Florida Stormwater Association

Adaptive Nutrient Source Identification Programs

March 9, 2023

10:30 a.m. – 11:30 a.m. (Eastern)

www.florida-stormwater.org

APPLIED SCIENCES

Civil Engineering
Watershed Planning
Urban Design
Resiliency Strategies

OneWaterFL.com

Florida Stormwater Association

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Nutrient Source Tracking

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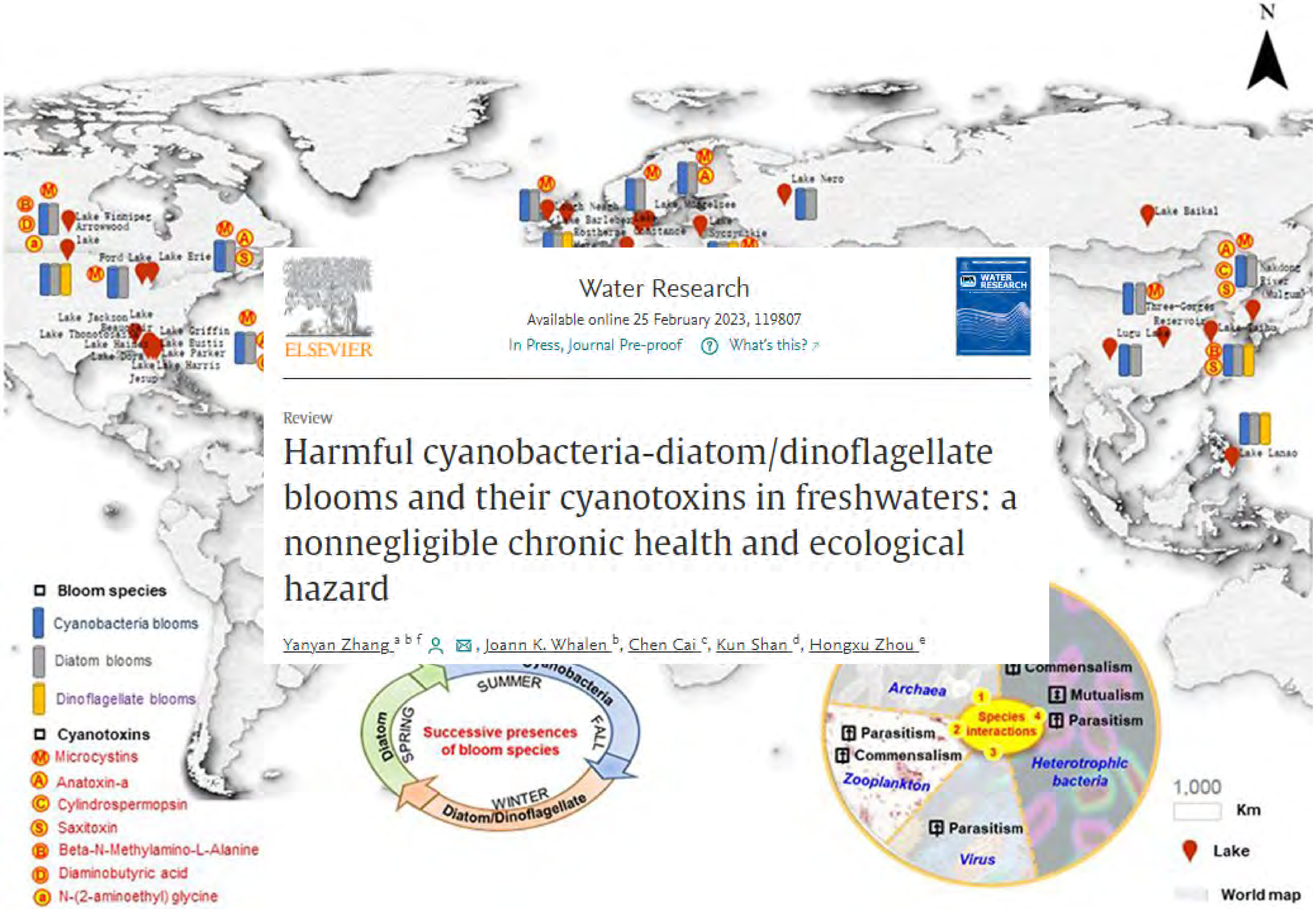
Nutrient Source Tracking (NST) Overview

- Introduction
- Background
- Sampling for NST
- Challenges & Limitations

Introduction

Water full of algae laps along the Sewell's Point shore on the St. Lucie River under an Ocean Boulevard bridge in Martin County. [Richard Graulich |The Palm Beach Post via the Associated Press (2016)]

- Nutrient Loading to Waterbodies
- Nitrogen and Phosphorus
- Harmful algae blooms
- Impacts to biodiversity, recreation, and property value
- How do we identify these sources of nutrients?



ELSEVIER

Water Research

Available online 25 February 2023, 119807

In Press, Journal Pre-proof What's this?

