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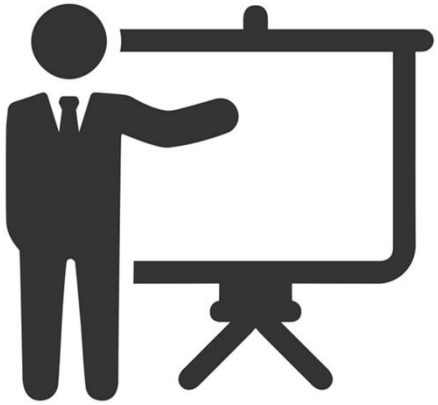
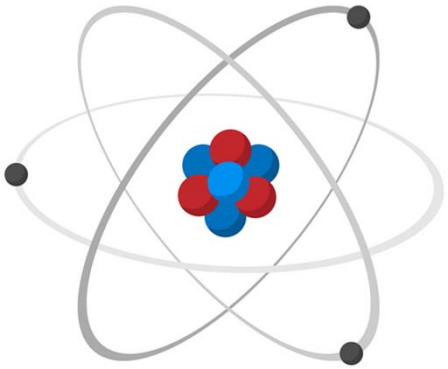
An Introduction to Isotopic Tracers in Stormwater Runoff

Sean P. Ahearn, MSc

The Goals

- ❑ Define isotopic fingerprinting of water and nutrients.
- ❑ Explain how fingerprinting is used to ID and track water and nutrient sources.
- ❑ Review case study applications.





BETA

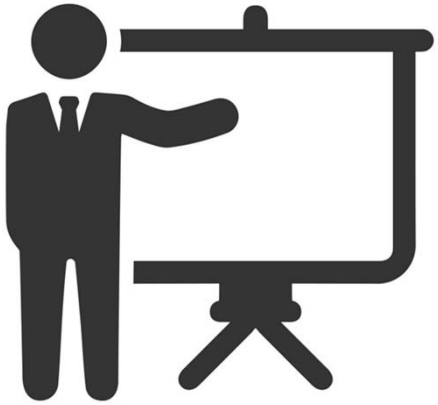
Our Road Map

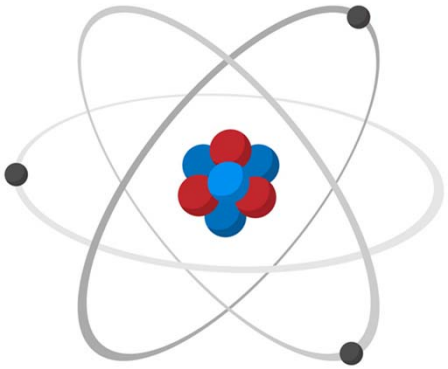
Introduction & Background

- ❑ Beta Analytic
  - ❑ What is an isotope?
    - ❑ What is a delta value?
      - ❑ Fingerprinting
        - ❑ The Water Cycle

Nutrient Source Tracking

- ❑ Why Track Nutrients?
  - ❑ Nitrate (NO_3^-) $\delta^{18}O$ & $\delta^{15}N$
    - ❑ Stormwater Applications
      - ❑ Review
        - ❑ Questions?





BETA

Beta Analytic
TESTING LABORATORY

- The **ISO/IEC 17025:2005 accreditation** is the highest level of recognized quality any testing or calibration laboratory can attain.

ISO 17025

BETA is celebrating **40** years of testing

- **Radiocarbon age/activity** in archaeological, geological, and water samples

- **Stable isotope ratios** of carbon, deuterium, nitrogen, and oxygen in organic and carbonate materials and water via IRMS/CRDS

BETA is the certifying body for bio-based testing for the following

BIOBASED > 85 % DIN Geprüft
I'm green™
100% biobased
KBMP CERTIFIED BIOBASED PRODUCT PRODUCT CONTENT
OK biobased VINÇOTTE
BP BiomassPla
USDA CERTIFIED BIOBASED PRODUCT PRODUCT 65%

Environmental Science & Technology

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$\delta^{15}N$ and $\delta^{18}O$ Reveal the Sources of Nitrate-Nitrogen in Urban Residential Stormwater Runoff

Yun-Ya Yang and Gurpal S. Toor*

Soil and Water Quality Laboratory, Gulf Coast Research and Education Center, University of Florida, Institute of Food and Agricultural Sciences, 14625 CR 672, Wimauma, Florida 33598, United States

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Water (H_2O) → $\delta^{18}O_{H2O}$ and $\delta^{2}H_{H2O}$

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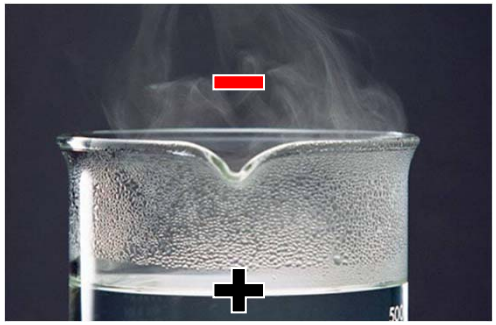
Stable Isotopes Review

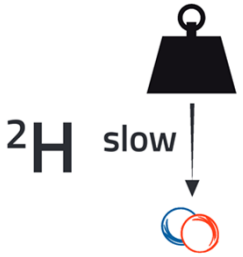
-**Stable isotopes** are variations of the same element but with differing number of neutrons and therefore mass. This changes the mass of the element without changing the element's identity or overall reactivity.

-Changes in delta values suggest that a reaction or phase change has taken place, fractionating the atom pool, expressed as the delta value and referred to as **depleted** and **enriched**.

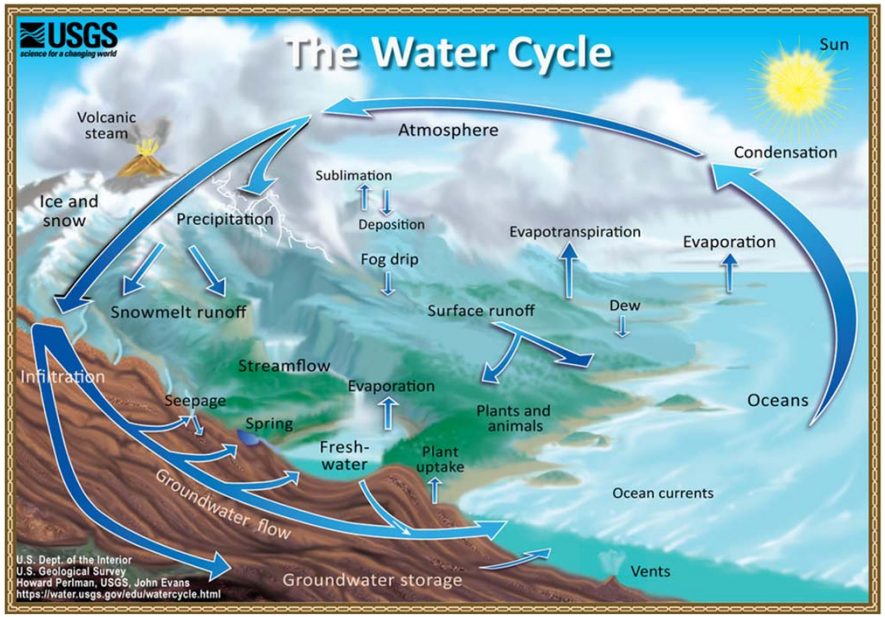
^{1}H	^{2}H
1.00794 99.985%	2.0141 0.015%
Stable	Stable

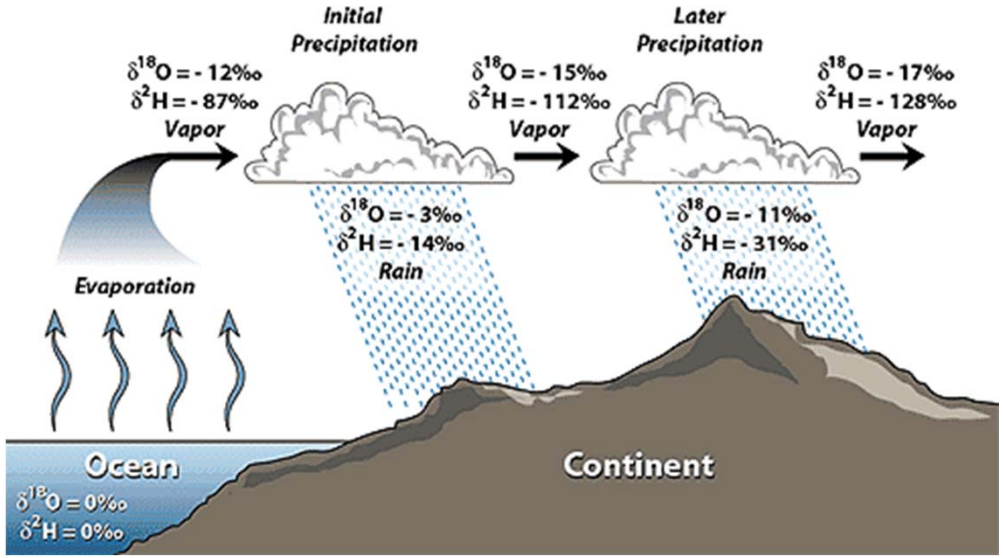
$$\delta\ ^{2}H = \left(\frac{\left(\frac{^{2}H}{^{1}H}\right)_{Unknown}}{\left(\frac{^{2}H}{^{1}H}\right)_{Standard}} - 1 \right) * 1000\ ‰$$





Fingerprinting & The Water Cycle





http://web.sahra.arizona.edu/programs/isotopes/oxygen.html

-Natural processes imprint on the O and H delta values.

