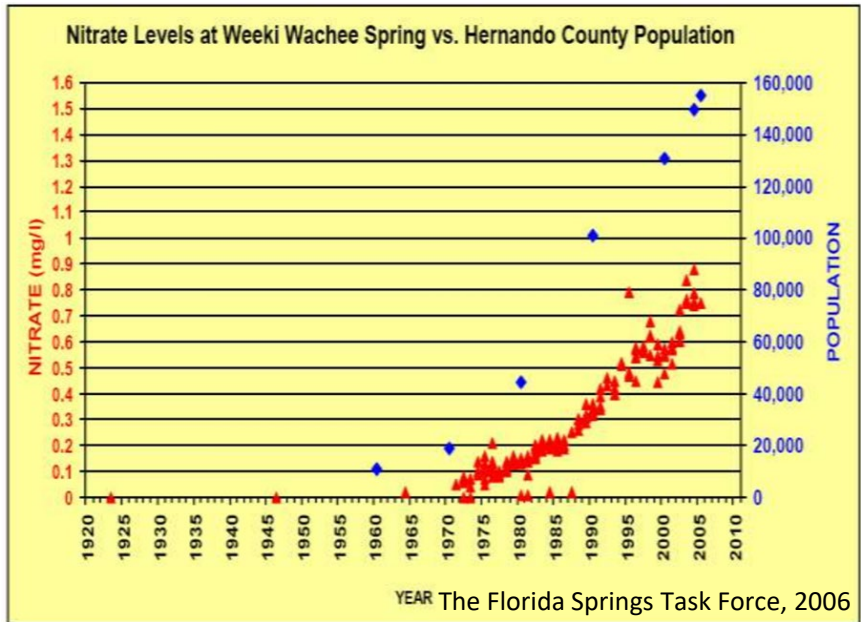
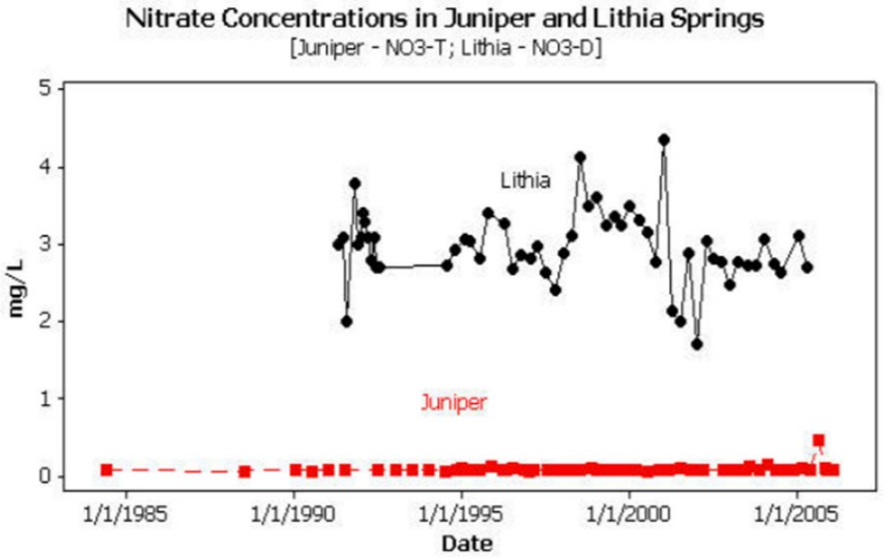
Nitrogen is naturally "fixed" in the soil, but natural / background (non-human input) groundwater nitrate concentrations are very low.



Nitrate-N concentrations at Weeki Wachee Spring (red triangles) and Population (blue diamonds) Hernando County.



Nitrate-N concentrations in Juniper (conservation lands) and Lithia (mix of agriculture, urban/ residential).

The Florida Springs Task Force, 2006

"…..Throughout the karst areas of north and central Florida where artesian springs are common, groundwater nitrate nitrogen concentrations have increased from a normal background of *less than 0.02 parts per million* to widespread concentrations over 1.0 parts per million (a fifty-fold increase)…" *(from Florida, Land of 1,000 Springs, Howard T. Odum Florida Springs Institute, http://www.lake.wateratlas.usf.edu/upload/documents/Springs-Facts-FSI-012414.pdf*

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- **Dual Nitrate Isotopes**
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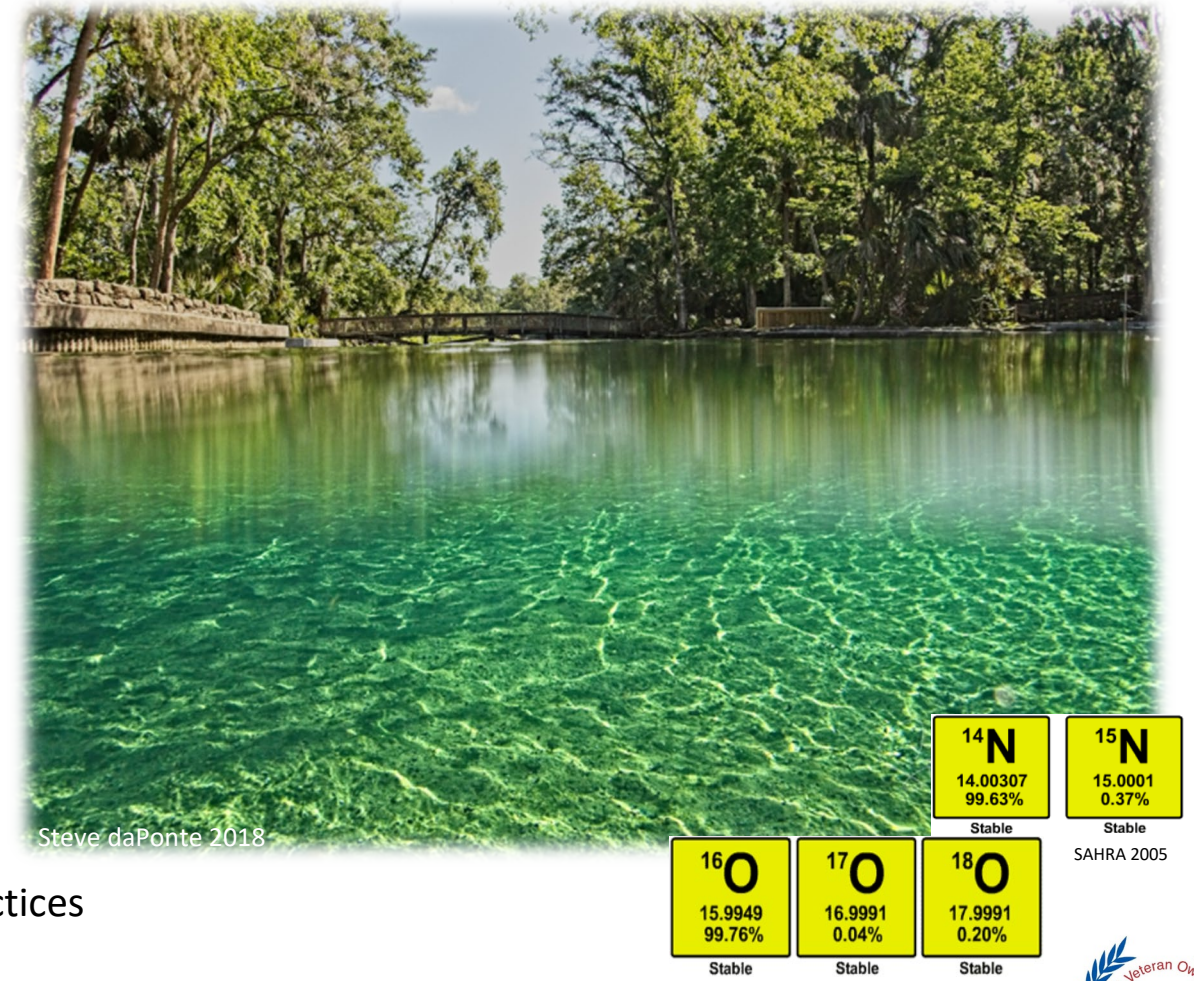

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- Mass differences cause different reaction rates or “fractionations” during chemical and biological reactions.
- Fractionations allow fingerprinting of sources and reactions.
- δ (Delta) Notation: $\delta_{Sample} = ((R_{sample}-R_{standard})/R_{standard})*1000$

where "R" is the ratio of the heavy to light isotope in the sample or standard.

A positive “δ” value means the sample is heavier than a standard, negative “δ” values indicates the sample is lighter than the standard.

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Analytical advances have **transformed** our capacity for analyzing nitrate isotopes.

Sample mass requirements decreased by
3 orders of magnitude

$AgNO_3$ Method
100-200 µmol NO_3^-

Denitrifier Method
10-20 nmol NO_3^-

Slide courtesy of Dr. Emily Elliott, University of Pittsburgh

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Analytical advances have **transformed** our capacity for analyzing nitrate isotopes.

https://syringefilter.com/

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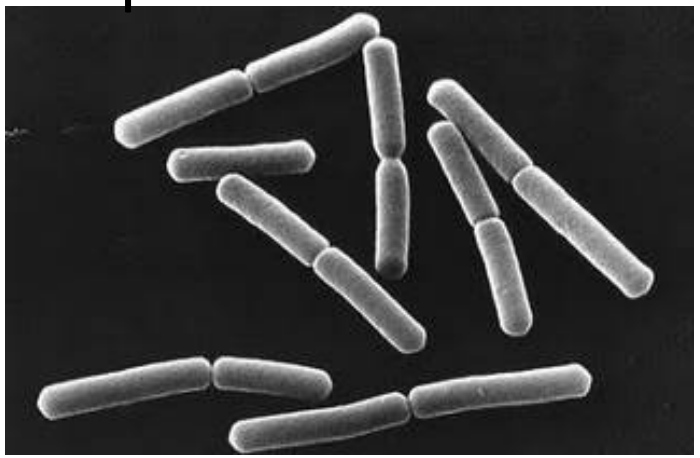

Pseudomonas aureofaciens
Photo courtesy of "Microbe wiki"

$NO_3^- \rightarrow NO_2^- \rightarrow N_2O$

$\delta^{15}N$ (***Sigman et al., 2001***)

$\delta^{18}O$ (***Casciotti et al., 2002***)

$\Delta^{17}O$ (***Kaiser et al., 2007***)