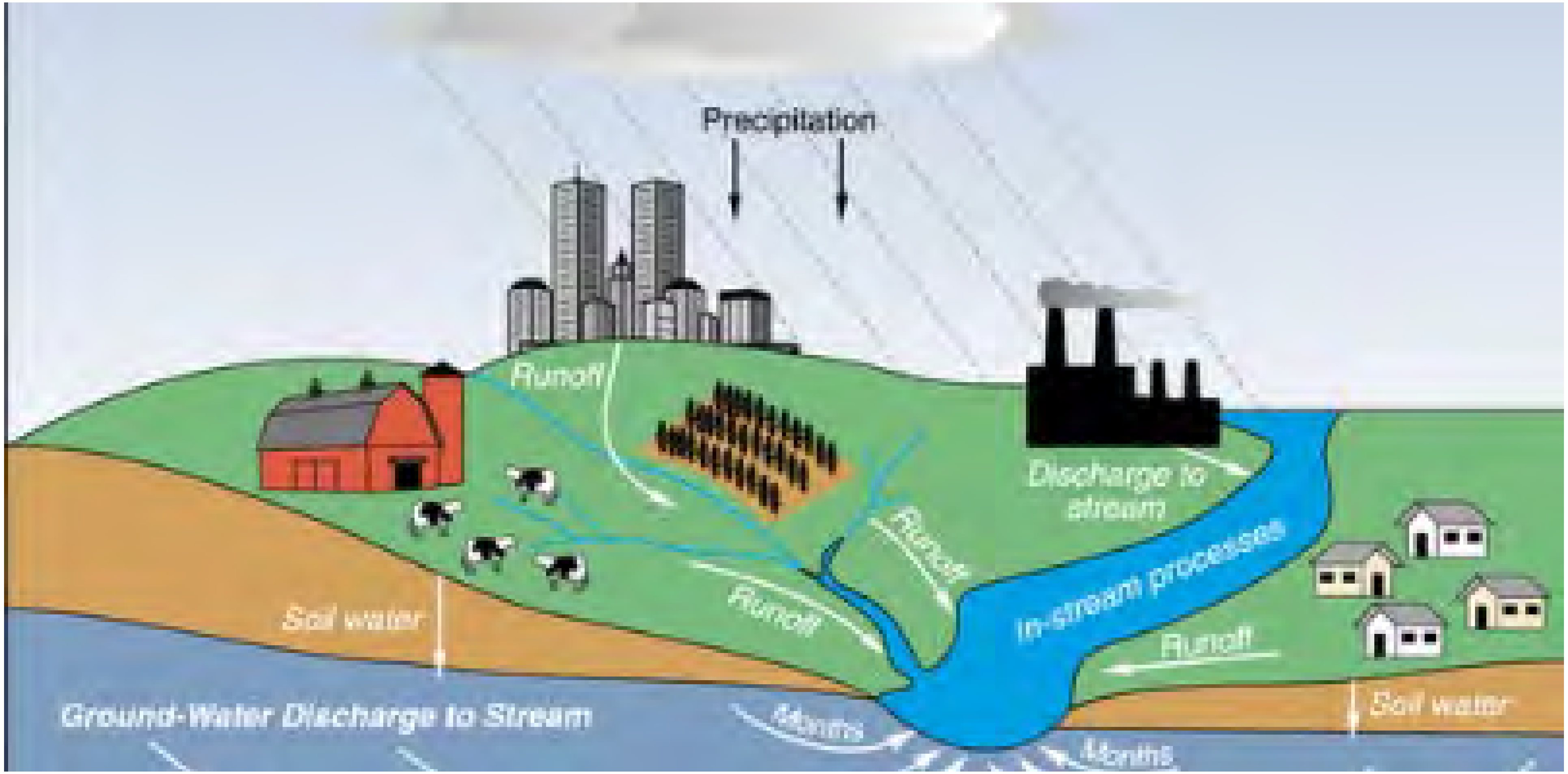
Review

Harmful cyanobacteria-diatom/dinoflagellate blooms and their cyanotoxins in freshwaters: a nonnegligible chronic health and ecological hazard

Yanyan Zhang[a b f], Joann K. Whalen[b], Chen Cai[c], Kun Shan[d], Hongxu Zhou[e]

Where are nutrients coming from?