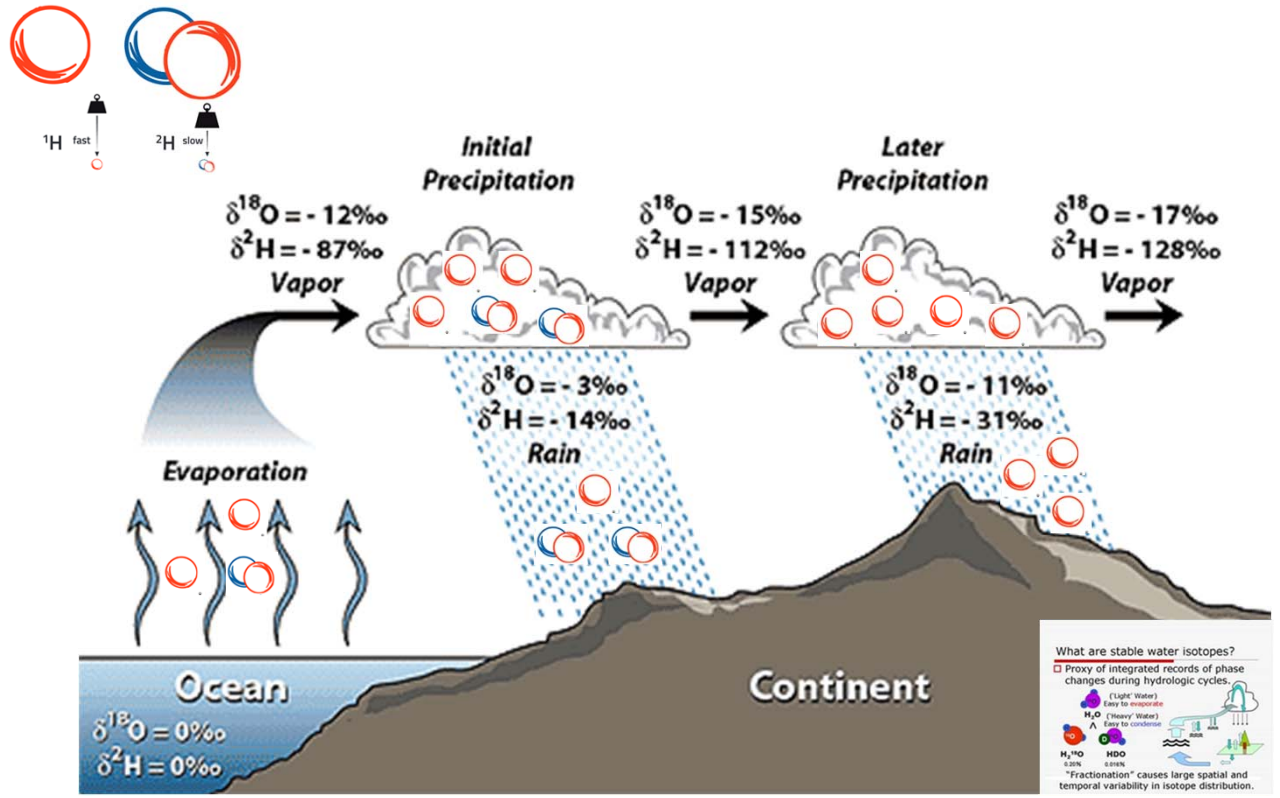
Fingerprinting & The Water Cycle

-Marine sources of water are fairly uniform and measure 0‰

-Vapor will favor ^{1}H and ^{16}O depleting the delta values.

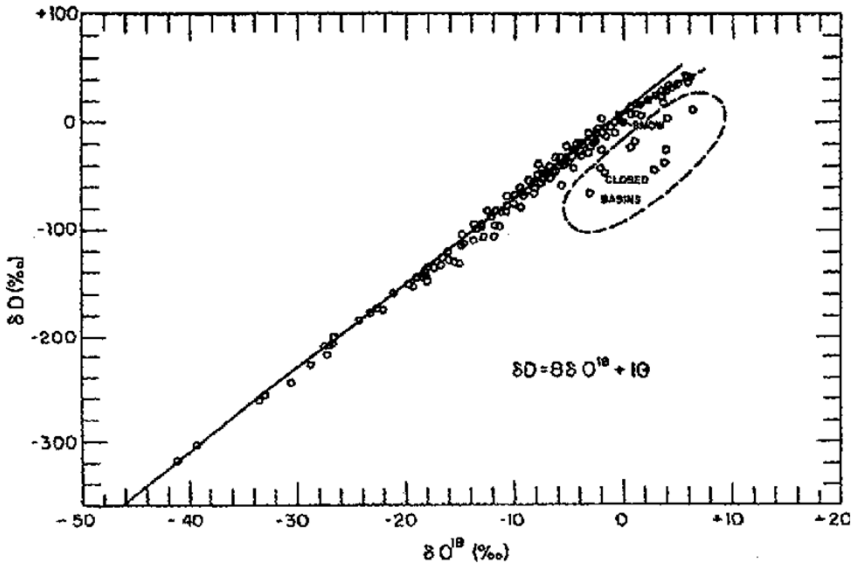
-Precipitation is generally depleted but condensation will favor ^{2}H and ^{18}O enriching the delta values.

-Ground water from snow melt in high altitudes and polar regions will show significant depletion in delta values.



The Global Meteoric Water Line

-In **1961** Dr. Harmon Craig introduced the concept of the Global Meteoric Water Line which describes the relationship of $\delta^{18}O$ and $\delta^{2}H$ isotopes of natural waters.



Performing shipboard titrations on the 1961 MONSOON expedition to the Antarctic Ocean.

The Geochemical News #98, January 1999

$$\delta D = 8 * \delta^{18}O + 10$$

Craig, H. (1961). Isotopic variations in meteoric waters. *Science*, *133*(3465), 1702-1703.

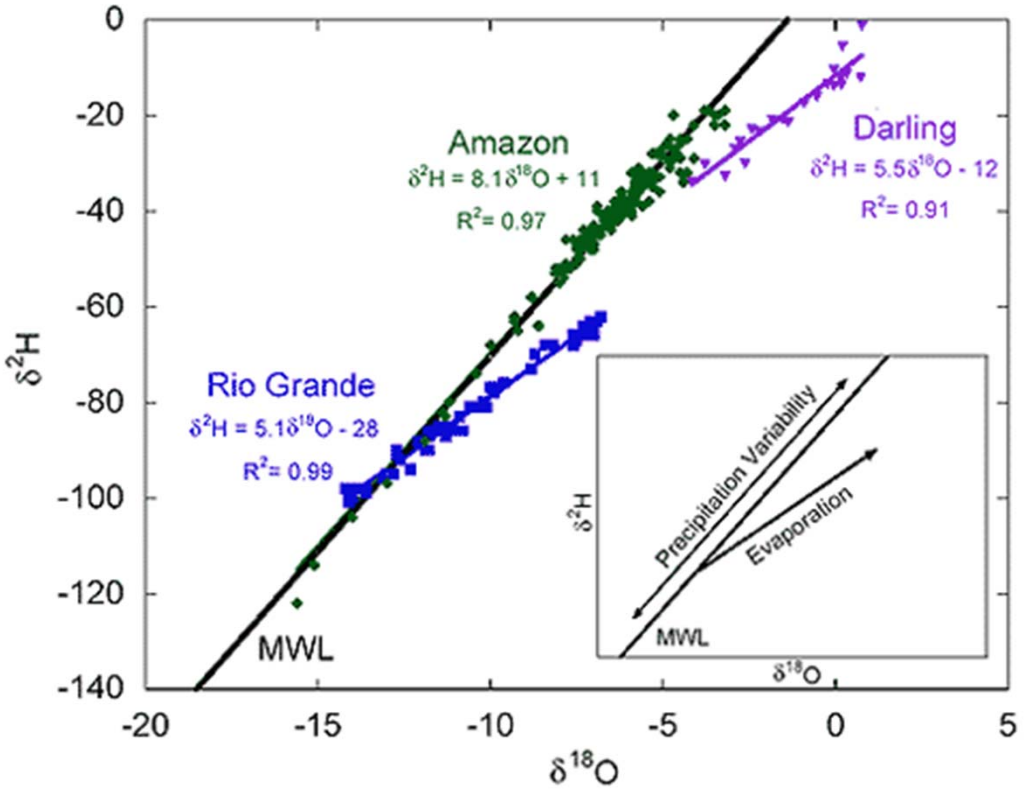
Fingerprinting & The Water Cycle

-The Global Meteoric Water Line

-The GMWL describe the relationship (slope) between $\delta^{18}O$ and $\delta^{2}H$ values of water samples from around the globe and is considered the general trend that is expected within the water cycle.

-This relationship is key in utilizing isotopic data to source water.

-A Local Meteoric Water Line (LMWL) describe this relationship on a regional scale.

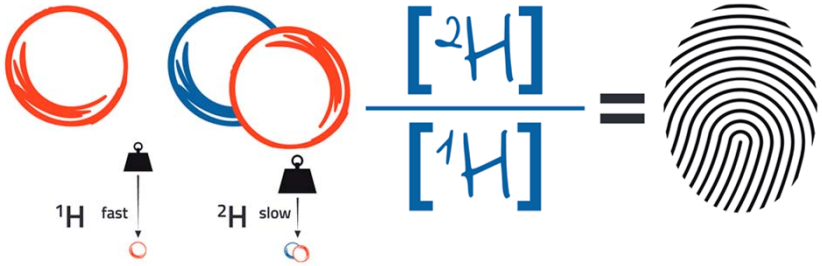


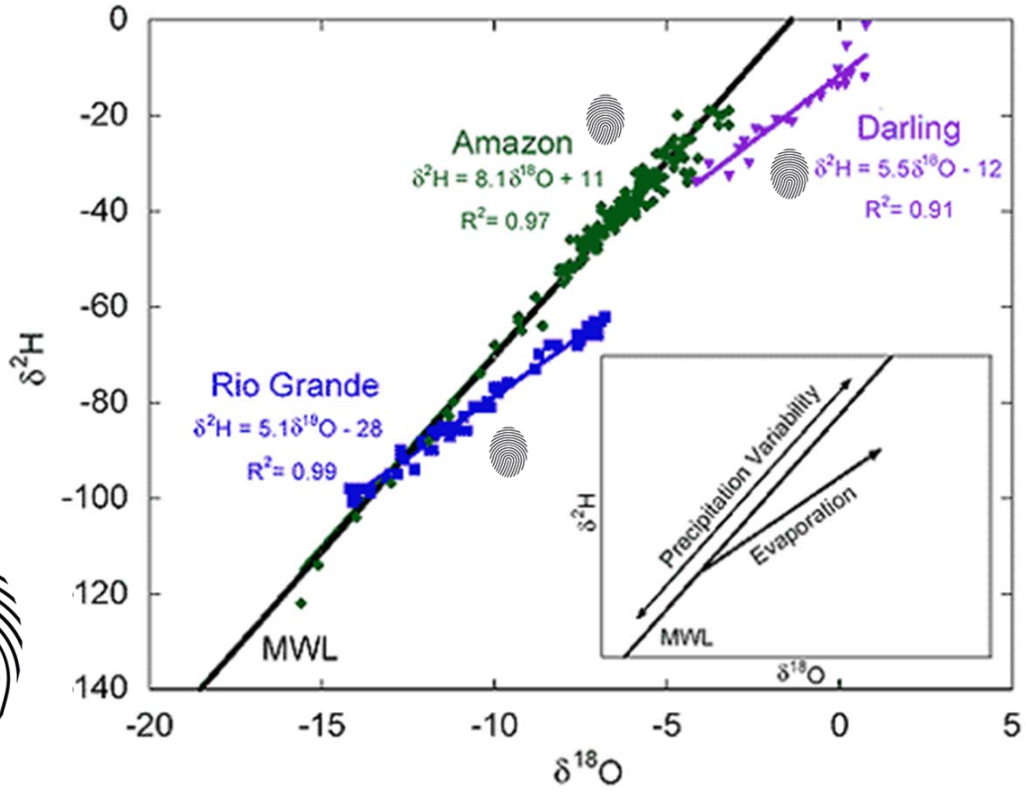
http://web.sahra.arizona.edu/programs/isotopes/oxygen.html

Fingerprinting & The Water Cycle

-Since it has been discovered that waters from different geographic regions have natural and distinct isotopic ratios, these ratios have been used to identify water sources.

-**Utilizing the isotopic value and their covariance as a tracer or fingerprint** has since become a very standard application of water isotopes.