Slide courtesy of Dr. Emily Elliott, University of Pittsburgh

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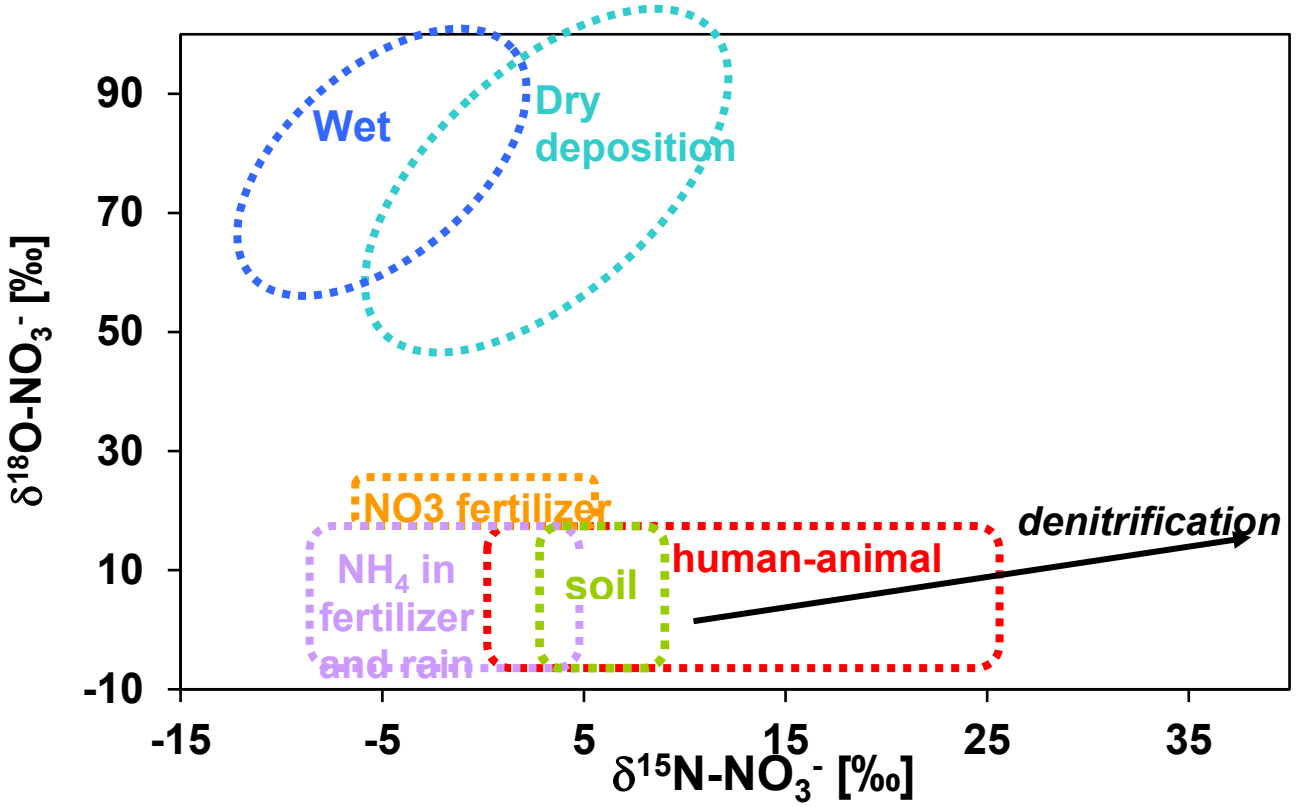
Nitrate isotopes can provide information about what sources contribute to observed nitrate.

- Nitrate sources show distinct ranges of reported values.
- Some overlapping signatures



(After Kendall et al 2007)

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DUAL NITRATE ISOTOPES

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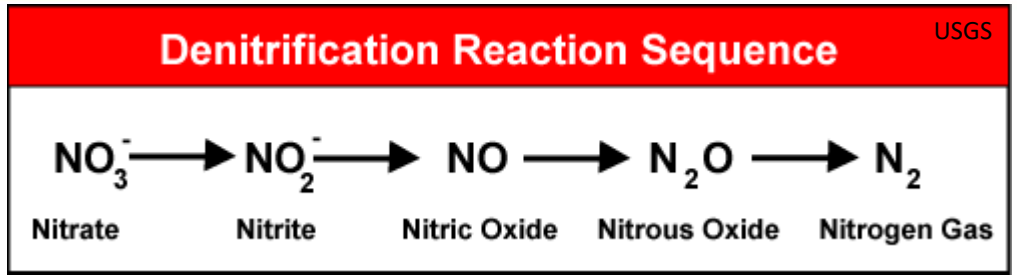
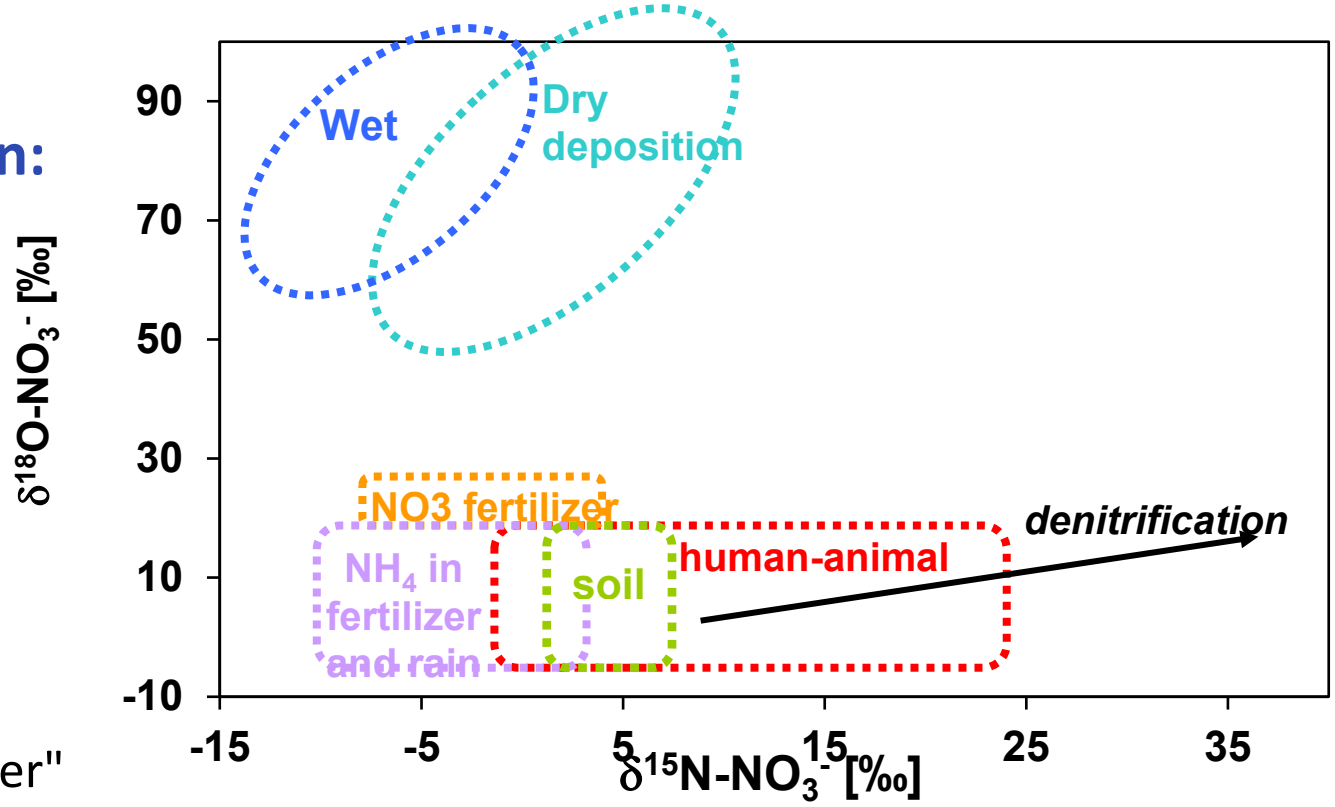


Conditions that promote denitrification:

- Presence of denitrifying bacteria
- Low dissolved oxygen
- Presence of electron donor (carbon)

Denitrification enriches $\delta^{15}N$ & $\delta^{18}O$

- Lighter isotopes are preferentially used by bacteria
- Remaining nitrate pool is isotopically "heavier"



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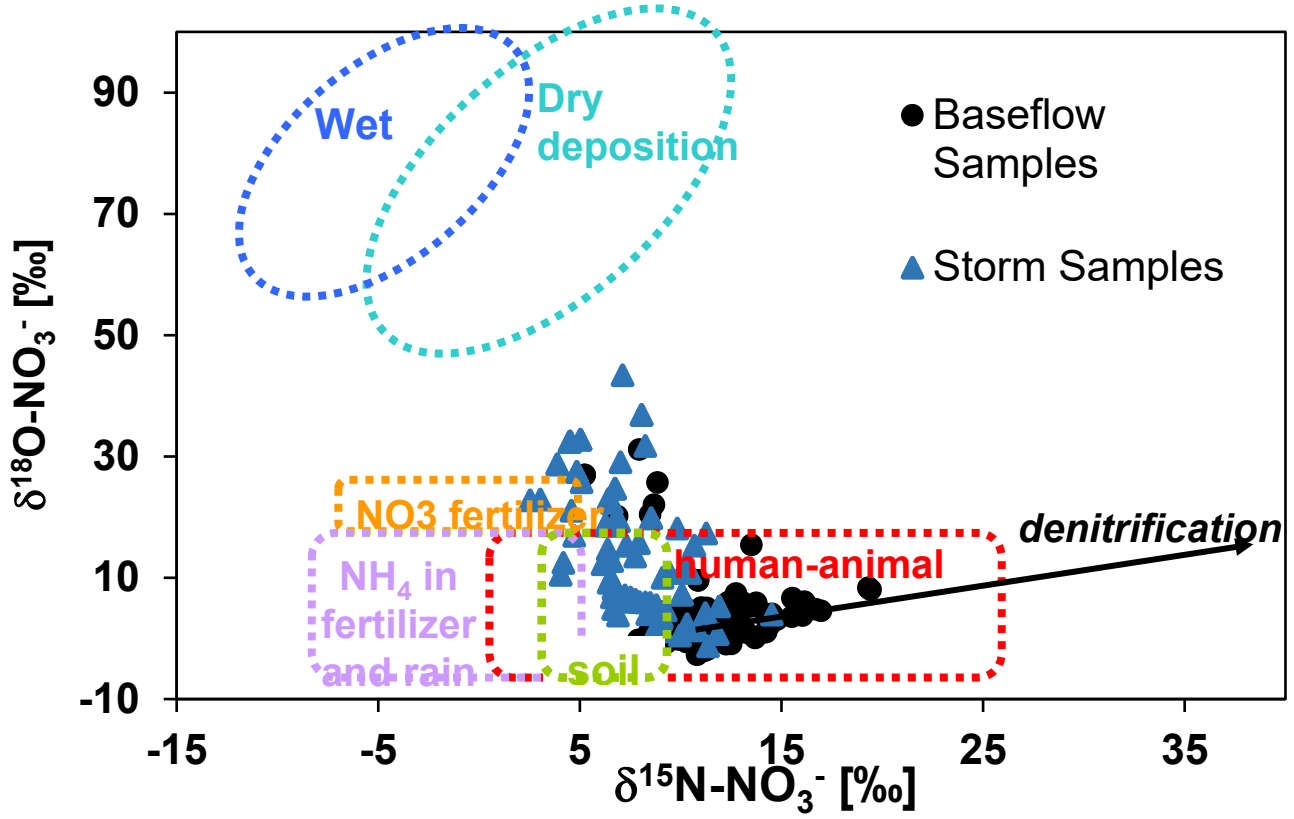
Nitrate isotopes can provide information about what sources contribute to observed nitrate.