Sources of Nutrients

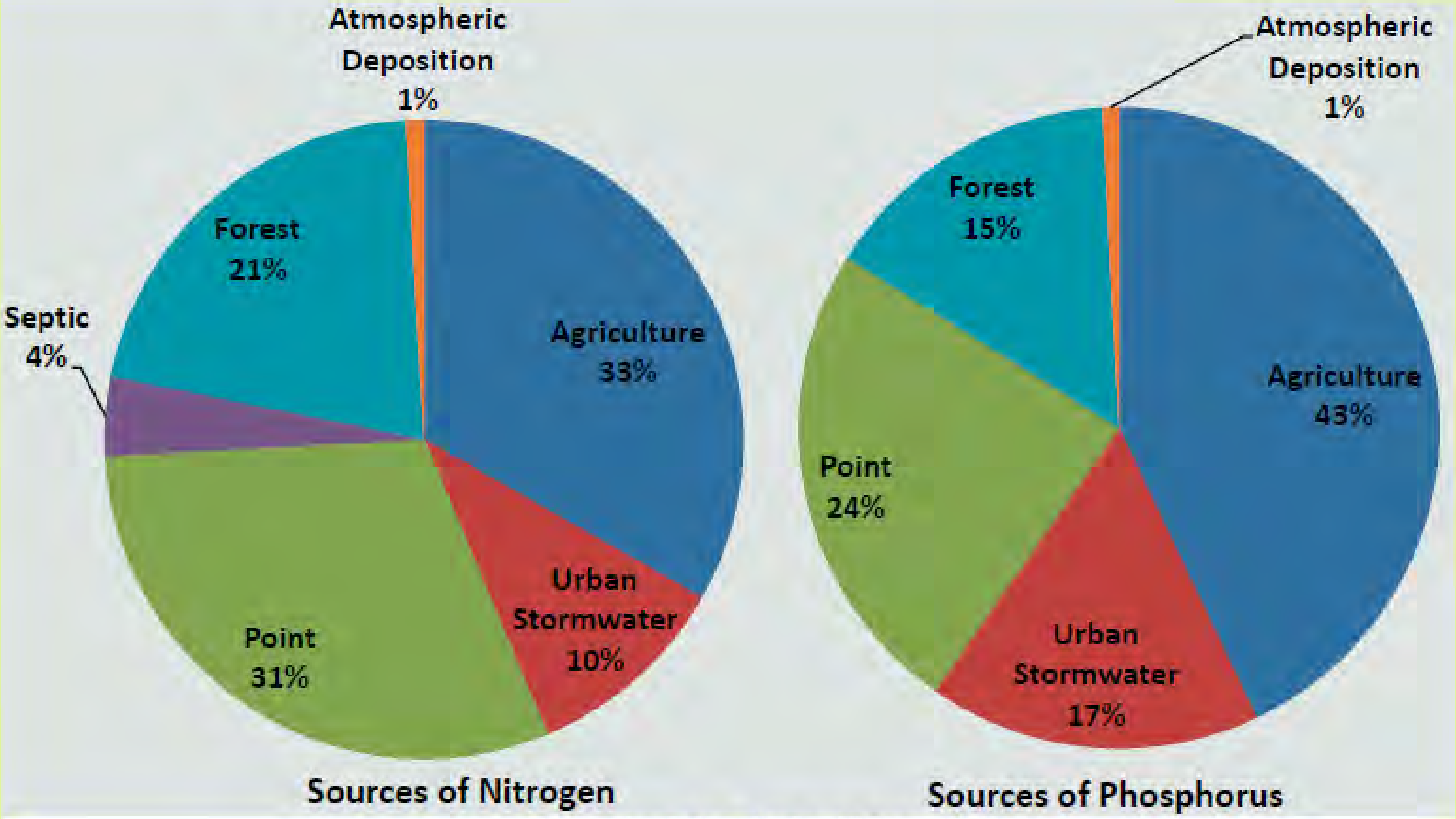


Nutrient Source Tracking

- Wastewater
- Stormwater
- Agriculture
- Atmospheric Deposition

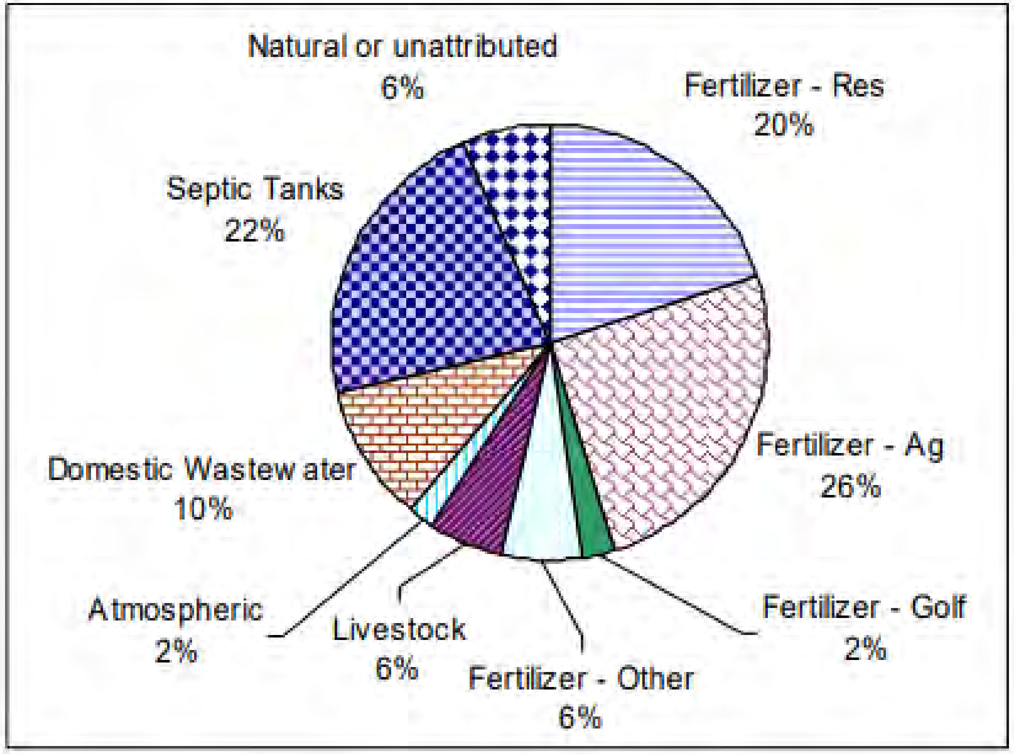
Nutrient Source Tracking Approaches

-Land use/runoff models



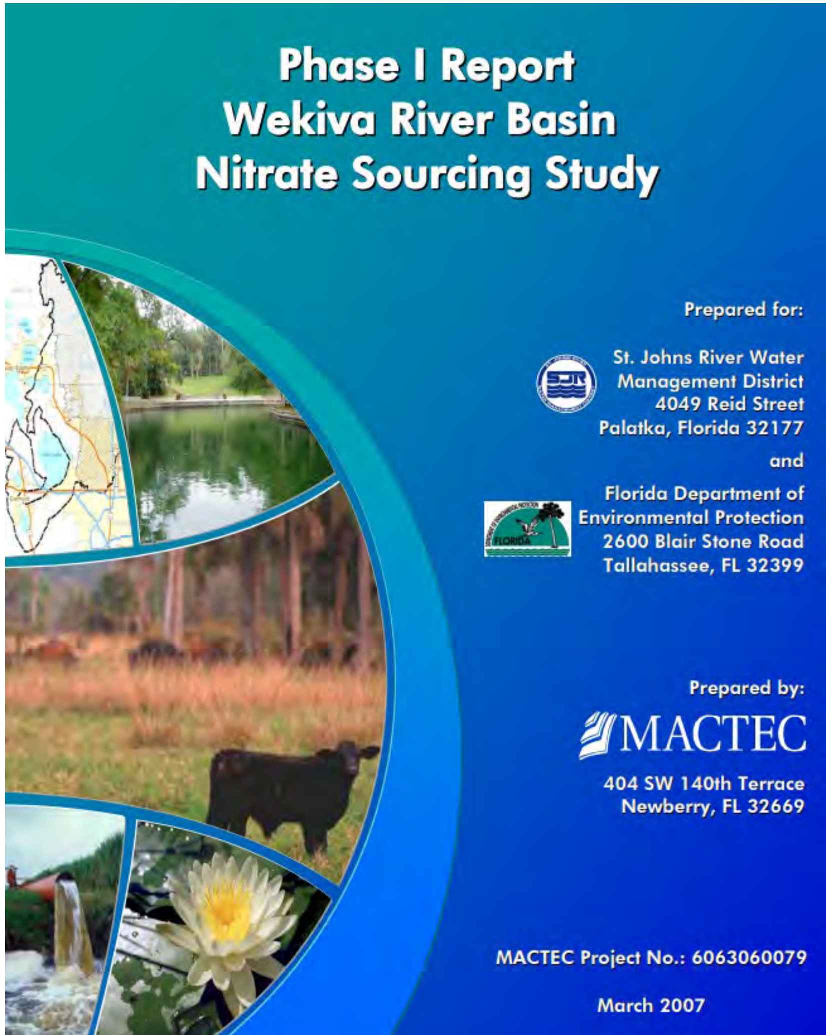
sources of nutrient pollution affecting Chesapeake Bay
Source: Hampton Roads Planning District Commission,
Chesapeake Bay Total Maximum Daily Load and Watershed Implementation Plan (September 15, 2010)