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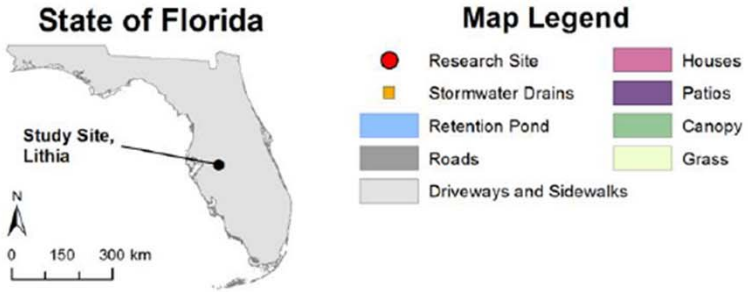


Water Isotope Fingerprint of Local Stormwaters

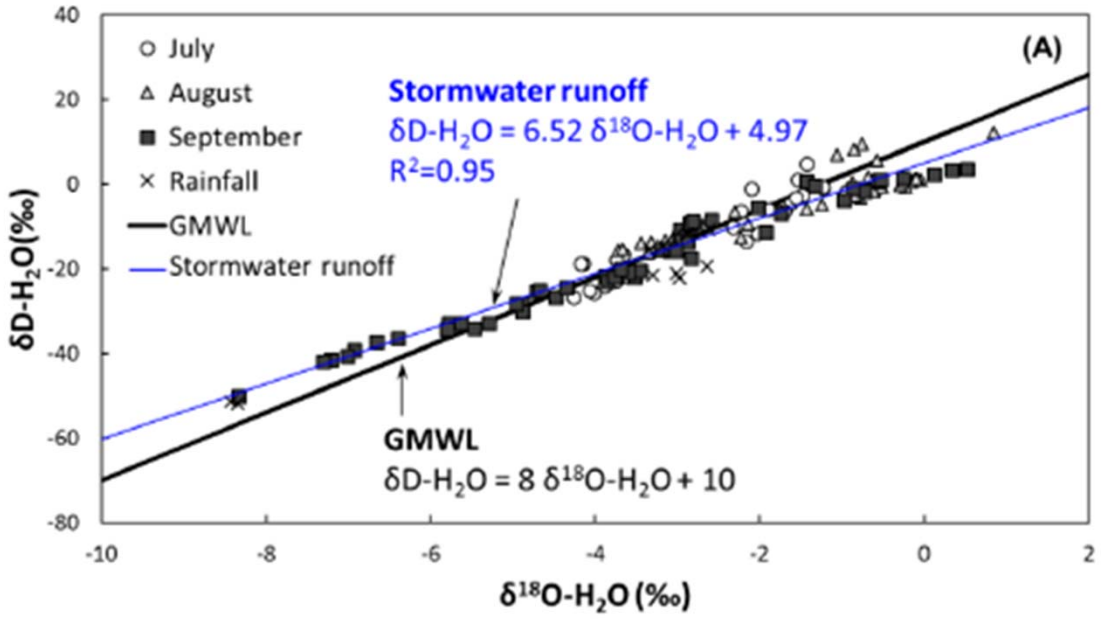
-Stormwater runoff during **all 25 storm events**

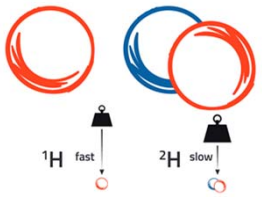
-Overall, our data indicated that all runoff water during 25 **stormwater events originated from the local rainfall and evaporation slightly changed the isotopic composition.**

-This suggests that no other sources of water (e.g., groundwater, municipal water, reclaimed water, leaking sanitary sewers) contributed any water and thus N in our stormwater runoff samples.

-Water isotopes were used as a diagnostic tool to measure the contribution of evaporative moisture. The mean d-excess values were lower than that GMWL indicated enrichment due to evaporation.

-Evaporation and impermeable areas leads to enrichment of the δ^2H values





Nutrient Source Tracking (NST)

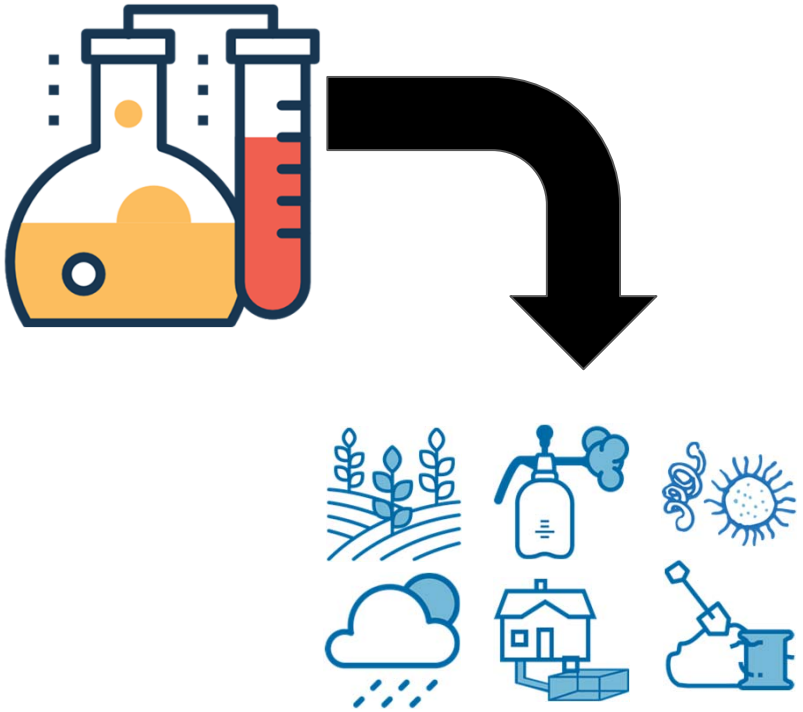
Nutrient Source Tracking

-Issues with excess nitrate Point Source vs. Nonpoint Source

-Nitrate(NO_3^-) $\delta^{18}O$ and $\delta^{15}N$

-Nitrate isotopic fingerprinting

-Stormwater Case Study

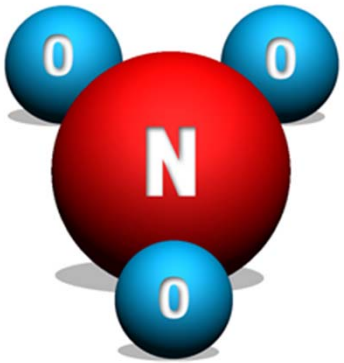


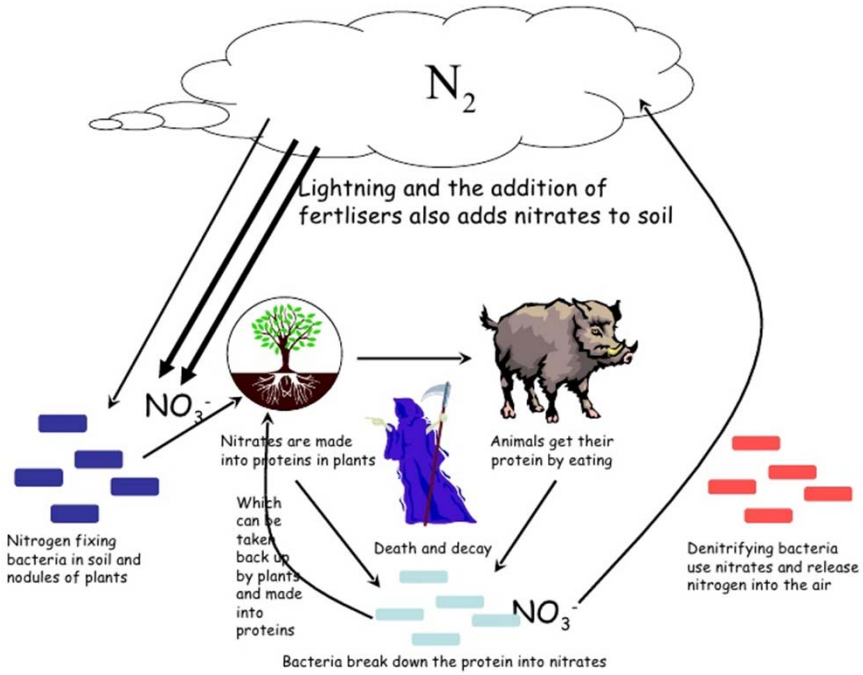
What is Nitrate?

-Nitrate, NO_3^-, is a naturally occurring molecule which contains 3 Oxygen atoms surrounding a central Nitrogen atom. In a trigonal planar structure.

-It is highly soluble in water

-Essentially a vehicle for nitrogen





Source: Dr. Shabeel Pn
URL:https://www.slideshare.net/shabeelpn/nitrogen-cycle-3614281

Long Term Environmental Hazards

-**Eutrophication can greatly impact recreational water quality, deterring tourism.**

-With eutrophication also comes **algal toxins**, marine algae produce toxins and cause large fish die offs. These poisons bioaccumulate and can eventually hit your dinner plate.

-Marine and Fishers industries struggle and due to a **dropping fish population**.

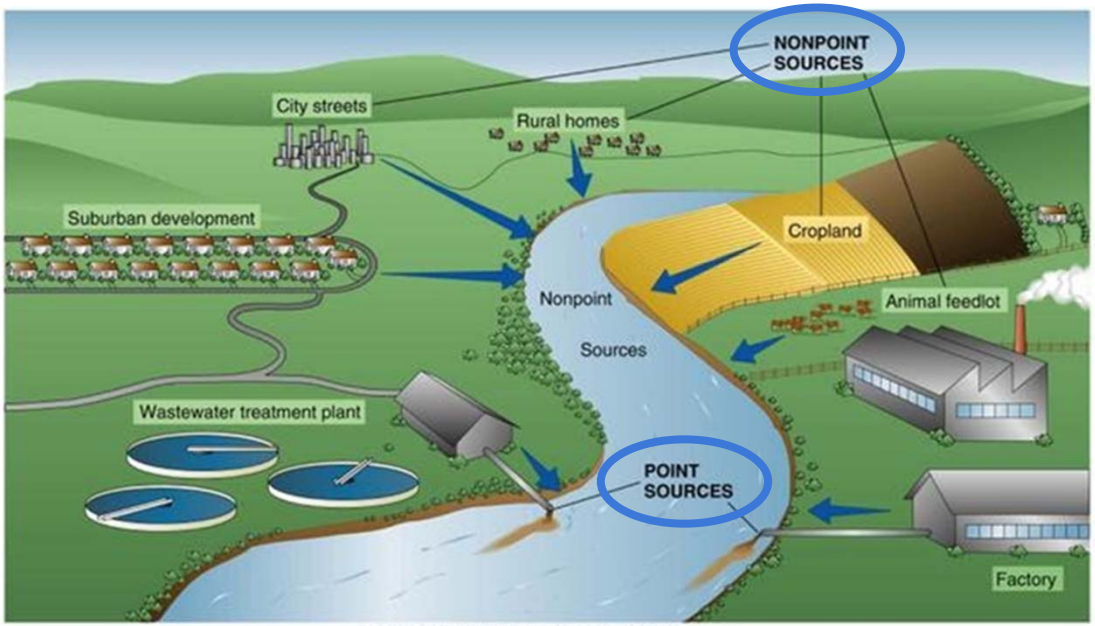
-All of which lead to **losses in revenue** for several industries which rely on

Nutrient Source Tracking

-**Nonpoint source and point source contamination can be difficult to distinguish**.