- Example Samples from Pittsburgh, PA.
- Surface waters plotted in the dual-isotope space.
- Baseflow, (for this water source) influenced by sewage.
- Mixes with atmospheric deposition during storms.
- Denitrification



(Divers et al 2014)

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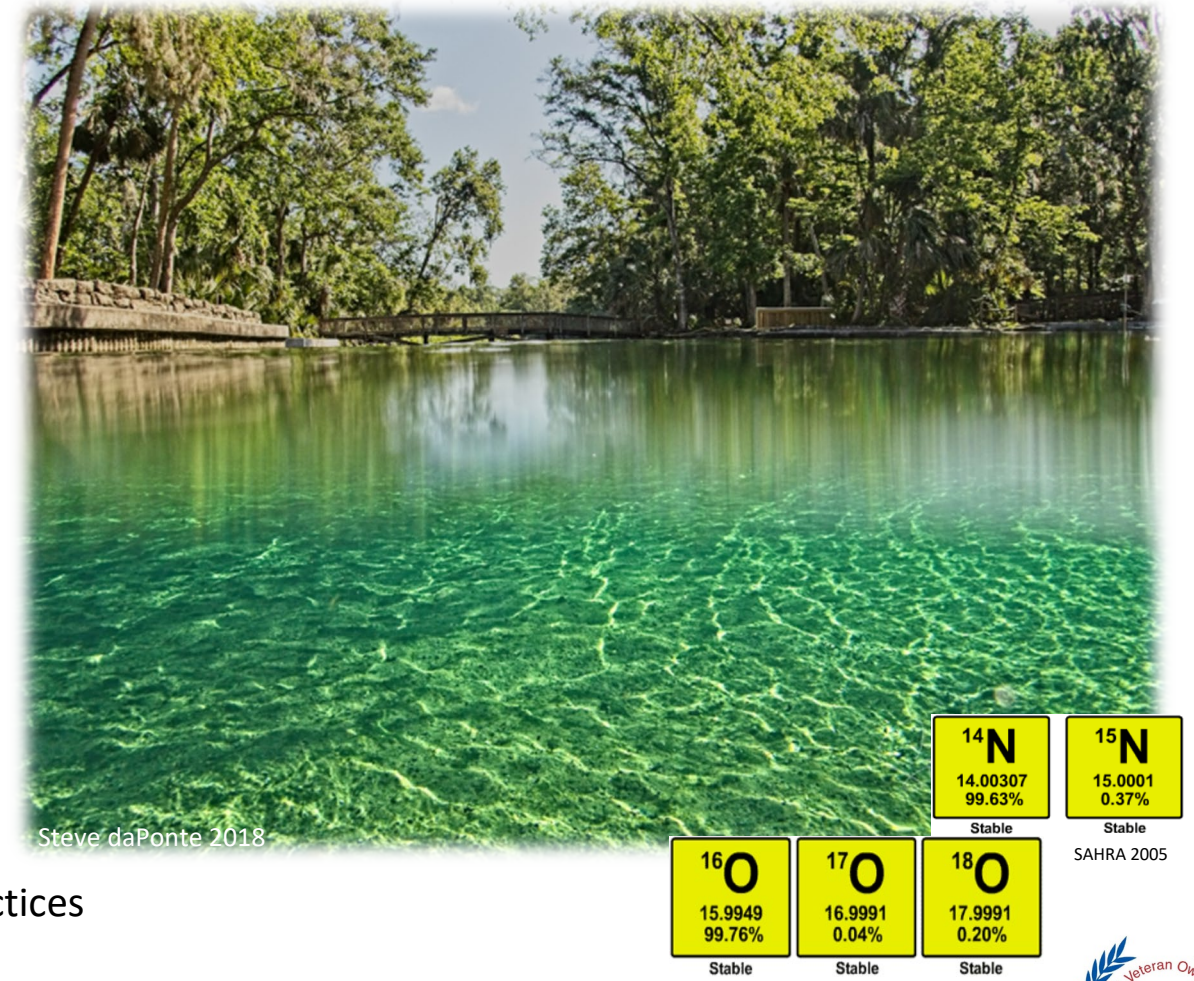

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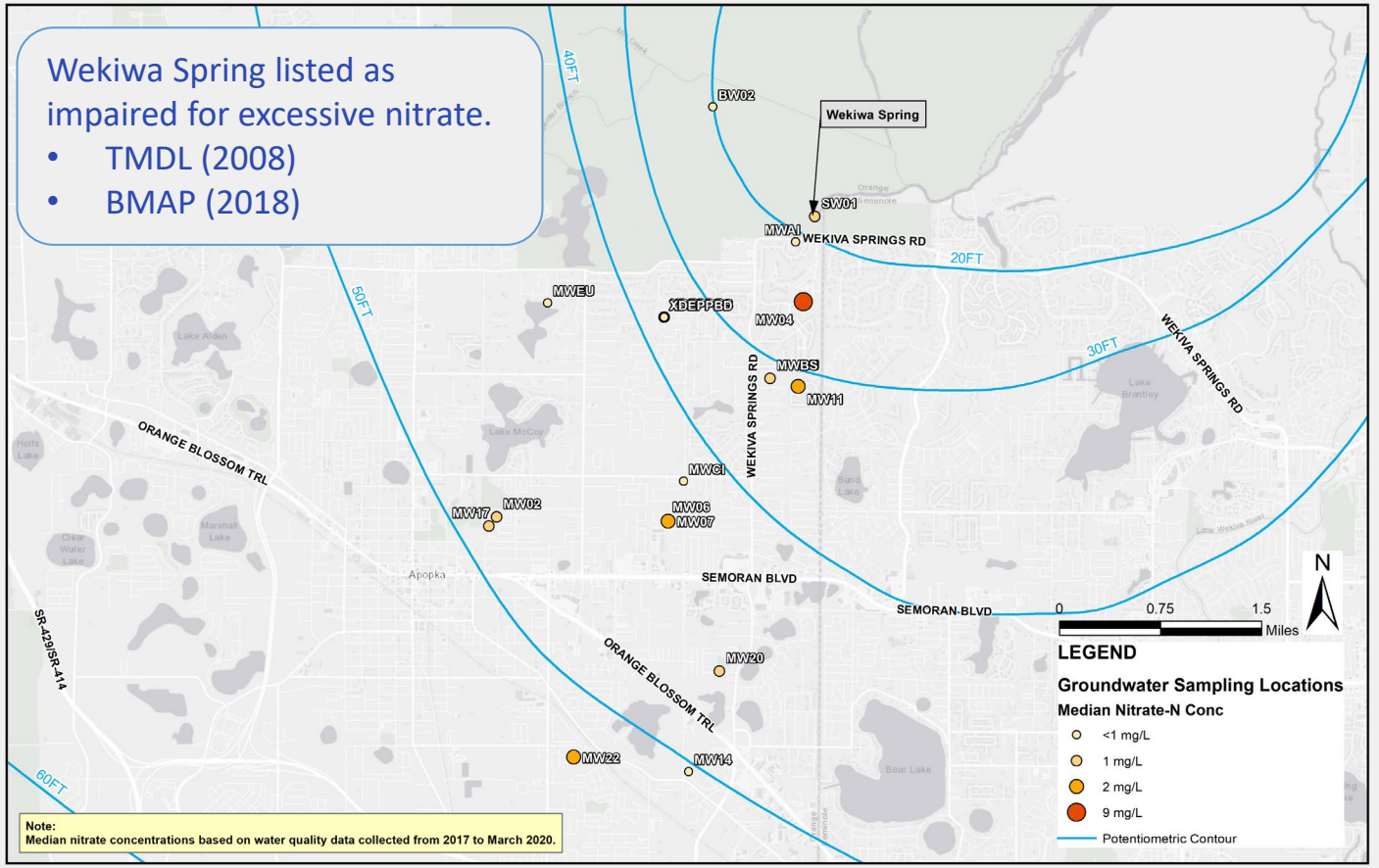
Is nitrate from fertilizer a significant nutrient source to Wekiwa Spring?

- Water quality data collected quarterly for 3+ years from 22 sampling locations
- Isotopic data collected for sampling locations with higher nitrate concentrations
- Does the data support restrictions on fertilizer practices?



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Springs Protection Assessment Using Nitrate Isotope Analysis

CASE STUDY: WEKIWA SPRING

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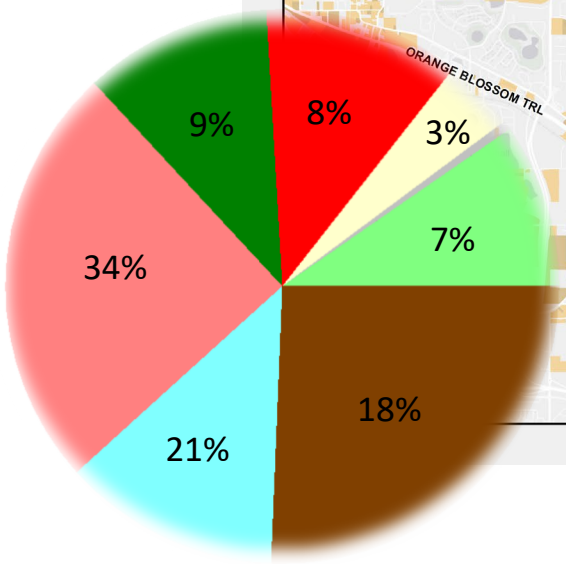
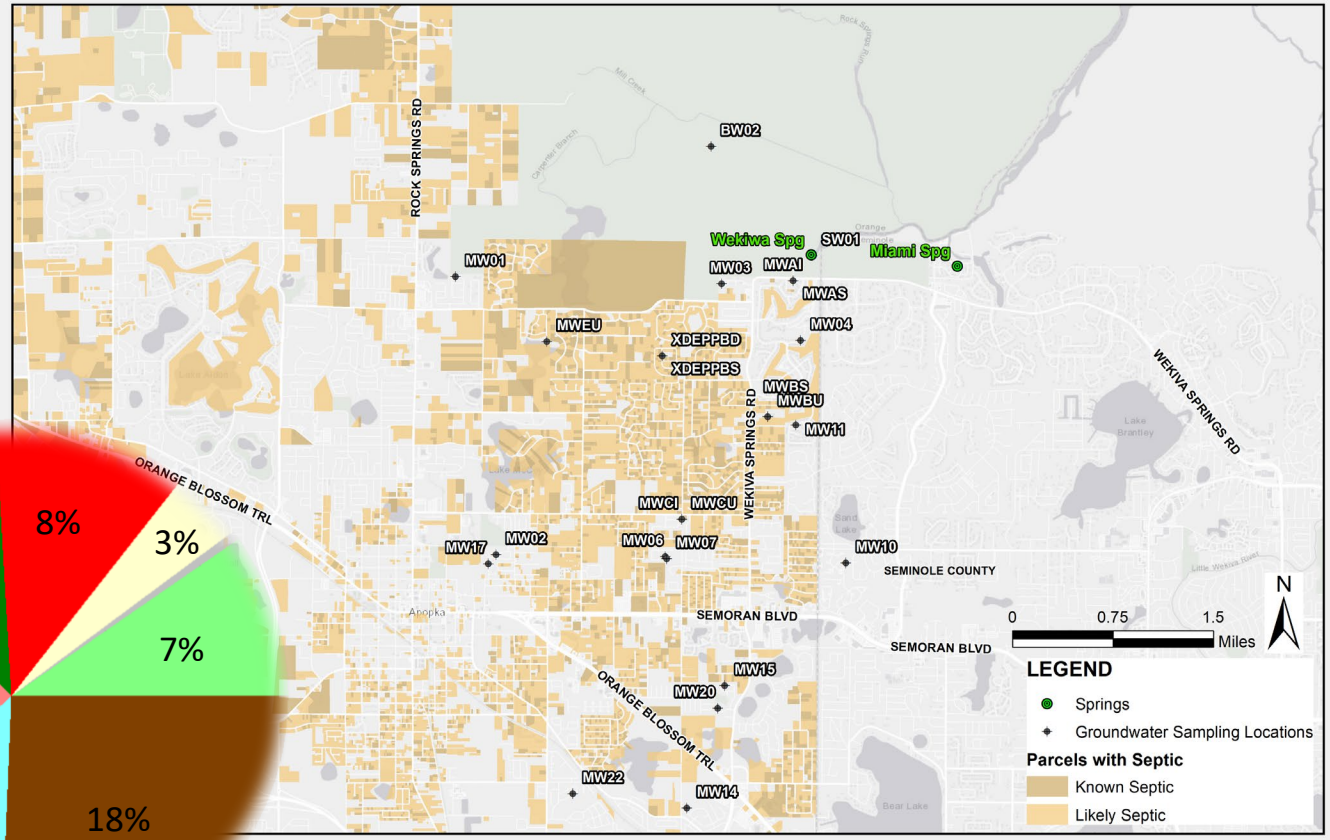
Land use in Wekiwa Priority Focus Area:

- 34% Urban and Built-Up
- 21% Water
- 18% Wetlands

Septic within Wekiwa Priority Focus Area:

- Study wells located on parcels connected to sewer





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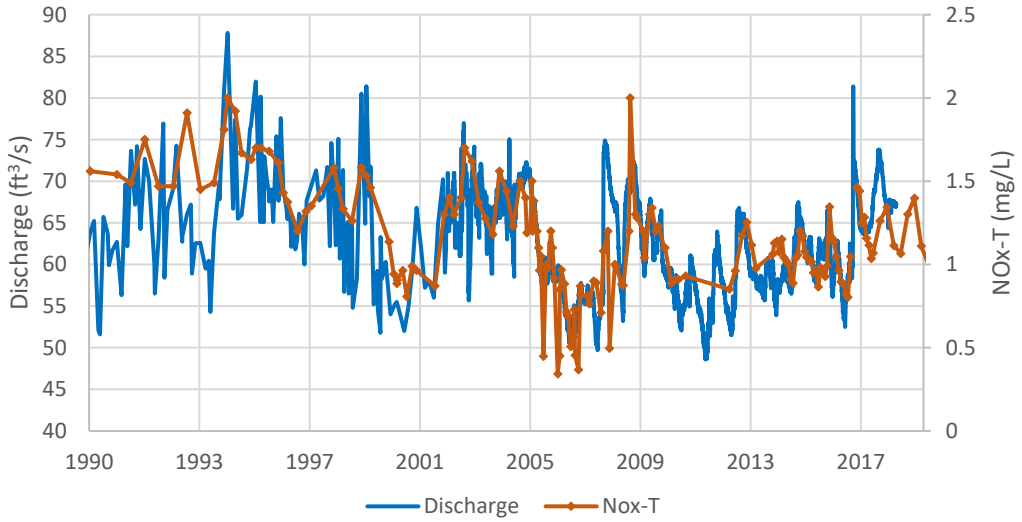
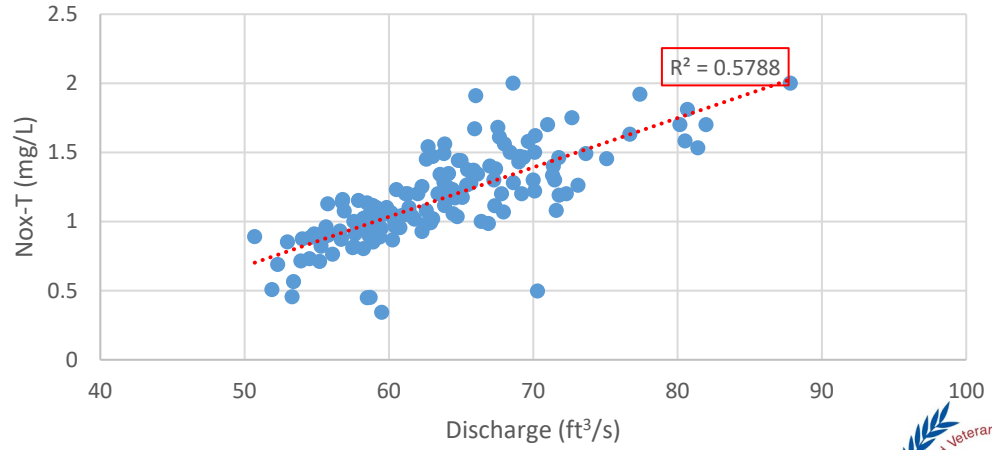
Nitrate reaching Wekiwa Springs via groundwater is dependent on a mix of factors:

- Source
  - Continuous = leaky septic
  - Intermittent = fertilizer application
- Groundwater travel times
  - Longer travel time = more denitrification potential
- Hydrogeologic conditions
  - Infiltration rate
  - Conditions to promote or inhibit denitrification





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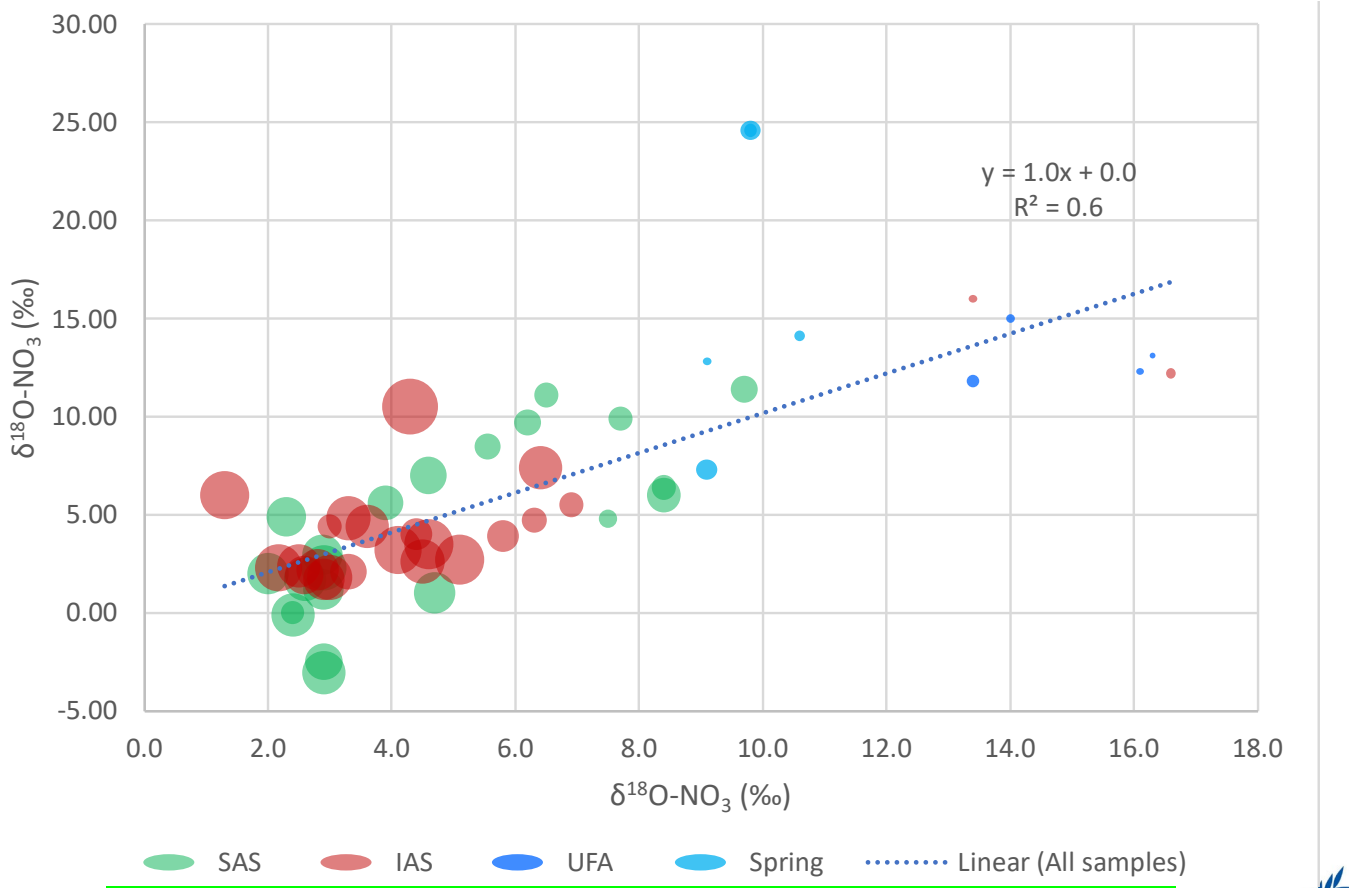
Data suggests mixing of groundwater originating from sources with various nitrogen loading and/or travel times.

- Samples from wells across Wekiwa Priority Focus area.
  - Spring water from Wekiwa Spring.
  - Wells from Surficial (n=4), Intermediate(n=6) and Upper Floridan (n=1) Aquifers.
- Dissolved oxygen (DO) decreases along denitrification trajectory.



Note: Bubble size positively correlated with DO (mg/L)

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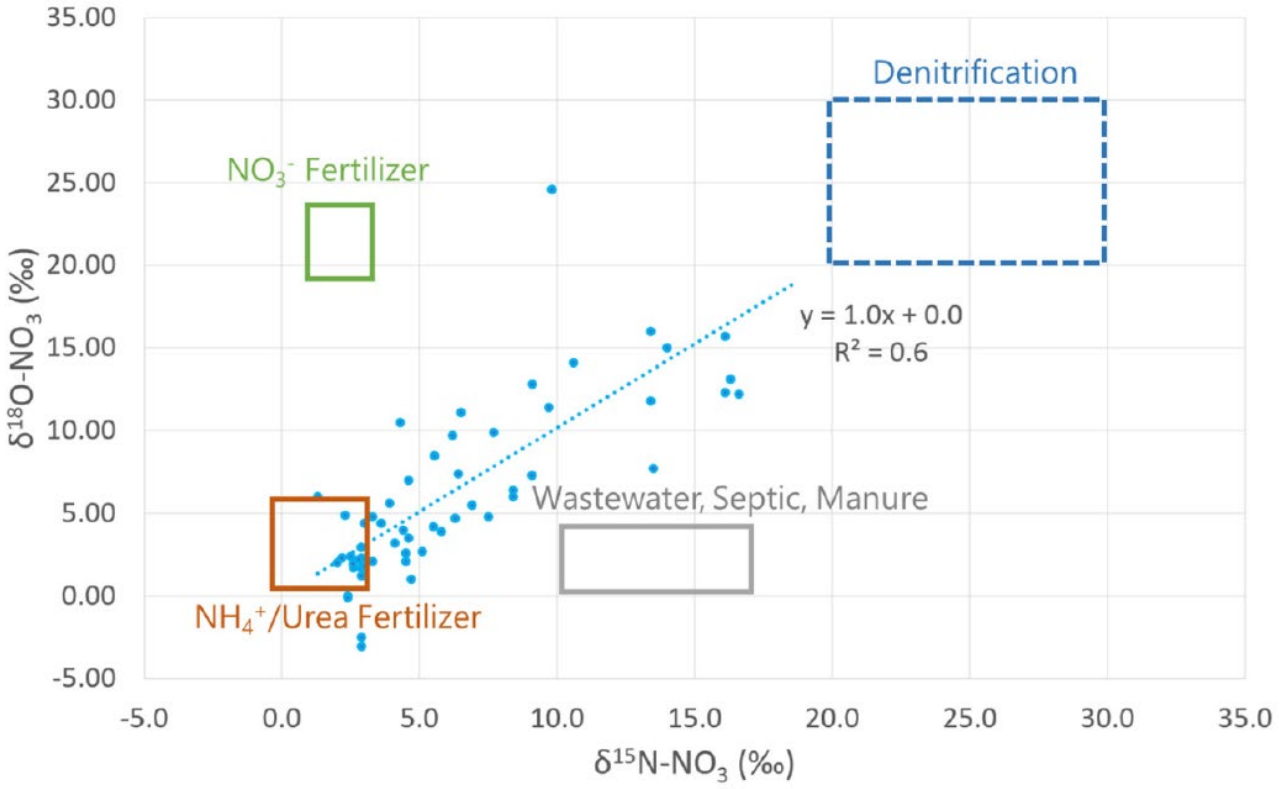
Nitrate Isotope values indicate strong fertilizer signal and denitrification.