Figure ES-3. Nitrate Loadings to the Wekiva Basin, Partitioned by Source



Source: MACTEC

Created by: SAR Checked by: WAT



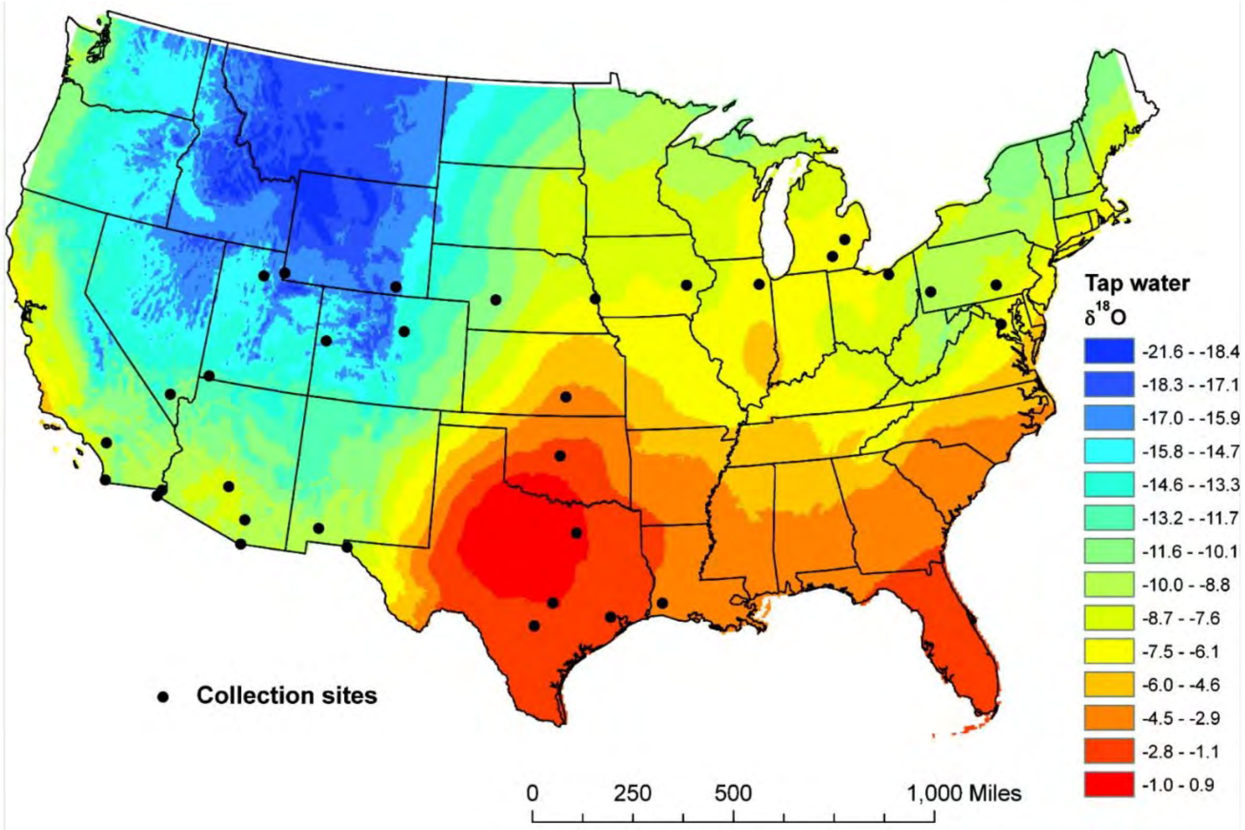
Nutrient Source Tracking Approaches

-Chemical Signatures

Chemical Beverage Signatures Allow Geographical Tracking of People By What They've Been Drinking

Your beer can tell you where you've been, according to a new study by researchers in Utah. No, not because...

BY REBECCA BOYLE | PUBLISHED JUN 30, 2010 10:13 PM EDT



How do we detect and differentiate nutrients?