-Aside from obvious point sources such as wastewater treatment plants there are also less obvious groundwater **nonpoint sources which can be difficult to account for**.

-When mitigating nutrients or developing wetland projects it is necessary to understand the sources of nutrients into and out of a system.

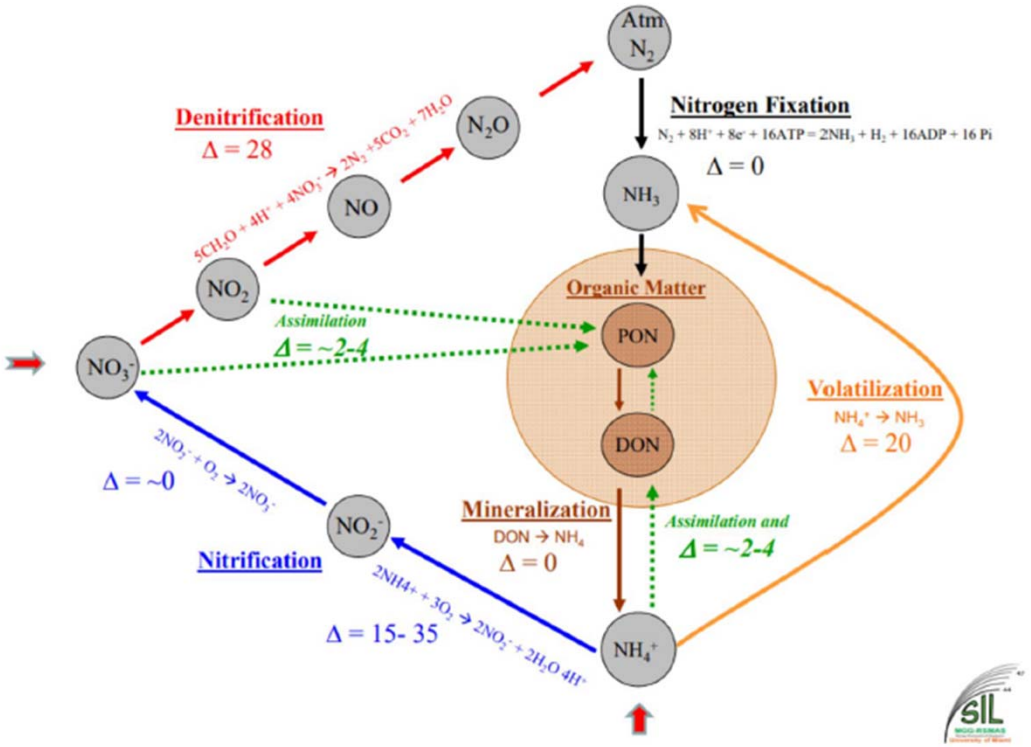


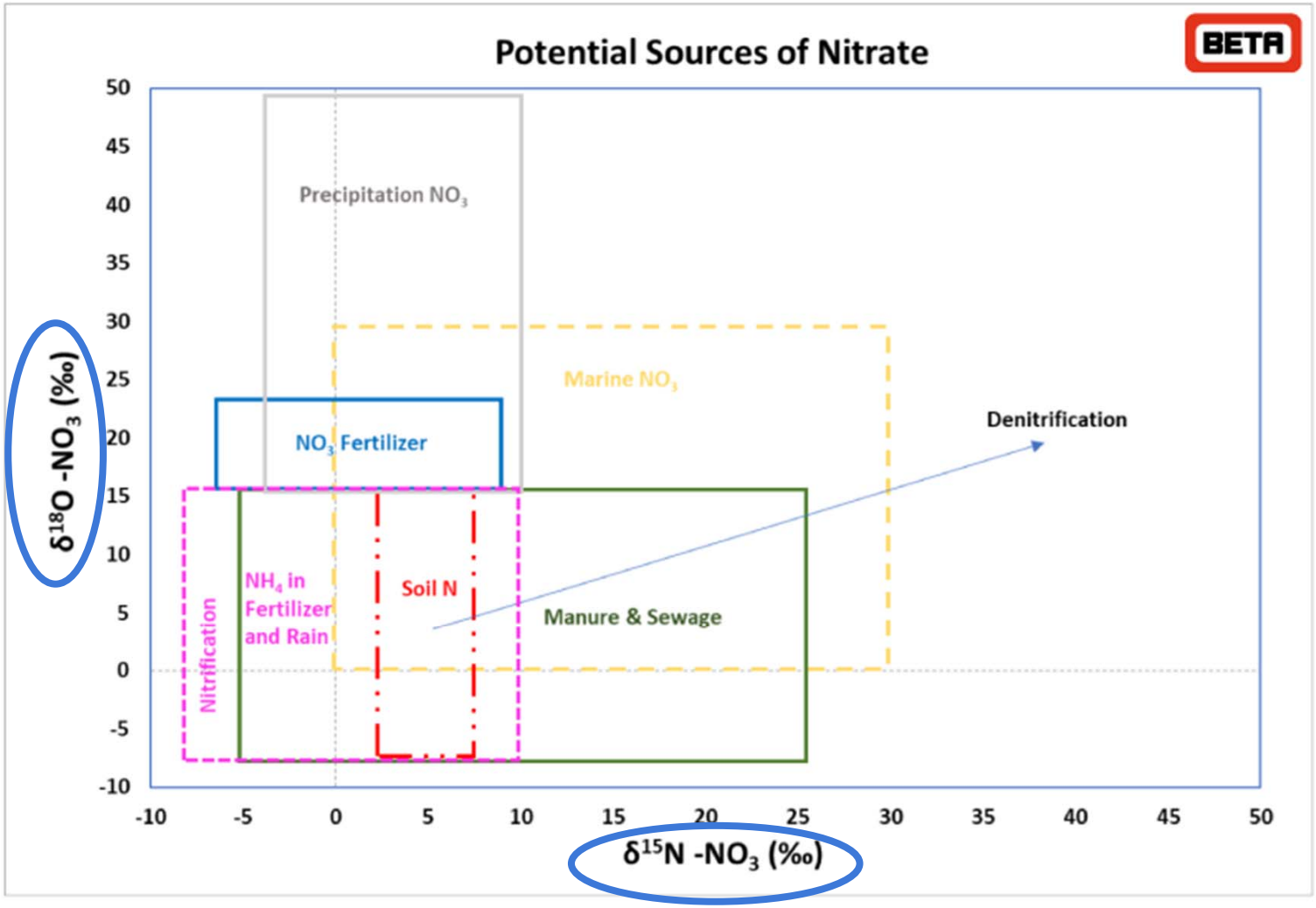
Isotopic Tracers Why Nitrate?

-Nitrate analysis allows for the **clearest understanding of fate** of nitrogen by giving insight into what pathway nitrogen is following.

-By having both oxygen and nitrogen isotopic values a **dual isotopic approach** can be made, similar to water, there is more evidence then compared to using one isotopes alone.

-Wether being nitrified or denitrified the **fractionation imposed on both isotopes is evident.**




Potential Sources of Nitrate
BETA
Precipitation NO_3
Marine NO_3
NO_3 Fertilizer
Denitrification
NH_4 in Fertilizer and Rain
Soil N
Manure & Sewage
Nitrification
$\delta^{18}O$ -NO_3 (‰)
$\delta^{15}N$ -NO_3 (‰)
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-10
-5
0
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10
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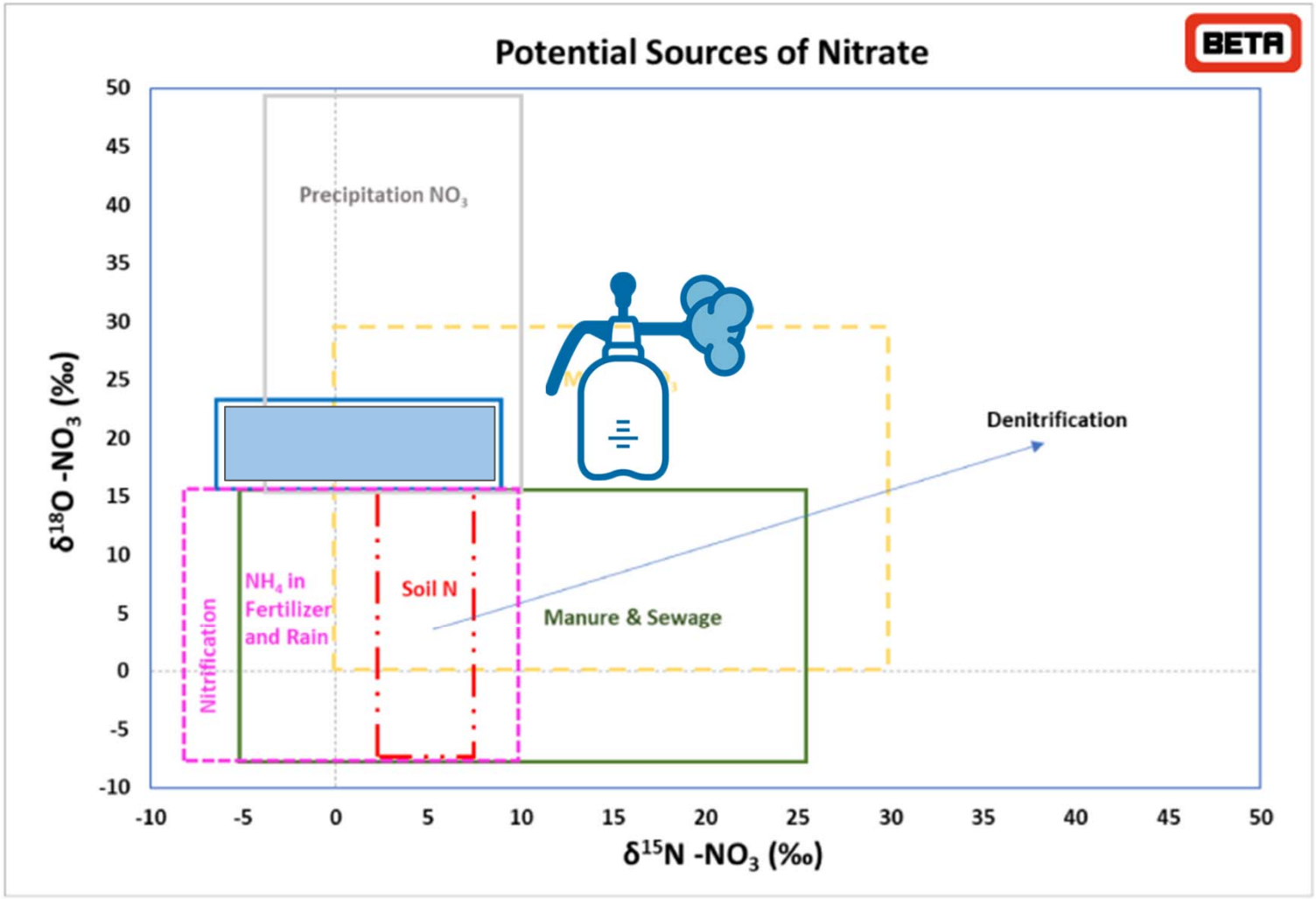