- Potential mixing with wastewater.
- Denitrification in action.
  - Albertin et al. (2012) calculated a 43% decline in nitrate concentrations (with increases in $\delta^{15}N$, $\delta^{18}O$) for Wekiva Spring from 2005 to 2008.
- Mixing models can help determine proportion of nitrate originating from each source.



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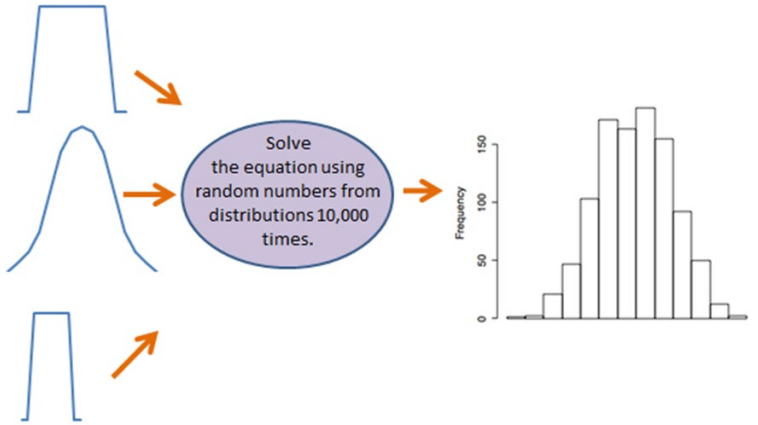
Bayesian Mixing Models can help untangle the proportion of nitrate by source and gain insight into biological processing.

Stable Isotope Analysis in R (SIAR)

- Developed for ecological food web studies
- Commonly used in nitrate sourcing studies

Model Inputs:

- Source Distributions
- Isotopic Data of Samples



Allows for overlapping source ‘fingerprints’
Allows for variability in source ‘fingerprints’

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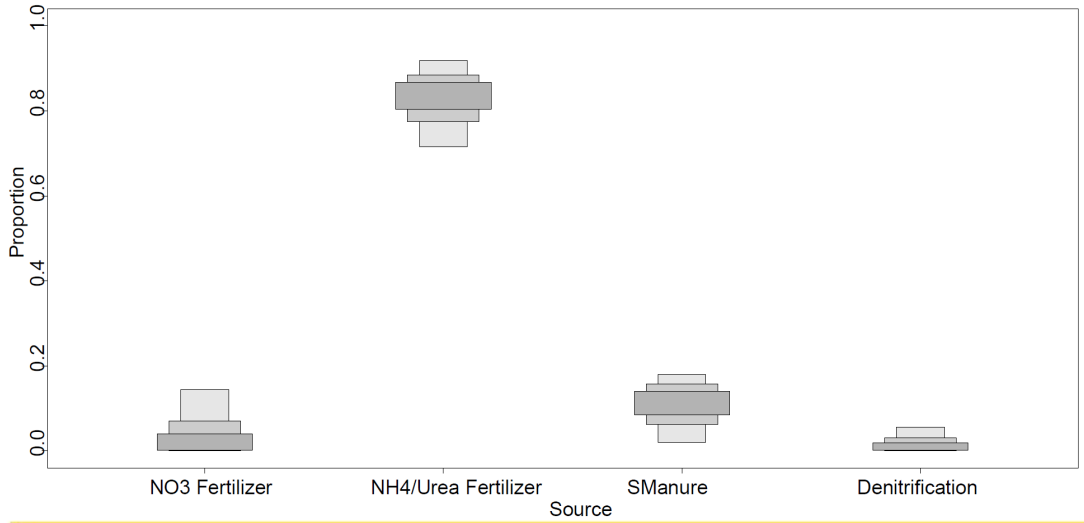
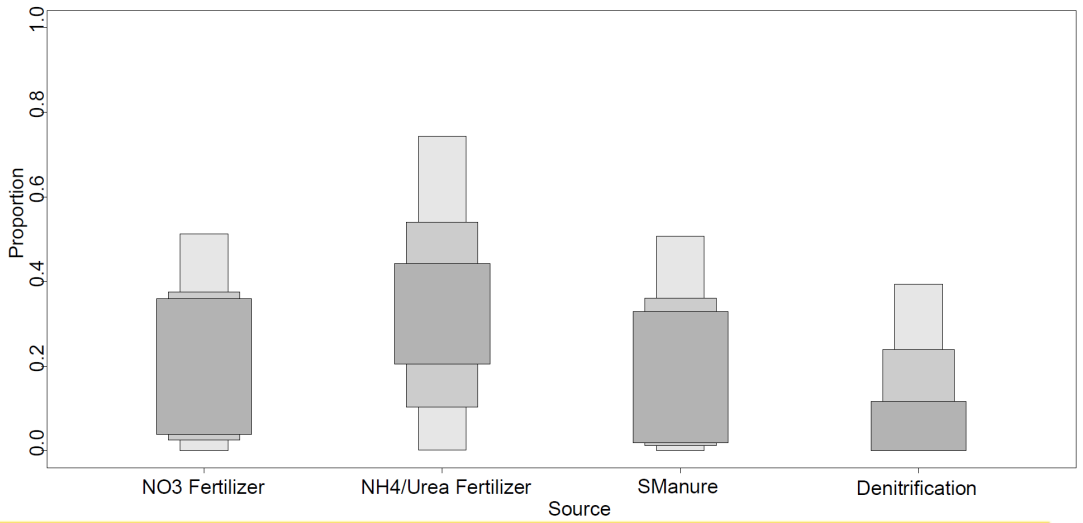
Mixing model results provide relative contributions of each source to total nitrate in each well sample set.

- Mixing model results commonly viewed as boxplots.
  - Allows for visualization of uncertainty.
- Larger sample size produces more certainty in model results.

Well X: Sample Size = 13



Well Y: Sample Size = 2



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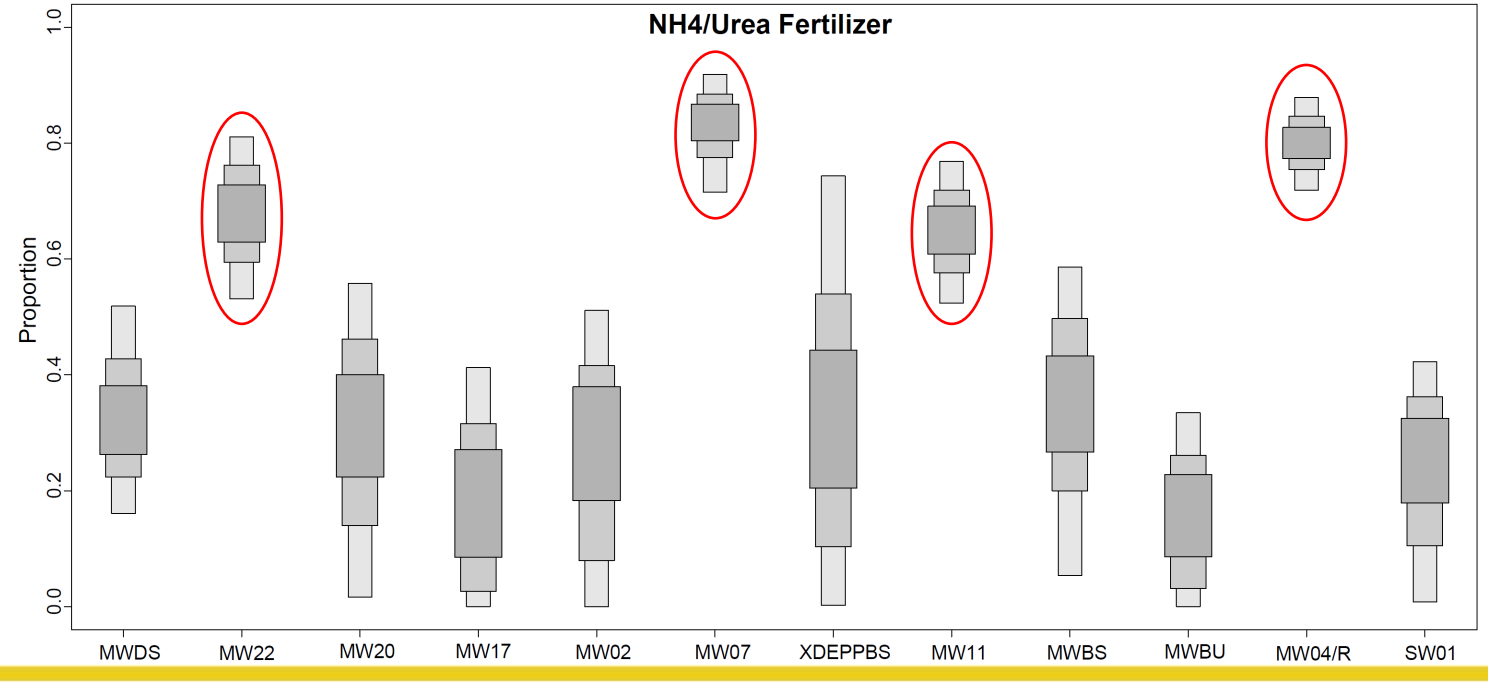
Mixing model results provide relative contributions of each source to total nitrate in each well sample set.

- Strong fertilizer signature across all sample locations.
- Wells with >60% attributed to fertilizer had average nitrate concentrations > 2 mg/L.