Nutrients

- Nitrogen species
- Phosphorus fractionations

Microbial Source Tracking

Anthropogenic Tracers

- Sweeteners
- Antibiotics
- Fragrance molecules

Indicators of wastewater

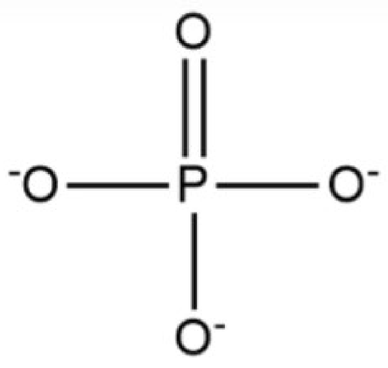
Stable Isotopes

Nitrogen and Phosphorus

Nutrient Measurements

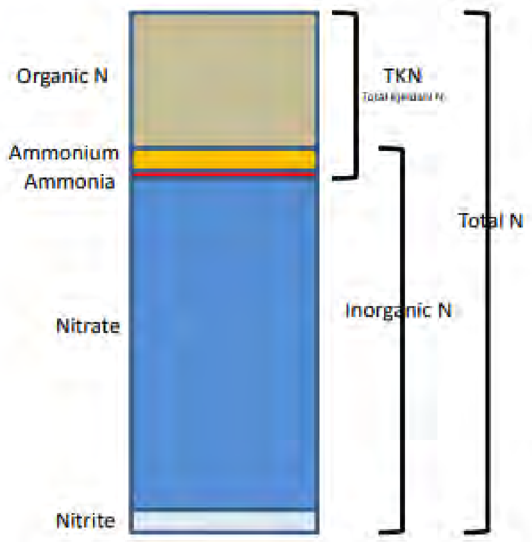
- Phosphorus: proportion of dissolved P can provide an indication of the source
- Nitrogen: proportion of species can provide an indication of the source:
  - Nitrate + Nitrite—associated with fertilizer and human wastes
  - Ammonia-N—associated with organic pollution
  - Organic N---associated with wetlands

Phosphorus



Phosphate

Nitrogen



Microbial Source Tracking

Not a nutrient, but an indicator of nutrients

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Water Research

Volume 41, Issue 16, August 2007, Pages 3747-3757

Confirmation of putative stormwater impact on water quality at a Florida beach by microbial source tracking methods and structure of indicator organism populations

M.J. Brownell [a], V.J. Harwood [a], R.C. Kurz [b], S.M. McQuaig [a], J. Lukasik [c], T.M. Scott [c]

Chemical Indicators

Chemical Indicators

- **Antibiotics and pharmaceuticals**
- **Anthropogenic tracers**
  - Sucralose and other sweeteners
  - Caffeine
- **Wastewater indicators**
  - Bromide
  - Chloride
- **Isotopes**
  - Phosphorus
  - Bromide
  - Nitrate

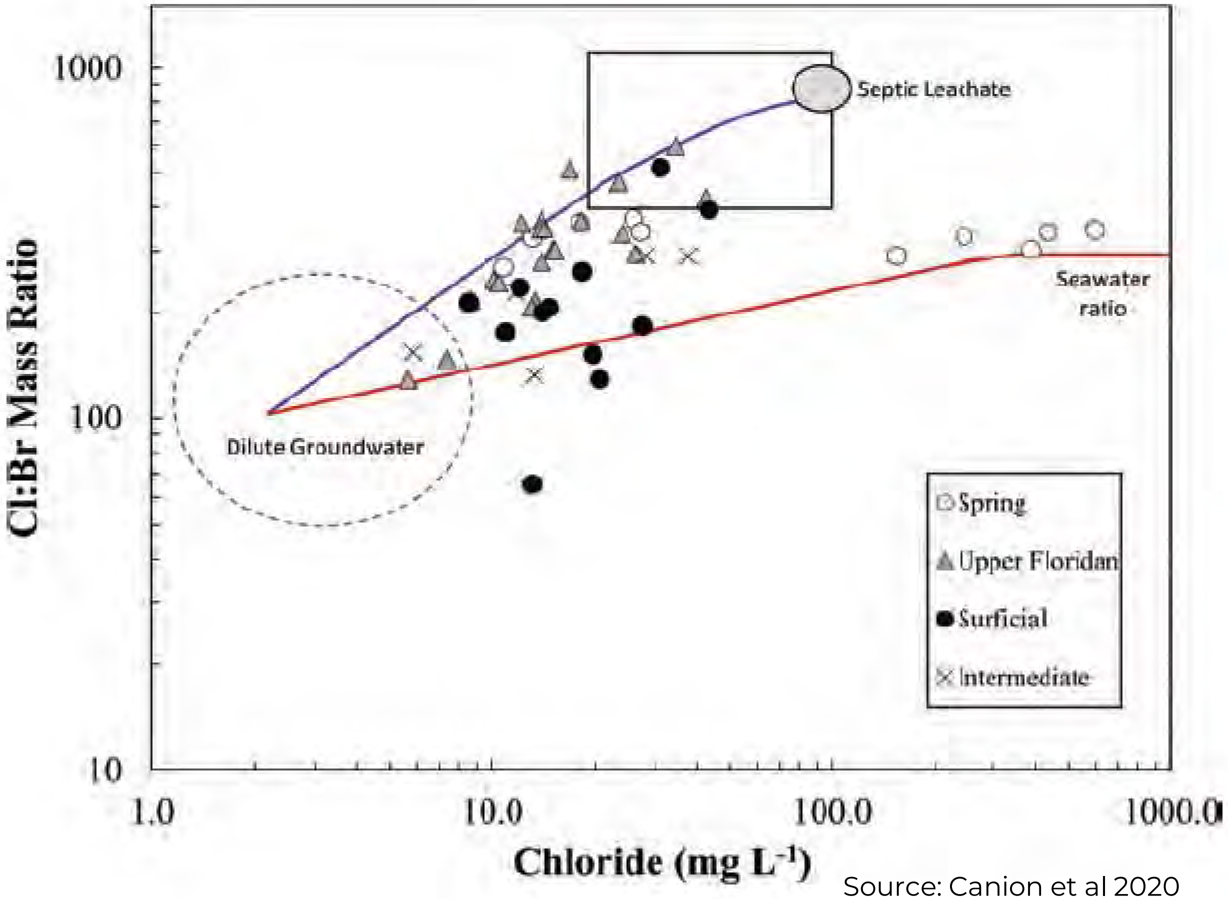
Chemical	CASRN[1]	Reporting level,[2] in µg/kg
Antibiotics and pharmaceuticals analyzed at USGS OGRL		
Azithromycin	117772-70-0	1
Carbamazepine	298-46-4	1
Chloramphenicol	56-75-7	1
Chlorotetracycline	64-72-2	1
Ciprofloxacin	85721-33-1	1
Doxycycline	564-25-0	1
Enrofloxacin	93106-60-6	1
Epichlorotetracycline	--	1
Epiisochlorotetracycline	--	1
Epioxytetracycline	--	1
Epitetracycline	79-85-6	1
Erythromycin	114-07-8	1
Erythromycin-H_2O	23893-13-2	1
Ibuprofen	15687-27-1	50
Isochlorotetracycline	514-53-4	1
Lincomycin	154-21-2	1
Lomefloxacin	98079-51-7	1
Norfloxacin	70458-96-7	1
Ofloxacin	82419-36-1	1
Ormetoprim	6981-18-6	1
Oxytetracycline	6153-64-6	1
Roxithromycin	80214-83-1	1
Sarafloxacin	98105-99-8	1
Sulfachloropyridazine	80-32-0	1
Sulfadiazine	68-35-9	1
Sulfadimethoxine	122-11-2	1
Sulfamethazine	57-68-1	1
Sulfamethoxazole	723-46-6	1
Sulfathiazole	72-14-0	1
Tetracycline	60-54-8	1
Total chlorotetracycline	--	1
Total erythromycin	--	1
Total oxytetracycline	--	1
Total tetracycline	--	1
Trimethoprim	738-70-5	1
Tylosin	1401-69-0	1
Virginiamycin	11006-76-1	5