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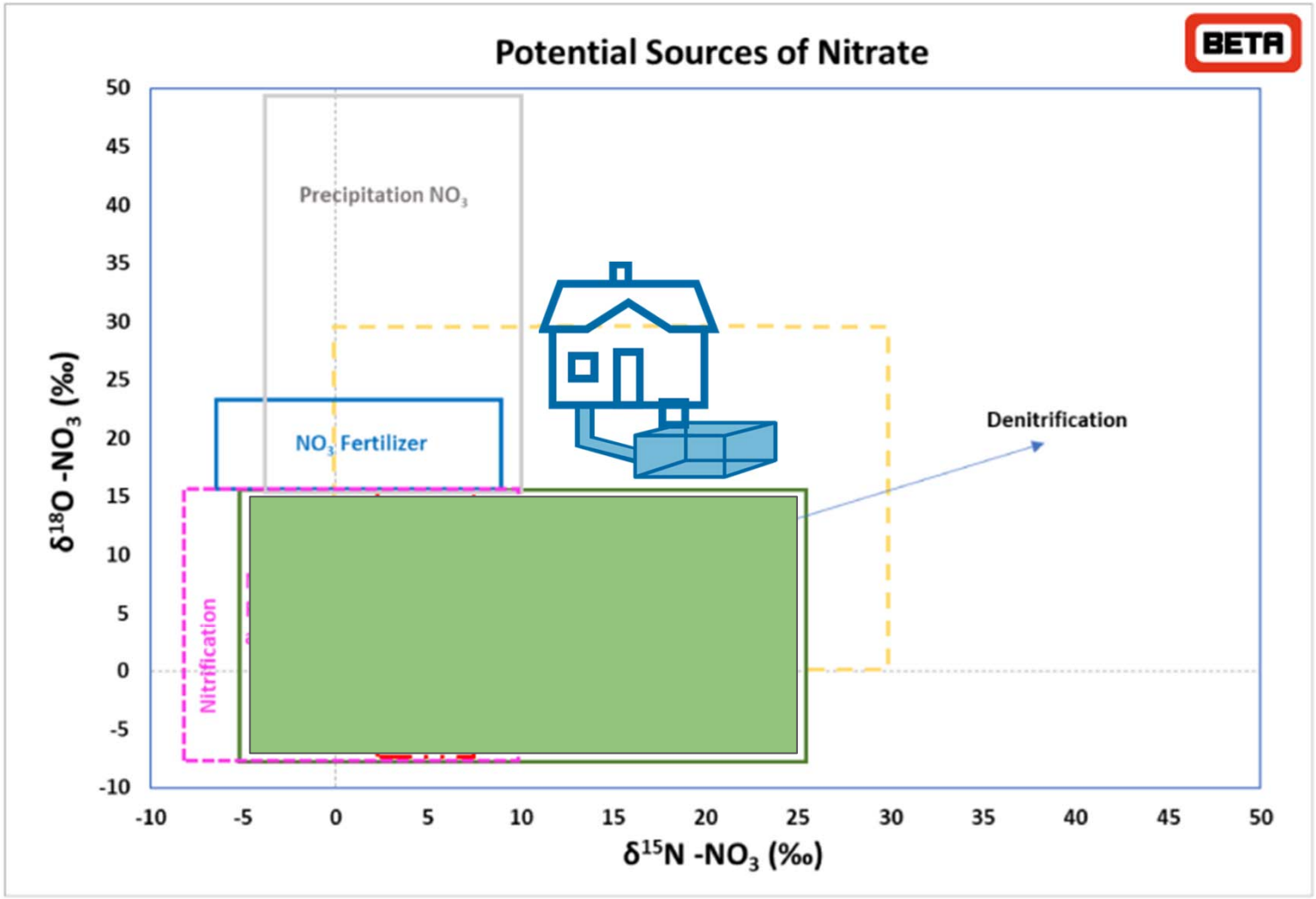

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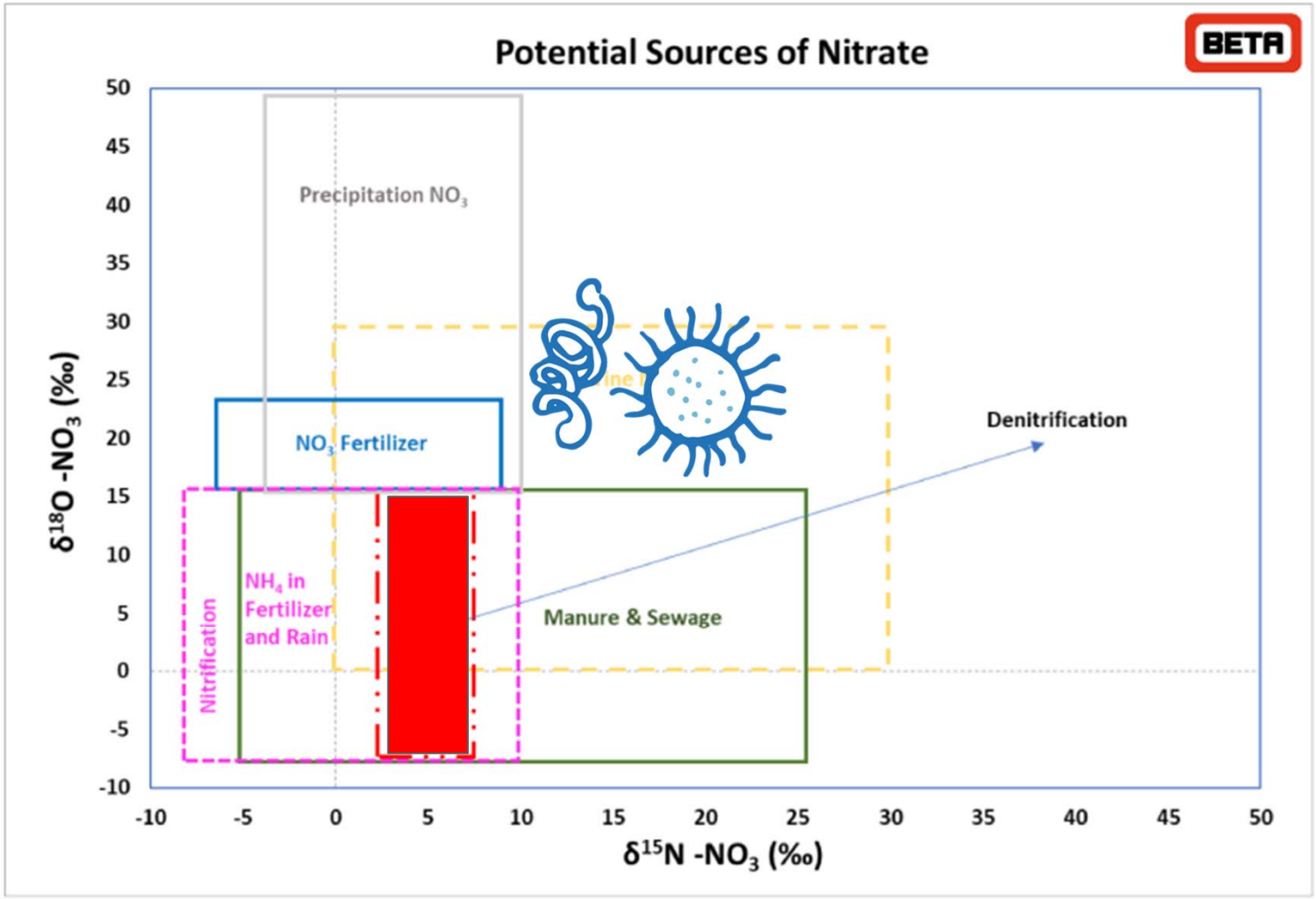

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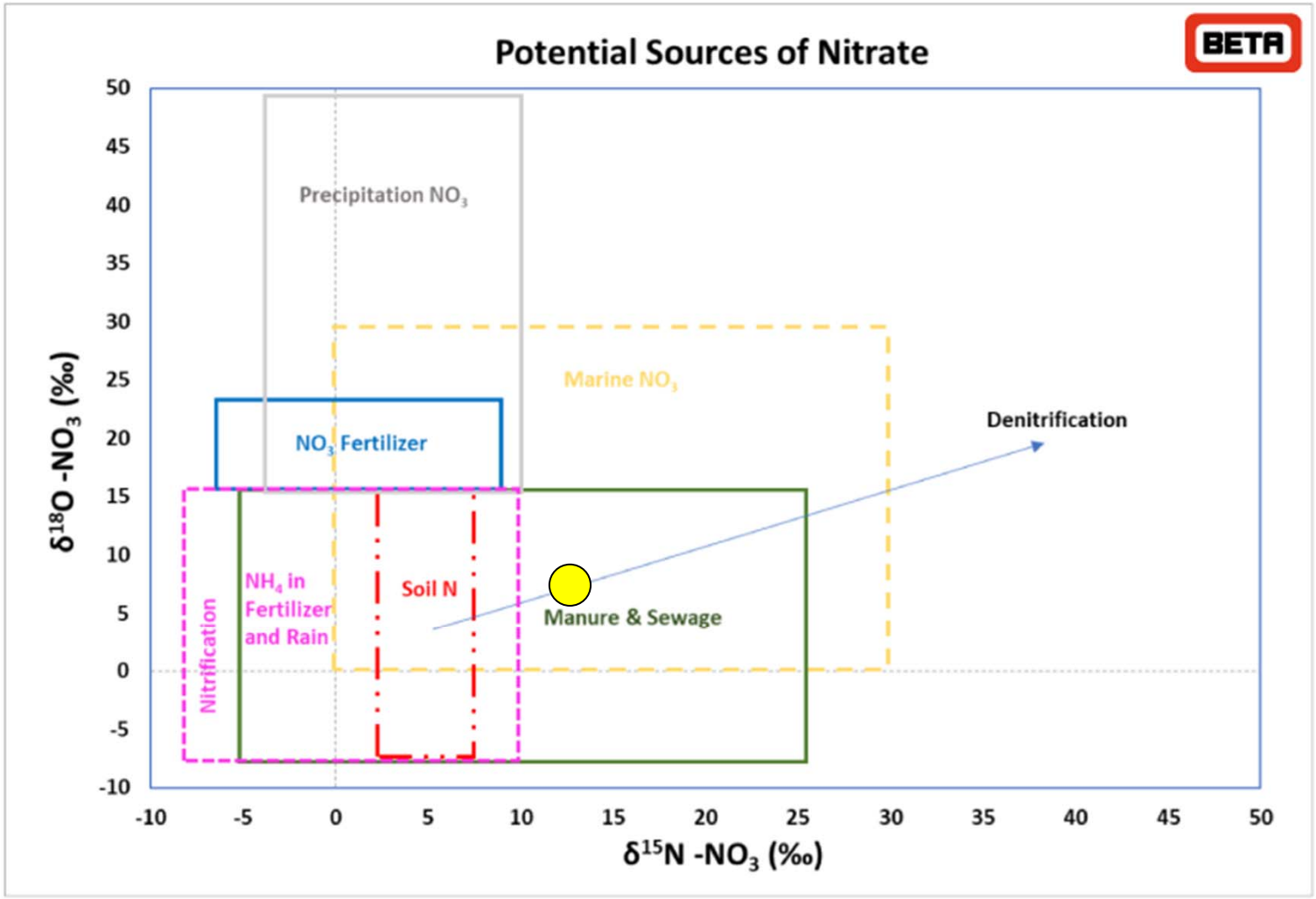