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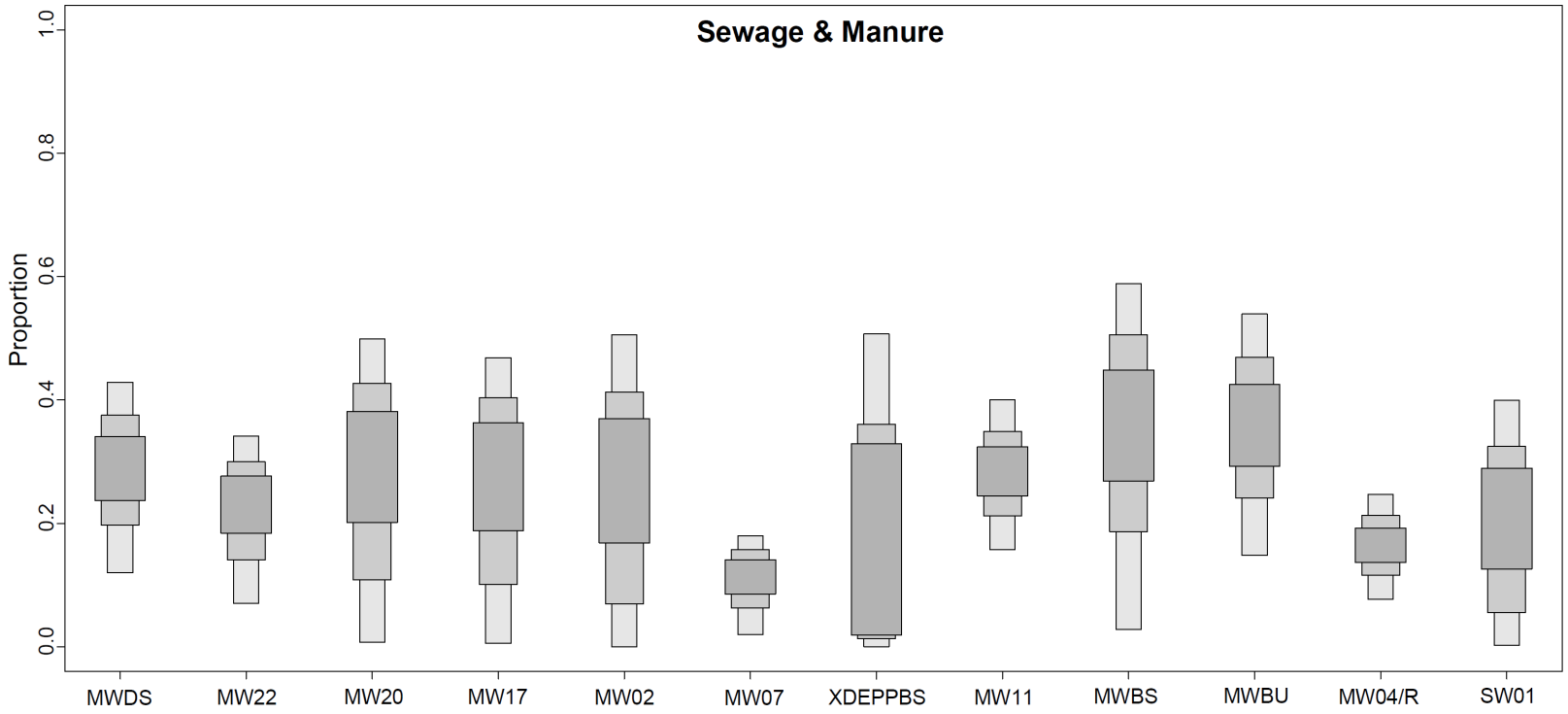
Mixing model results provide relative contributions of each source to total nitrate in each well sample set.

- Sewage signal present.



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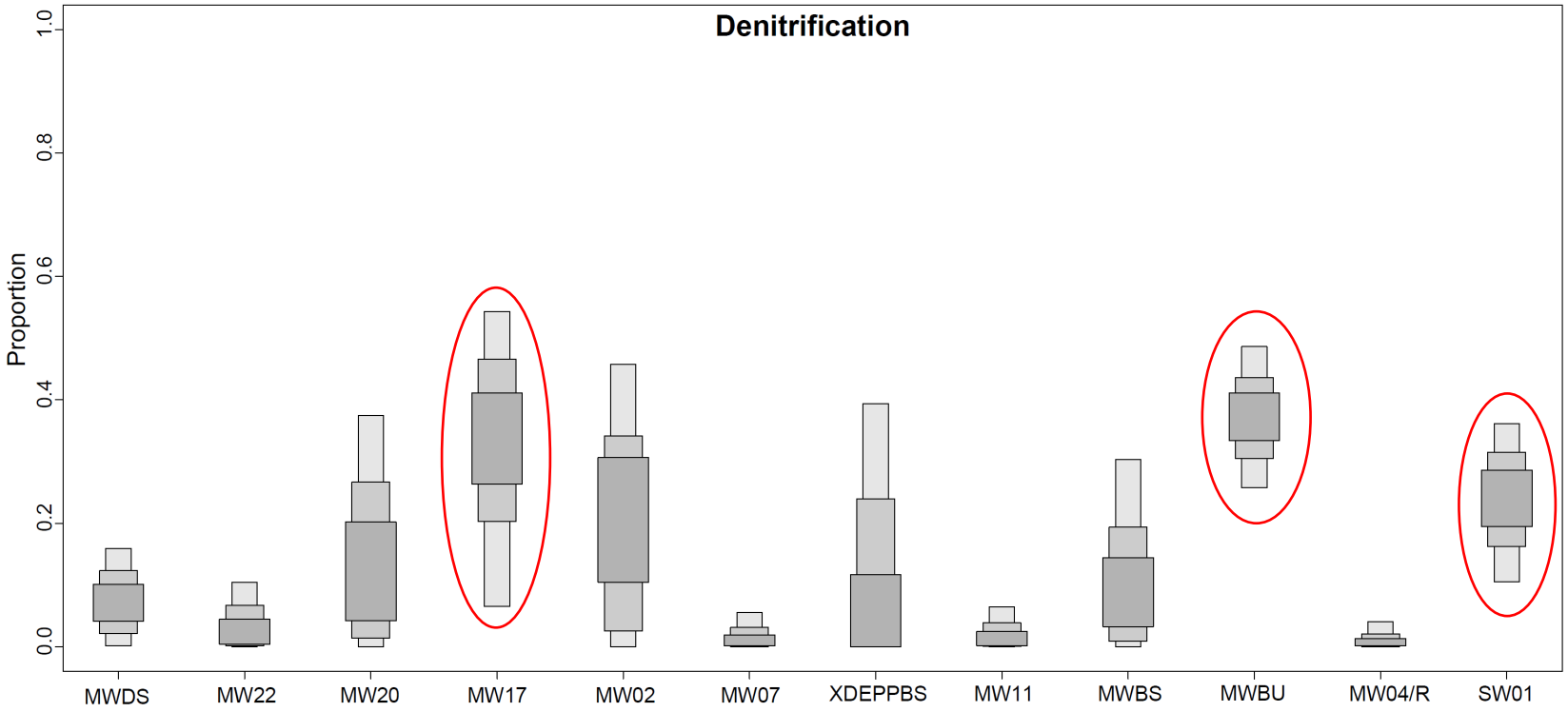
Mixing model results provide relative contributions of each source to total nitrate in each well sample set.

- Denitrification signal present.



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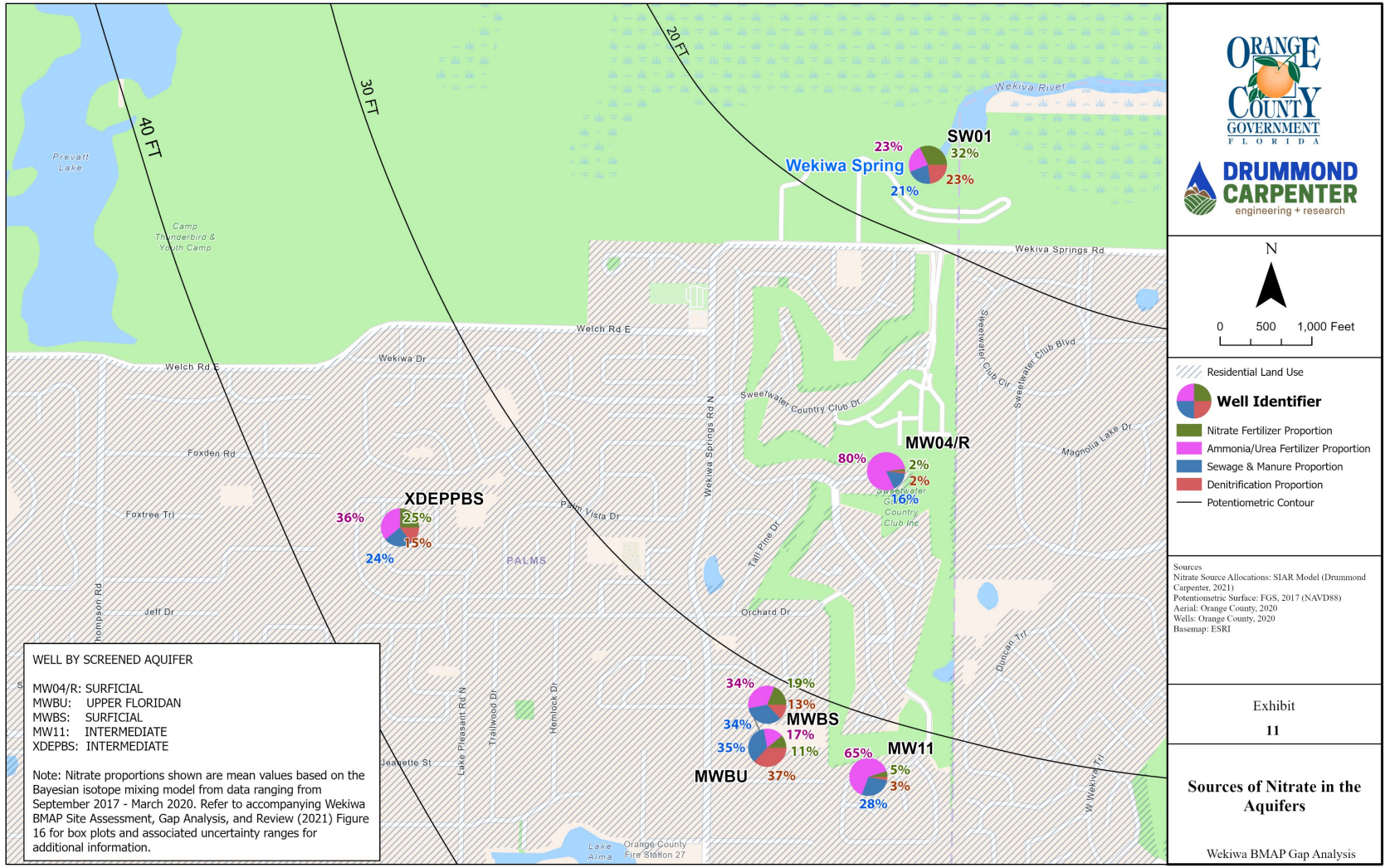
CASE STUDY: WEKIWA SPRING

Mixing model results can be viewed spatially.