Elliot et al 2018

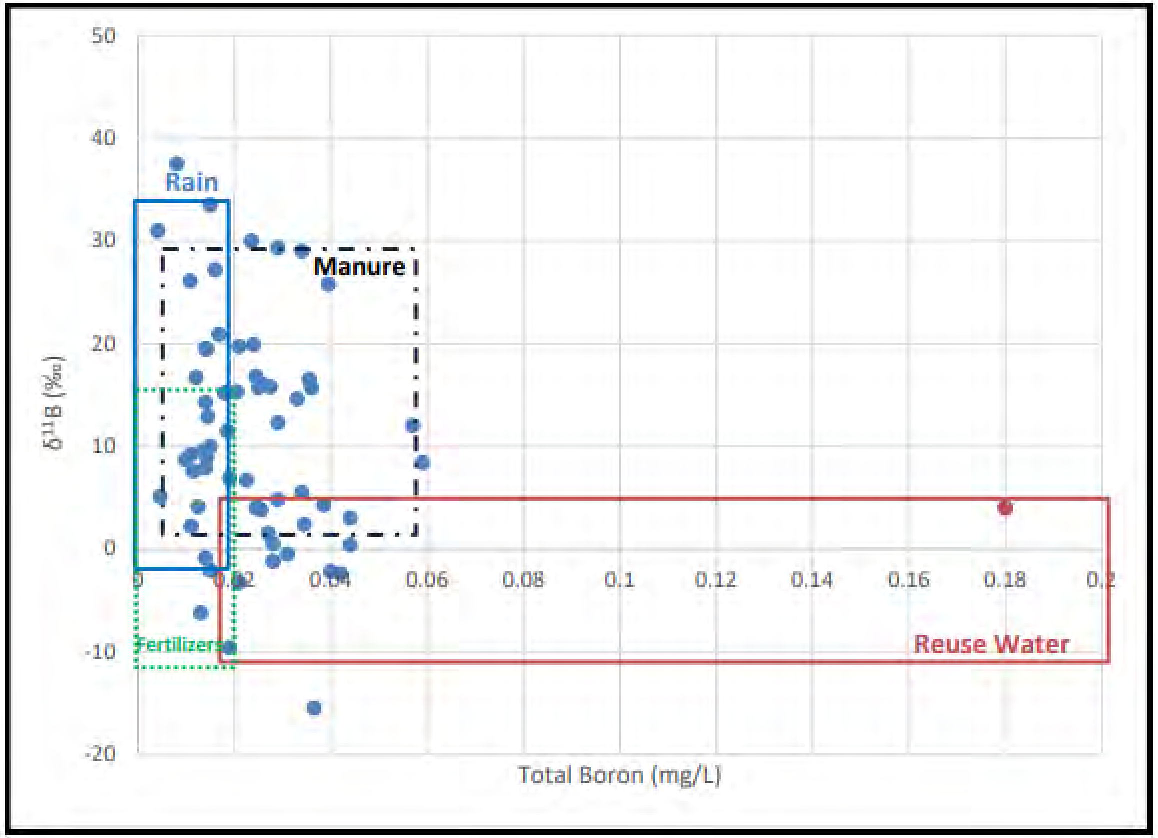
Chemical	Reporting level[1]	Sample concentration, in micrograms per kilogram			
		Soil site 1	Soil site 2	Soil site 3	Soil site 4
Wastewater indicators					
Sample weight (grams)	na	9.9	10	10	10
p-Cresol	250	50	40	40	nr
4-*tert*-Octylphenol	50	<50	<50	6	<50
BDE congener 47	50	<50	<50	3	<50
Tributyl phosphate	50	<50	10	<50	<50
3-Methyl-1*H*-indole	50	7	10	5	4
Acetyl hexamethyl tetrahydronaphthalene	50	<50	<50	11	2
Indole	100	60	110	90	70
Isophorone	50	<50	<50	11	6
Carbazole	50	<50	12	6	4
9,10-Anthraquinone	50	<50	10	7	5
Acetophenone	150	nr	nr	120	nr
2,6-Dimethylnaphthalene	50	<50	<50	<50	1
Benzo[*a*]pyrene	50	16	48	14	20
Fluoranthene	50	26	65	<50	<50
Pyrene	50	21	59	20	29
Triclosan	50	<50	nr	17	6
Bisphenol A[2]	50	<50	13	nr	nr
3β-Coprostanol[2]	500	1,140	1,470	nr	nr
β-Sitosterol	500	1,550	1,300	<500	<500
Hormones, sterols, and bisphenol A					
Sample weight (grams)	na	4.99	4.83	4.97	4.98
4-Androstene-3,17-dione	0.1	3.65	1.31	0.59	<0.43
cis-Androsterone	0.25	3.08	1.72	1.13	0.62
Dihydrotestosterone	0.1	3.9	1.82	1.13	0.9
Estrone	0.1	<0.36	<0.34	<0.20	0.21
Progesterone	0.5	<1.05	<1.45	0.91	<1.01
Bisphenol A[2]	10	E 35	E 27.7	E 10.9	E 36.3
3β-Coprostanol[2]	50	E 1,850	E 2,460	E 1,655	1,352
Cholesterol	50	702	E 1,031	731	326
Antibiotics and pharmaceuticals					
Sample weight (grams)	na	1	1	1	1
Carbamazepine	1.0	1.4	4.3	6.3	3.9
Norfloxacin	1.0	<1	10	24	<1
Ciprofloxacin	1.0	380	>1,000	>1,000	540
Ofloxacin	1.0	400	>1,000	>1,000	310
Epitetracycline	1.0	<1	3.1	5.7	1.8
Tetracycline	1.0	<1	3.3	6.6	2.2
Azithromycin	1.0	<1	180	540	<1