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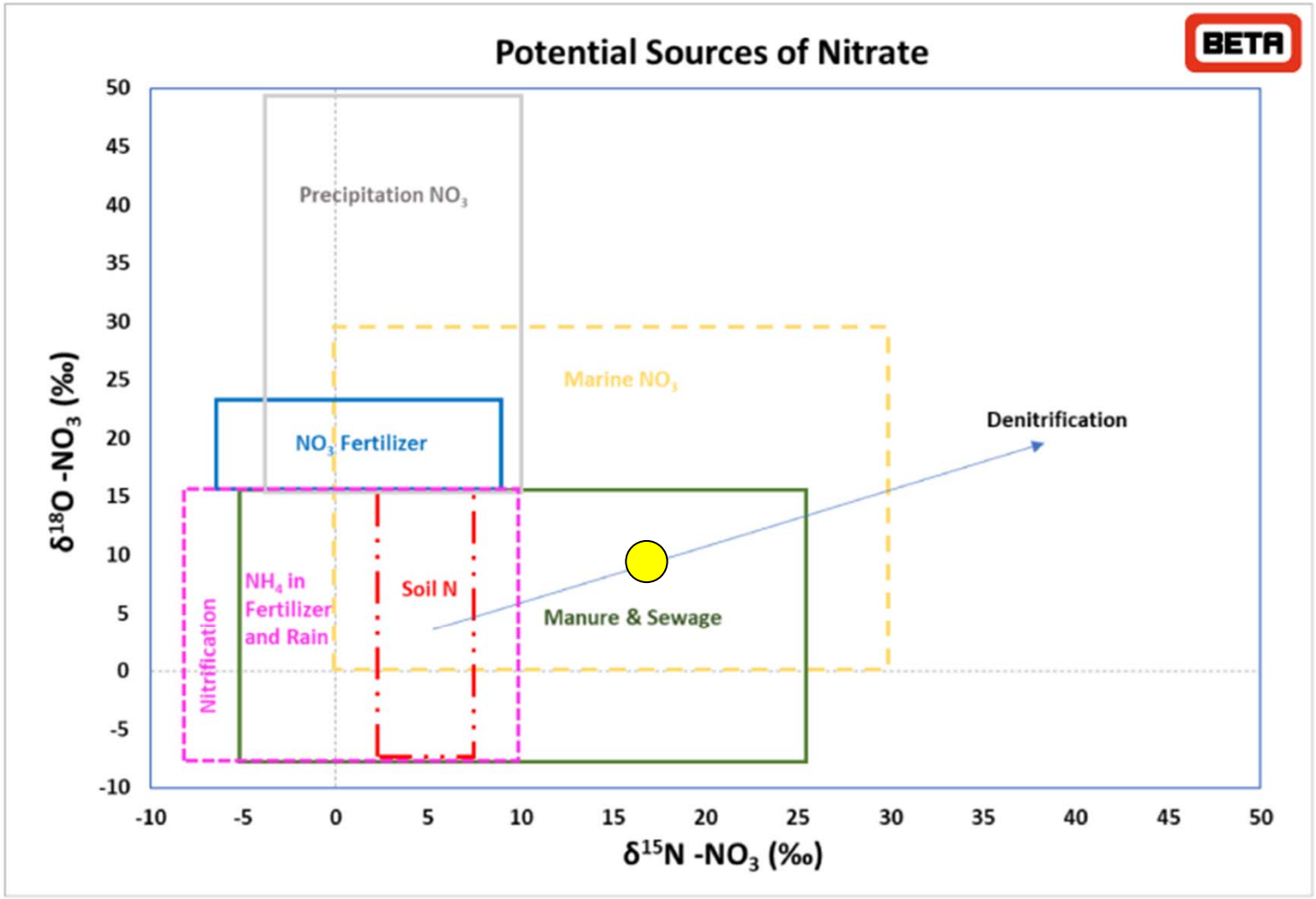

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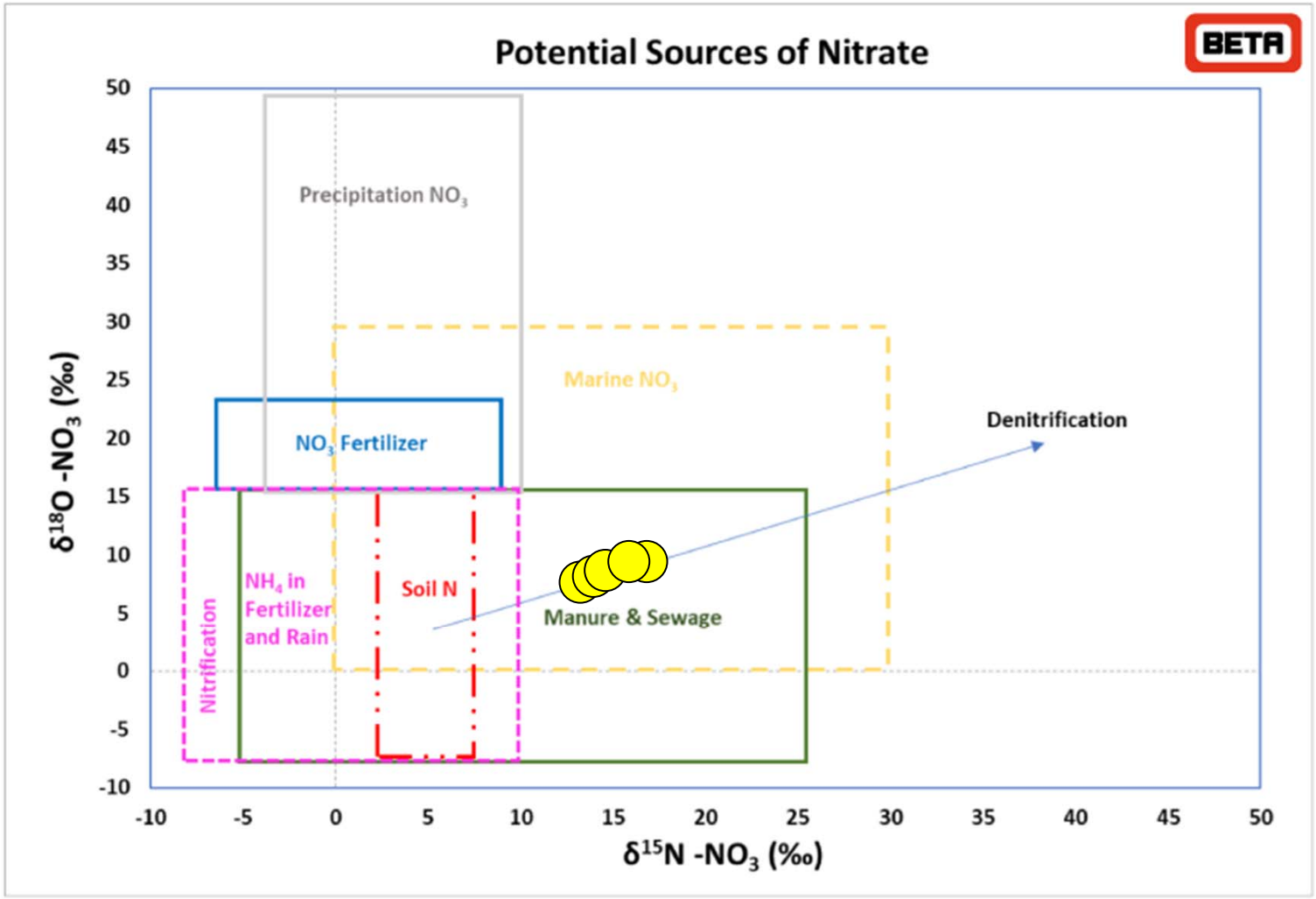

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Nitrate Isotope Dynamics

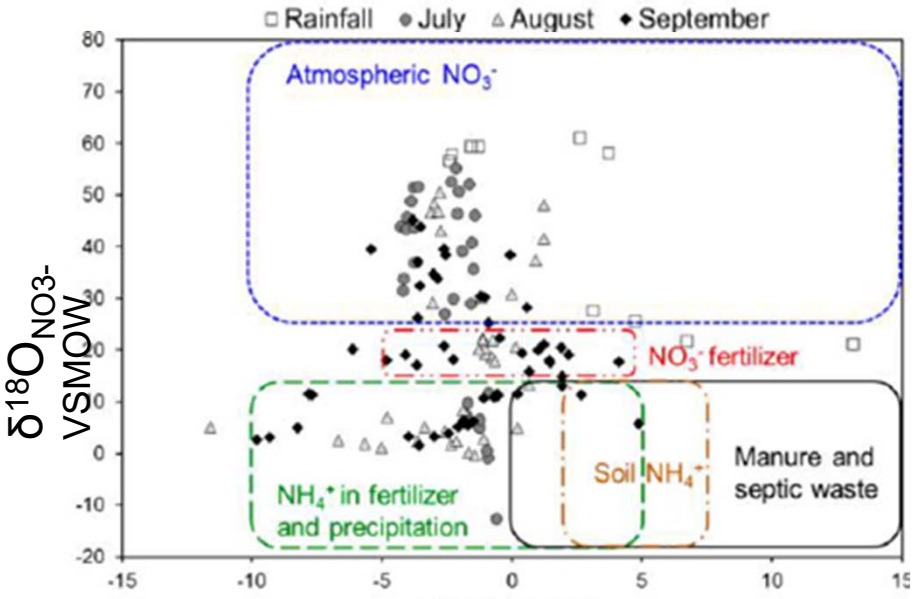
Nitrate Isotopic Results

Nitrate (NO_3^-) → $\delta^{18}O_{NO3-}$ values varied from ~0 to +60‰

Nitrate (NO_3^-) → $\delta^{15}N_{NO3-}$ values varied from ~-10 to ~+5‰

Rainfall results were on average enriched in $\delta^{18}O$ consistent with an atmospheric source.

Seasonally in July and August $\delta^{18}O$ results are on average more enriched then results in September.