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CASE STUDY: WEKIWA SPRING

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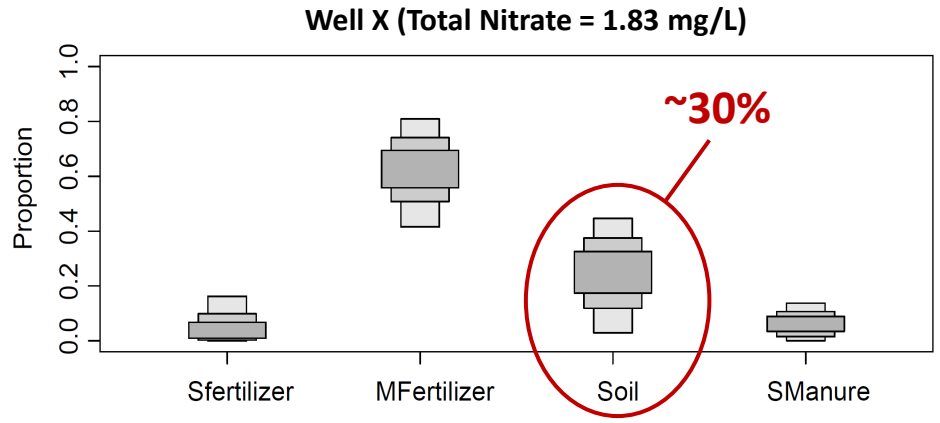
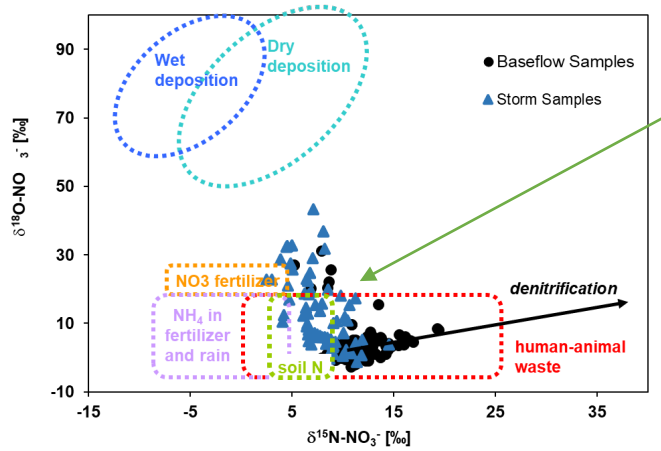
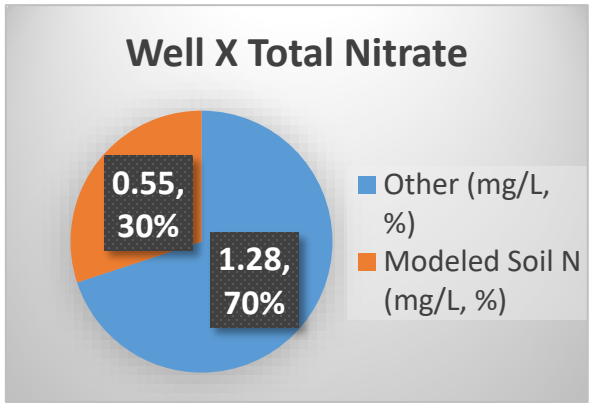
Real world 'check': do modeled proportions fall within expected or reasonable ranges based on knowledge of land use, fertilizer practices, septic systems present, atmospheric N, background soil N concentrations?



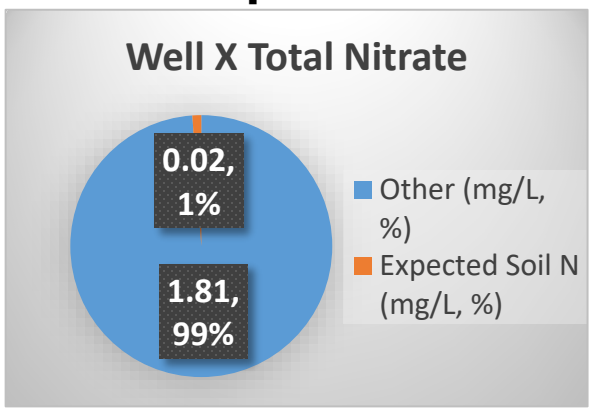


Overlapping soil isotopic signature

Modeled



Expected



Overlapping isotopic signatures create uncertainty in model and overestimation of soil contribution

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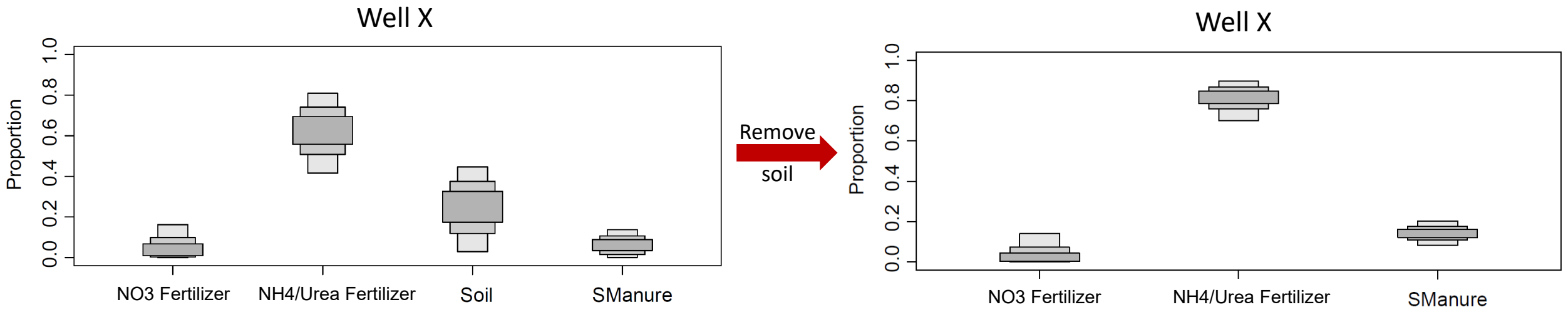
Real world 'check': do modeled proportions fall within expected or reasonable ranges based on knowledge of land use, fertilizer practices, septic systems present, atmospheric N, background soil N concentrations?

- Assuming soil-sourced nitrate is negligible reduces uncertainty in mixing model.



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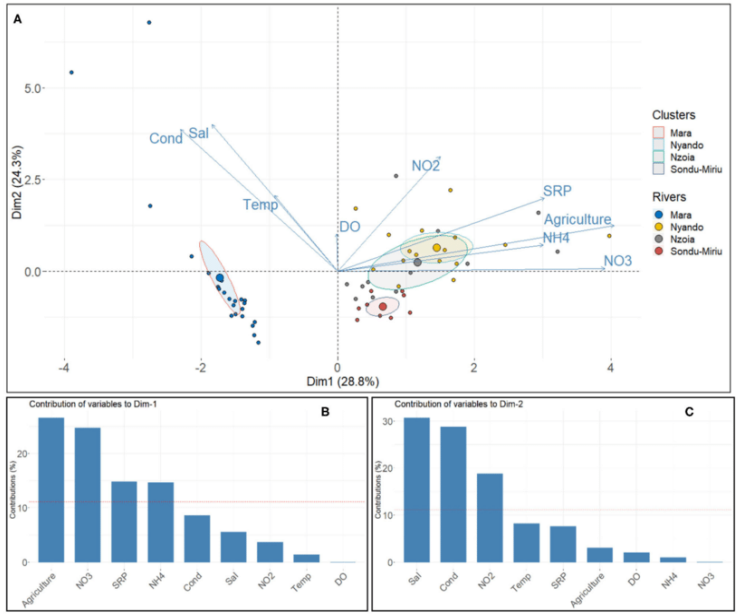
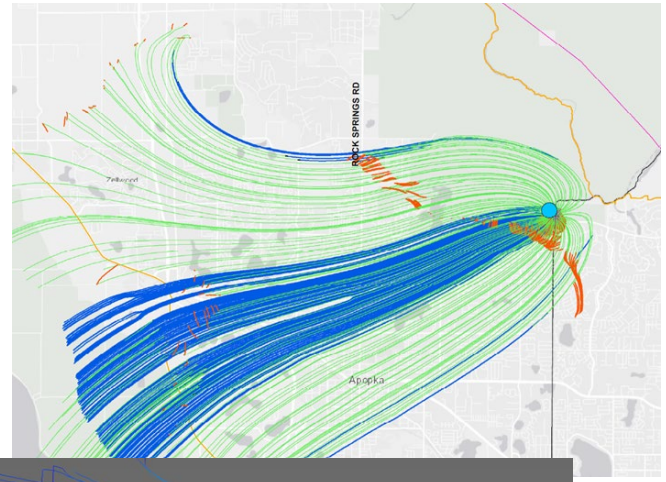
Multiple lines of evidence are helpful to compliment isotopic data.

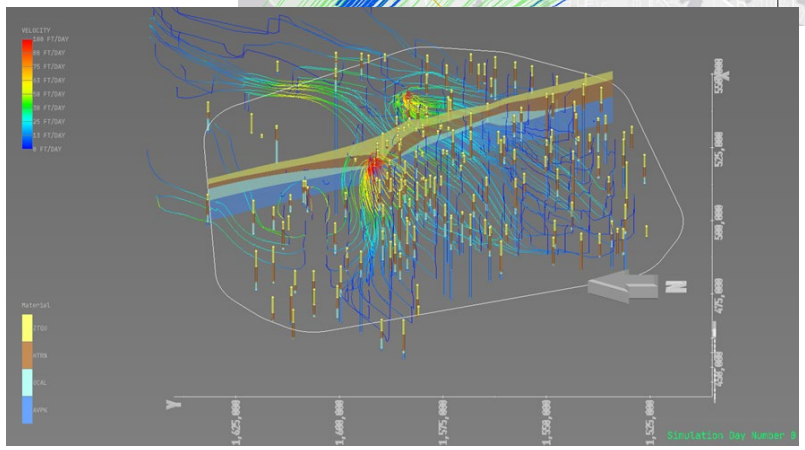
- Previous studies
- Historical values
- Additional tracers
- Water quality data
- Transport models

Images courtesy of Google Images



Otieno et al. 2021





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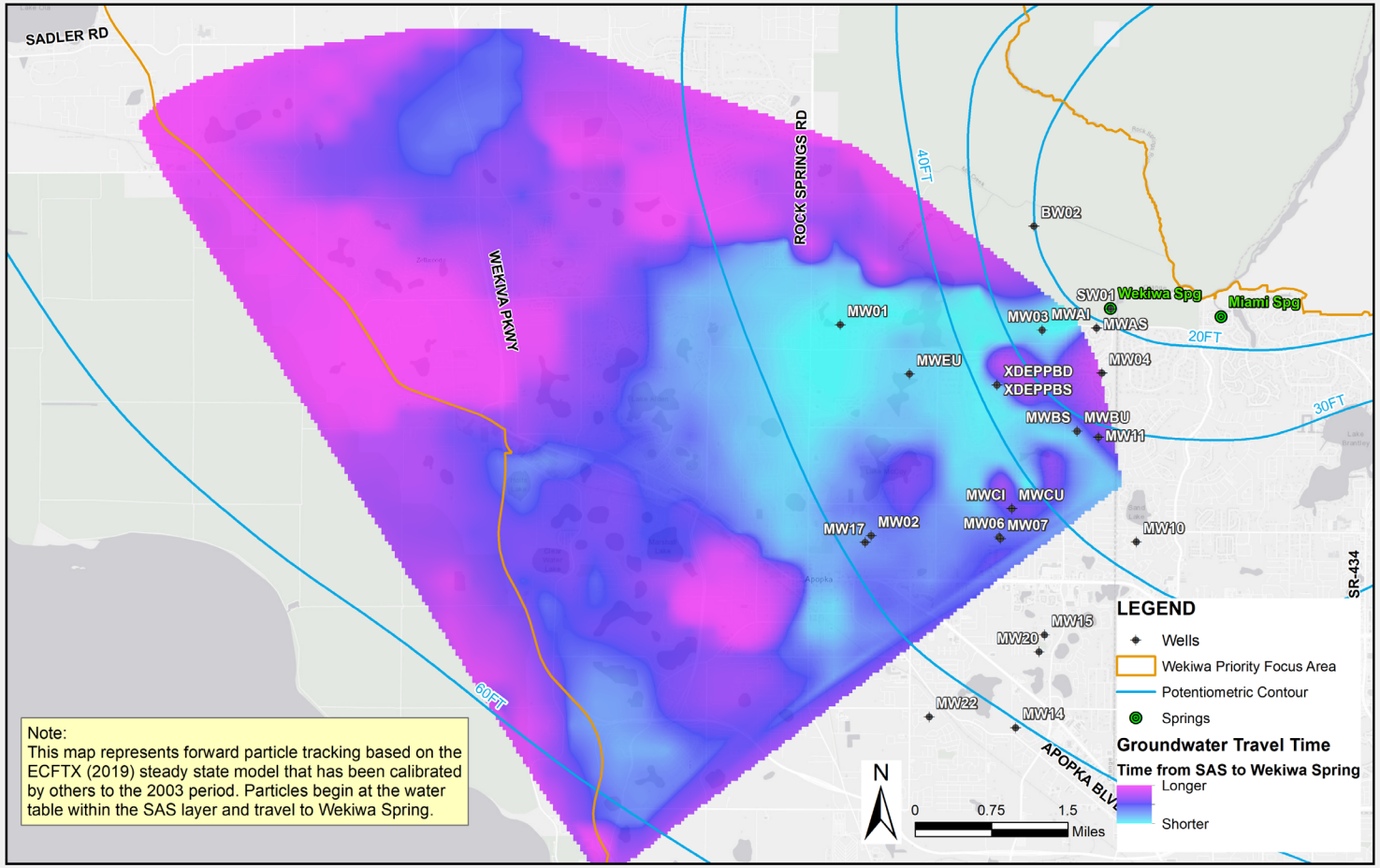
Multiple lines of evidence can be used to build a better conceptual model.