Elliot et al 2018

Chemical Indicators



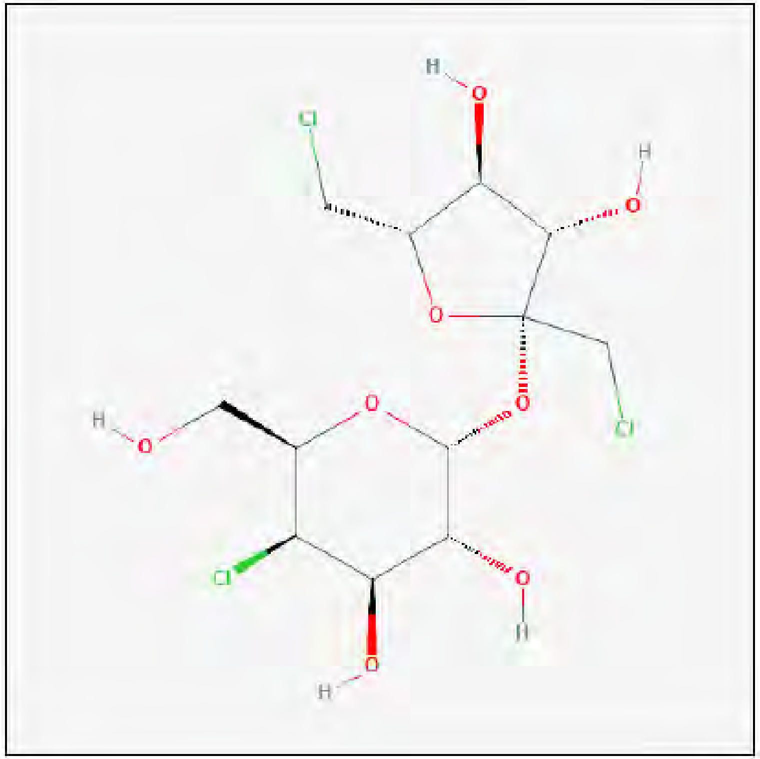
Source: Canion et al 2020



Source: OCEPD, 2022

Anthropogenic Tracers

SUCRALOSE



- Artificial sweetener
- Half Life of ~1 year

Reuse systems: 18,000 – 79,000 ng L^{-1}

Septic Tanks: 12,000 – 80,000 ng L^{-1}

FL surface water: 0 – 27,000 ng L^{-1}

FL unconfined aquifers: 0 – 3,700 ng L^{-1}

(Silvanima et al. 2018)

From: Canion et al 2020, UF Water Symposium

Sucralose

- Sucralose molecule is resistant to wastewater treatment processes (Torres et al., 2011)
- Found in areas influenced by septic (Herren et al., 2021)
- Commonly found in US waters (Bernot et al., 2016)
- Can be used to differentiate sources of anthropogenic loadings to impaired waters (Oppenheimer et al., 2012)