Nitrate Isotope Dynamics

Potential Sources of Nitrate

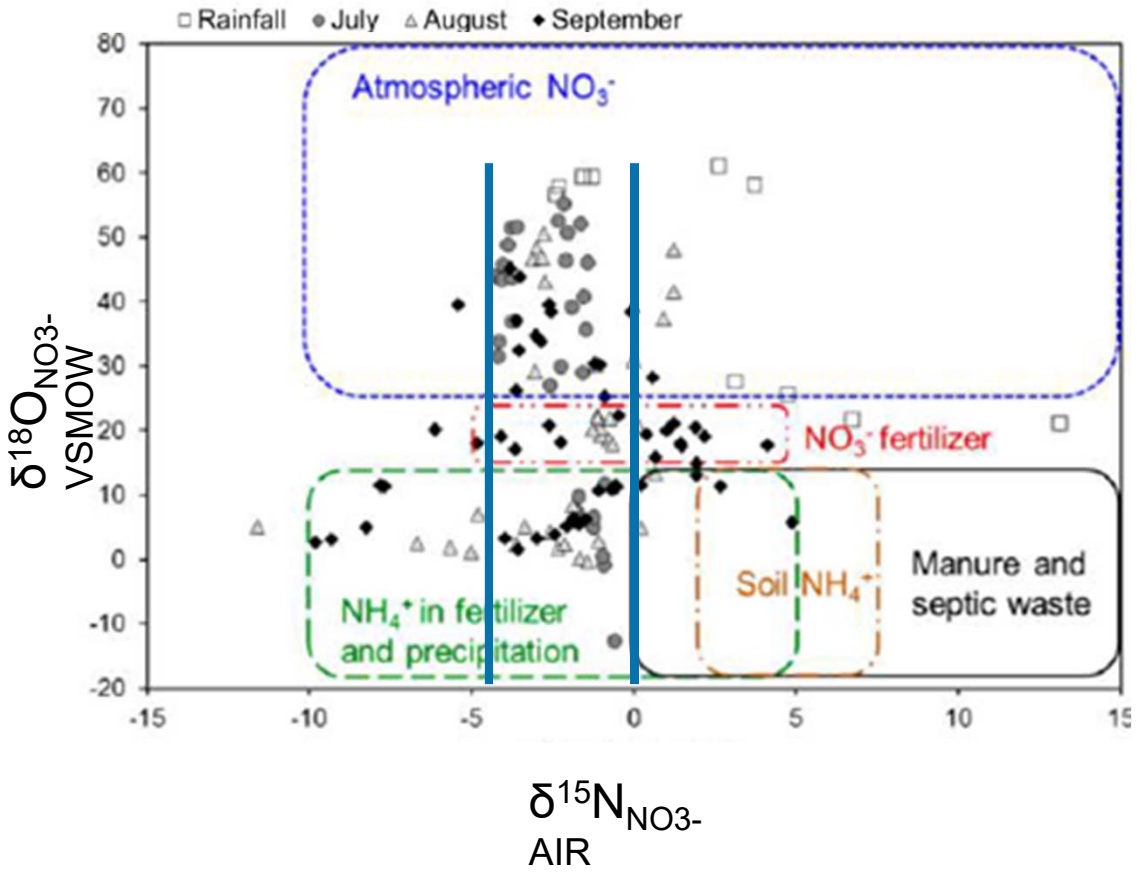
~60% of the runoff samples $\delta^{15}N_{NO3-}$ values varied from **0 to -4‰**

-The potential sources diagram suggests:

-Atmospheric deposition
-Chemical fertilizer
-Soil based N and
-Organic N

-Sources as the main contributors of NO_3^-

-**No evidence of Manure of Septic waste**.

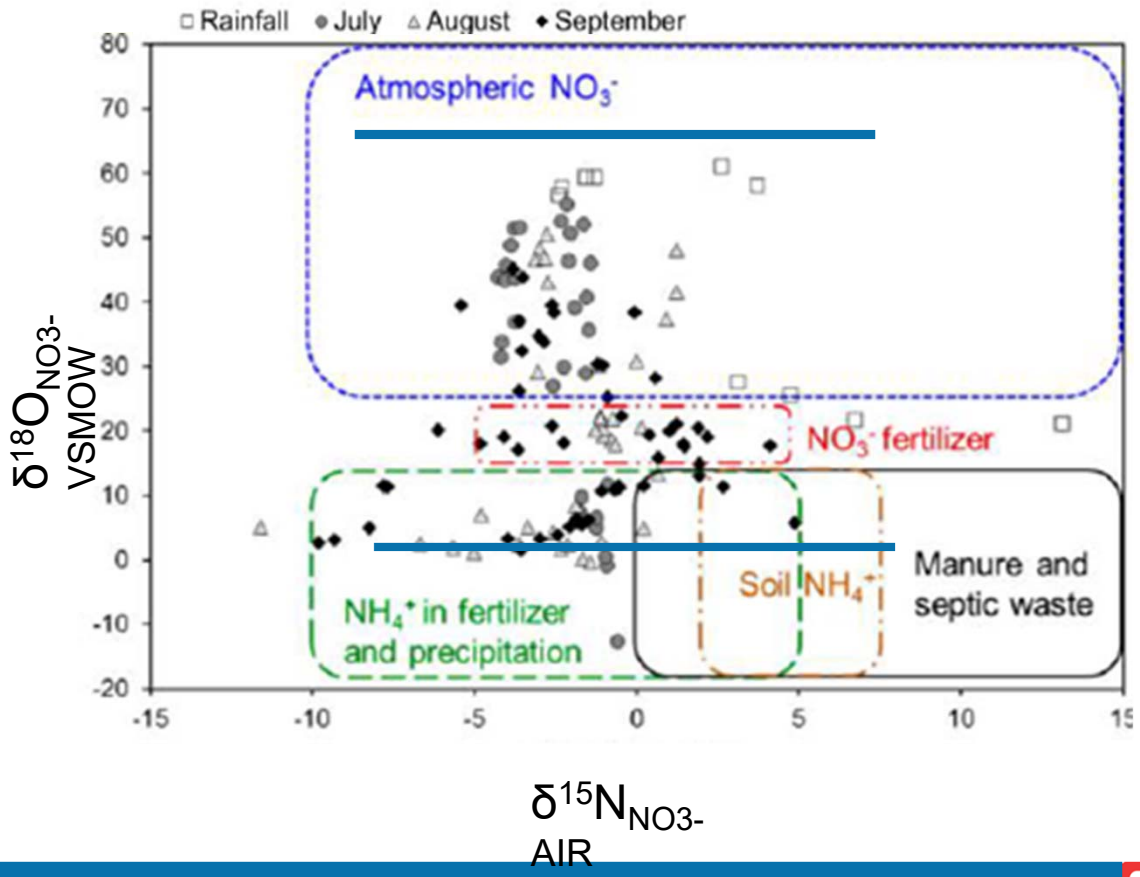


Nitrate Isotope Dynamics

Potential Sources of Nitrate

-Positive $\delta^{18}O_{NO3-}$ values suggest **atmospheric deposition as a major contributor of nitrate to stormwater.**

-$\delta^{18}O_{NO3-}$ values are known to be be more useful tools when $\delta^{15}N_{NO3-}$ have wide ranges.



Nitrate Isotope Dynamics

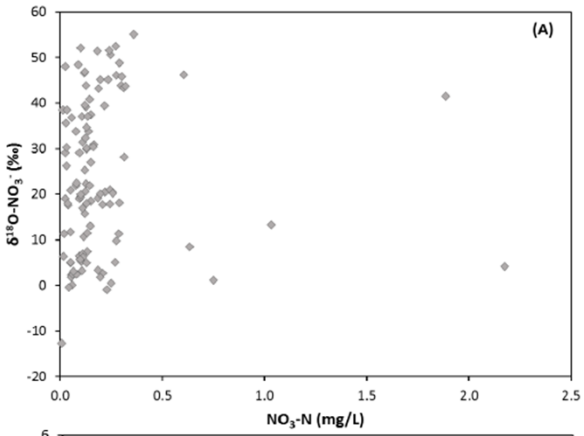
Mixing and Fate

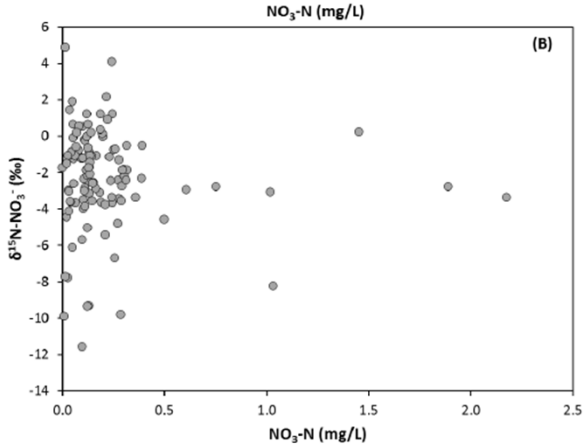
-By combining isotopic data with concentration data, **evidence for denitrification(transport out the system) and mixing (transport into the system)** can be assessed.

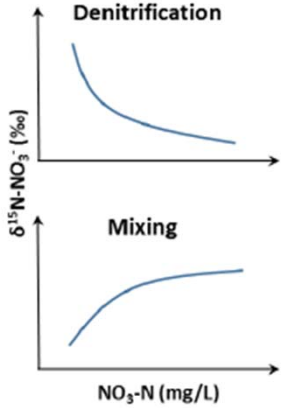
-Denitrification(DN) is expected to increase delta values as concentrations decrease

-Mixing tends to increase both delta values and concentrations

-**There was some evidence for mixing and no evidence for DN**







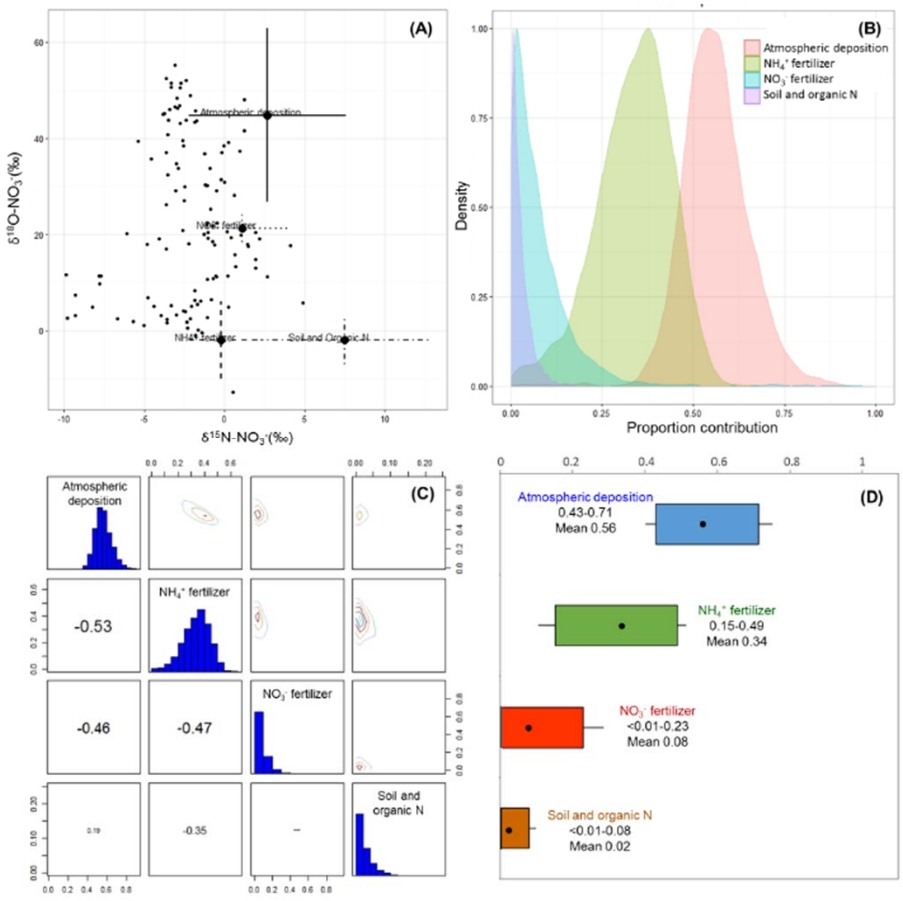
Nitrate Isotope Dynamics

Delineated Sources

-Statistical analysis was applied to the data sets to best determine sources in urban runoff.