- Identification of hotspots and vulnerable areas:
  - High recharge areas
  - Fast groundwater travel times
  - Elevated nitrate concentrations
  - Land use
- Management practices can be designed to target identified areas.



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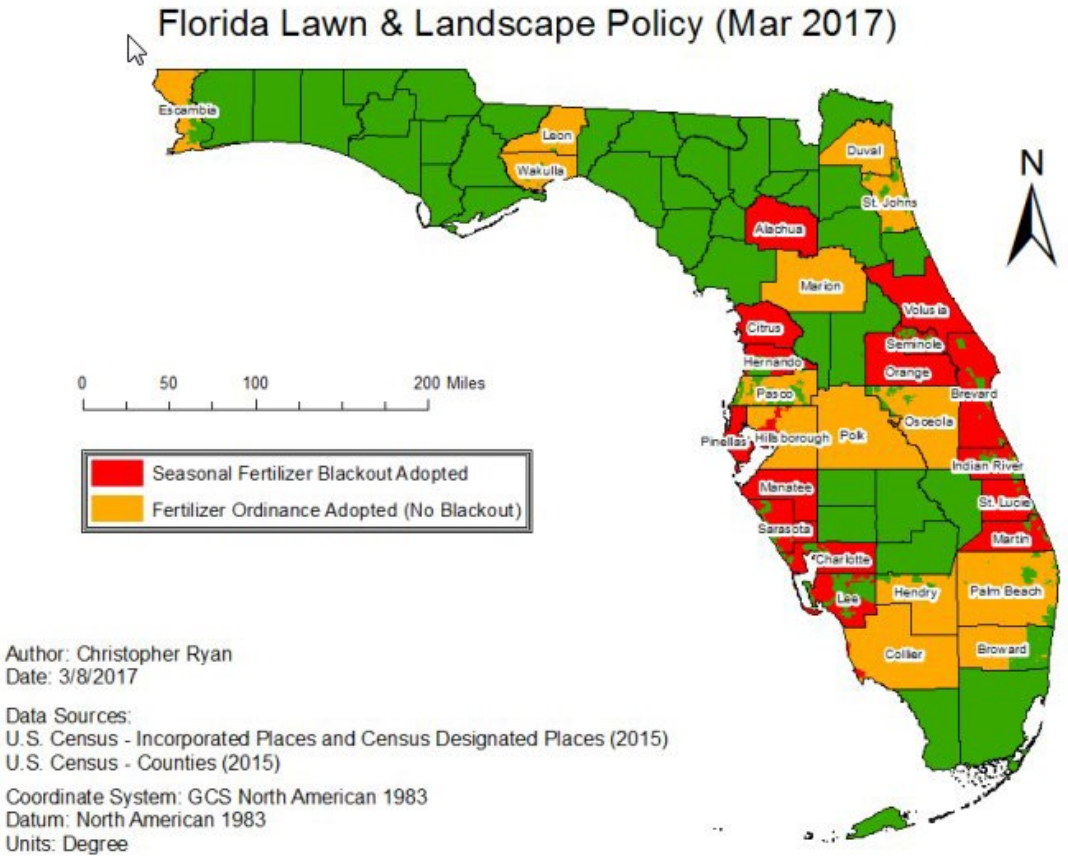
Implement management practices to reduce nitrogen loading in vulnerable areas.

Fertilizer ordinances:

- Restrictions on fertilizer application rates
- Restrictions on fertilizer timing
- Mandates for fertilizers with slow-release Nitrogen
- Bans on fertilizer during wet season



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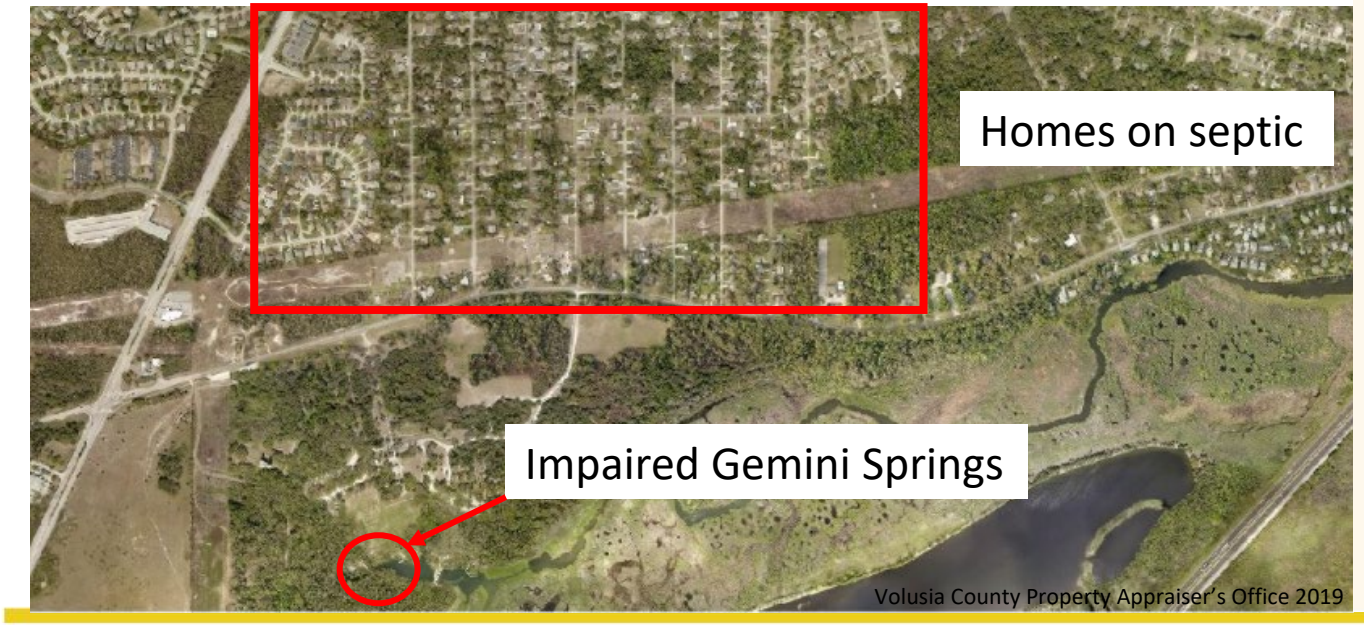
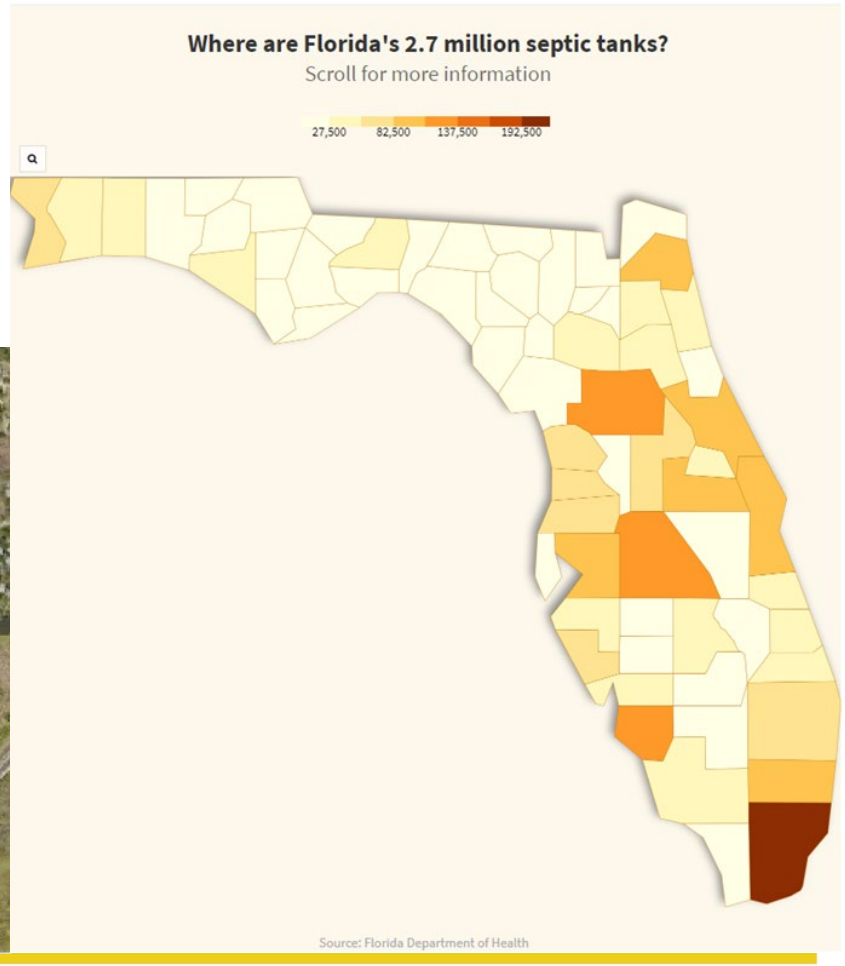
Implement management practices to reduce nitrogen loading in vulnerable areas.

Septic systems:

- Limit or prohibit permits for new septic
- Advanced treatment septic systems
- Septic-to-sewer retrofits





Springs Protection Assessment Using Nitrate Isotope Analysis

S U M M A R Y

- Nitrate from multiple human-influenced sources contributes to eutrophication in Florida Springs.
- Dual Nitrate Isotope Analysis can help untangle the mix of sources observed in water samples.
- Mixing models further help to define source proportions to each sampling site.
- Mixing models also provide important estimates about denitrification.
- Understanding the sources and proportion from each help target solutions.

Rules to Follow

Restricted Season: June 1 - September 30

- No fertilizer containing nitrogen or phosphorus may be applied in Orange County from June 1 through September 30, unless you comply with one of the following:
  - Residential applicators must have annual proof of training via completion of the online Orange County Fertilizer Application Education Course for Citizens.
  - Commercial applicators must have a valid FDACS Limited Fertilizer Applicator's License or proof of completion of Green Industries Best Management Practices (GI-BMP) within the previous 3 years.

Press release from Orange County, September 27, 2021

Orange County Awarded Millions for Septic Conversion and Upgrades

Approximately $41 million will go towards sewer conversion projects in Wekiwa Springs and Pine Hills

https://www.orangecountyfl.net/Environment/FertilizeResponsibly.aspx#.YYRCivnMKzU

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THANK YOU!

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Special thanks to:

Orange County Environmental Protection Division

Orange County Government Florida

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