-**Atmospheric deposition was** found to contribute more than half of the nitrate found in urban runoff at **~56%**.

-**Ammonia based fertilizer** was found to be the 2nd dominant source in urban runoff at **~34%**.



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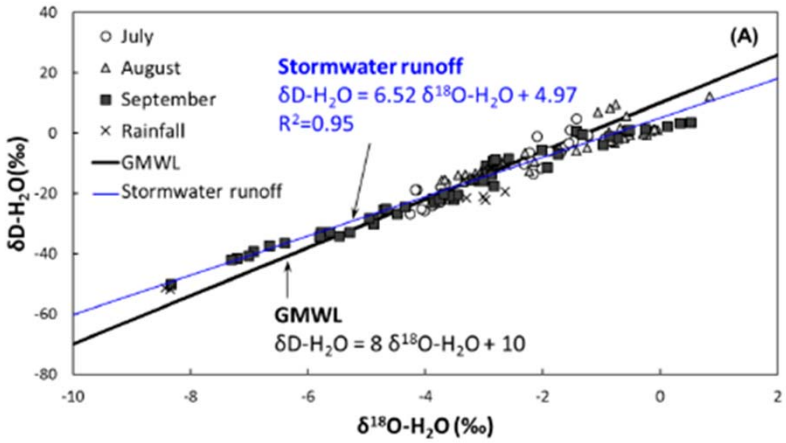
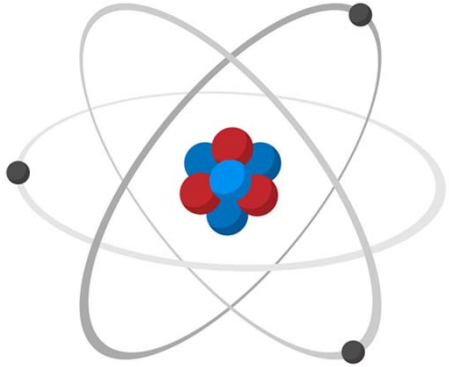
Isotopic Applications Review

$\delta^{18}O_{H20}$ & $\delta^{2}H_{H20}$

-Interpretation of water sources, mixing,and source heterogeneity.

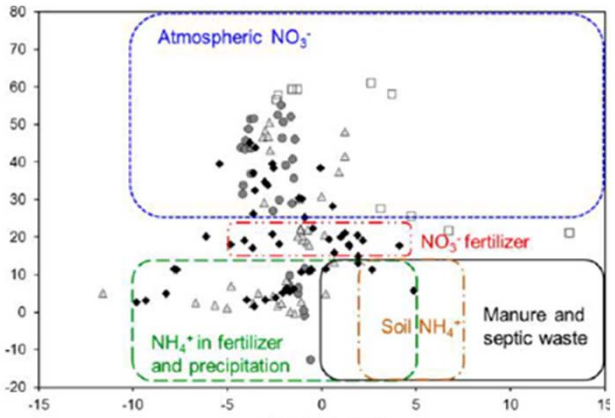


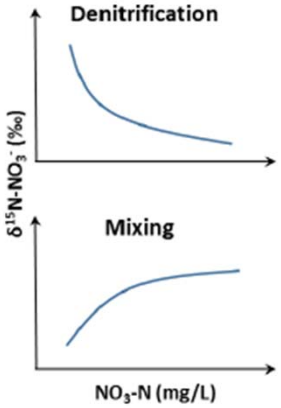


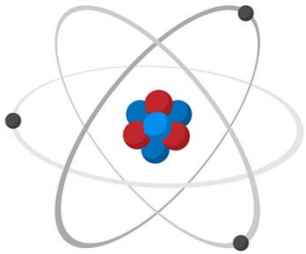
Isotopic Applications Review

$\delta^{18}O_{NO3-}$ & $\delta^{15}N_{NO3-}$

-Insight into source, transport mechanisms





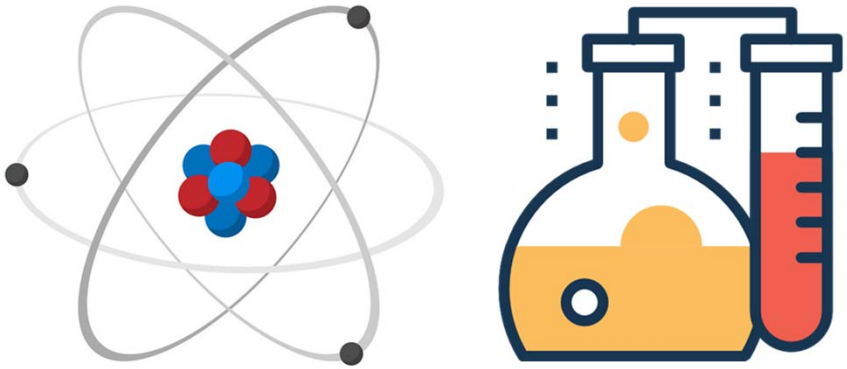


Isotopic Applications Review

-Insight provided by isotopic analysis into the source and transport of excess nutrients into stormwater system can help **optimize stormwater catchment areas.**

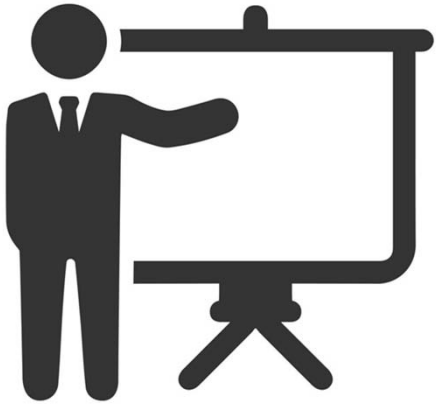
- This data can also be used to **suggest whether NPS or PS contamination** are the causes of elevated nutrients which may ultimately be introduced in groundwaters systems or directly into canals and estuaries.

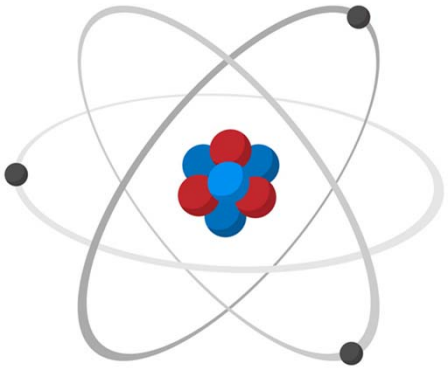
-All without the need for dosing or subsurface intervention.



The Goals of Our Next 30 mins

- ☑ Define isotopic fingerprinting of water and nutrients.
- ❑ Explain how fingerprinting is used to ID and track water and nutrient sources.
- ❑ Review case study applications





BETA

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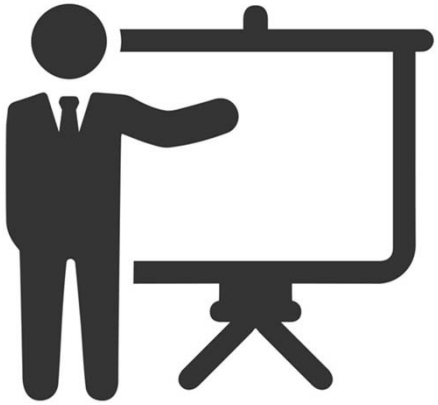

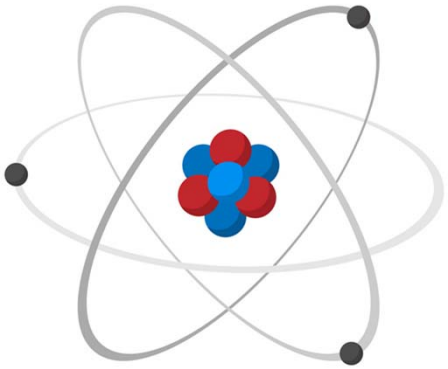

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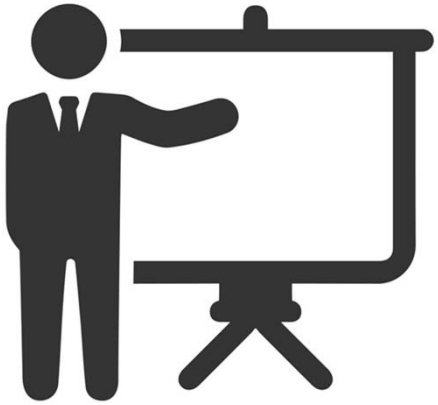

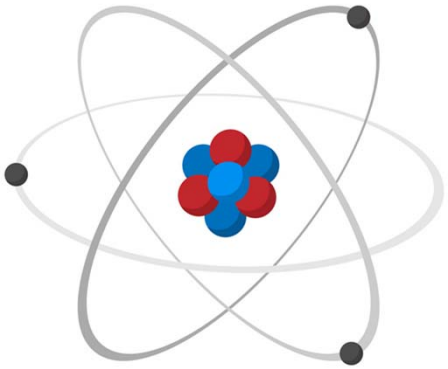

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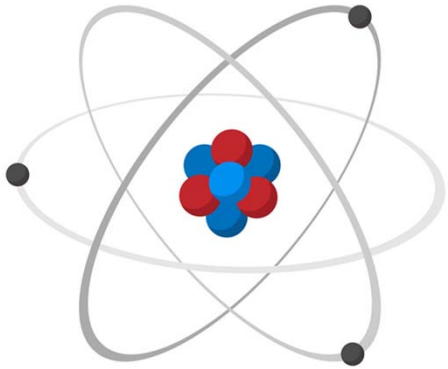
Summary and Review

Isotopic Tracers have allowed for:

-Insight into the source and transport of excess nutrients into stormwater system can help **optimize stormwater catchment areas** as well be used to suggest whether NPS or PS contamination are the causes of elevated nutrients which may ultimately be introduced in groundwaters systems or directly into canals and estuaries.

-These finding suggested **the importance of atmospheric contributions in the area, as well as mixing with fertilizers.**

- There was **evidence that fertilizer nitrification was promoting the formation of NO_3^{2-}** . With **no evidence for denitrification.**



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Questions?

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