WATER RESEARCH 45 (2011) 4019–4027

Available at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/watres

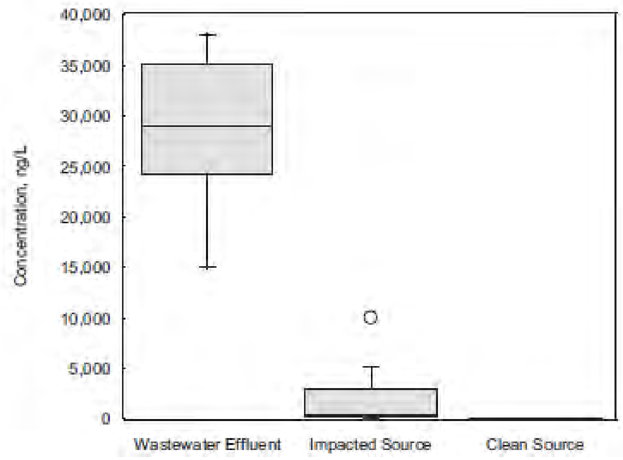
ELSEVIER

WATER RESEARCH

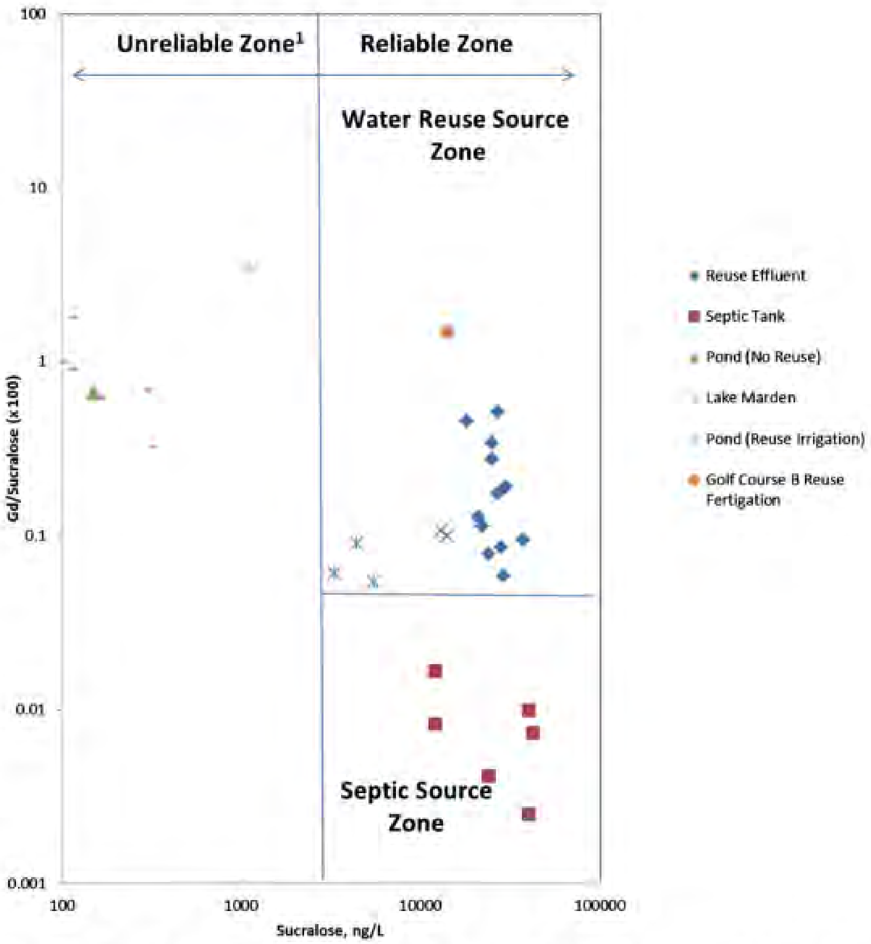
Occurrence and suitability of sucralose as an indicator compound of wastewater loading to surface waters in urbanized regions

Joan Oppenheimer [a,*], *Andrew Eaton* [b], *Mohammad Badruzzaman* [a], *Ali W. Haghani* [b], *Joseph G. Jacangelo* [a,c]

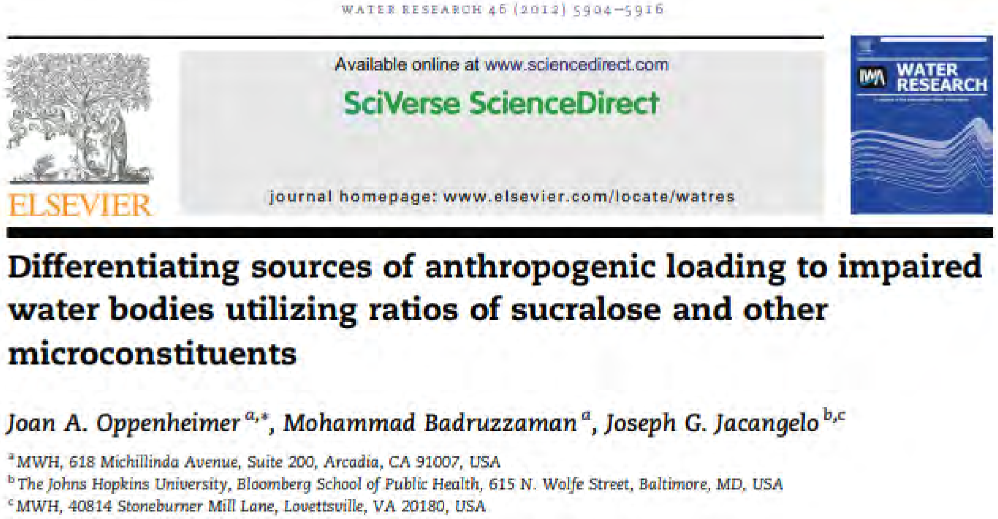
[a] *MWH Americas Inc., 618 Michillinda Avenue, Arcadia, CA 91007, USA*
[b] *MWH Laboratories, 750 Royal Oaks Avenue, Monrovia, CA 91016, USA*
[c] *The Johns Hopkins University, Baltimore, MD 21205, USA*



Gadolinium anomaly/sucrose ratio
(Oppenheimer et al 2014, Bertolotti et al 2014)



[1]Unreliable zone is the region where sucralose is <3,000 ng/L and the Gd anomaly concentrations are too low to provide a meaningful ratio.



WATER RESEARCH 46 (2012) 5904–5916

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WATER RESEARCH

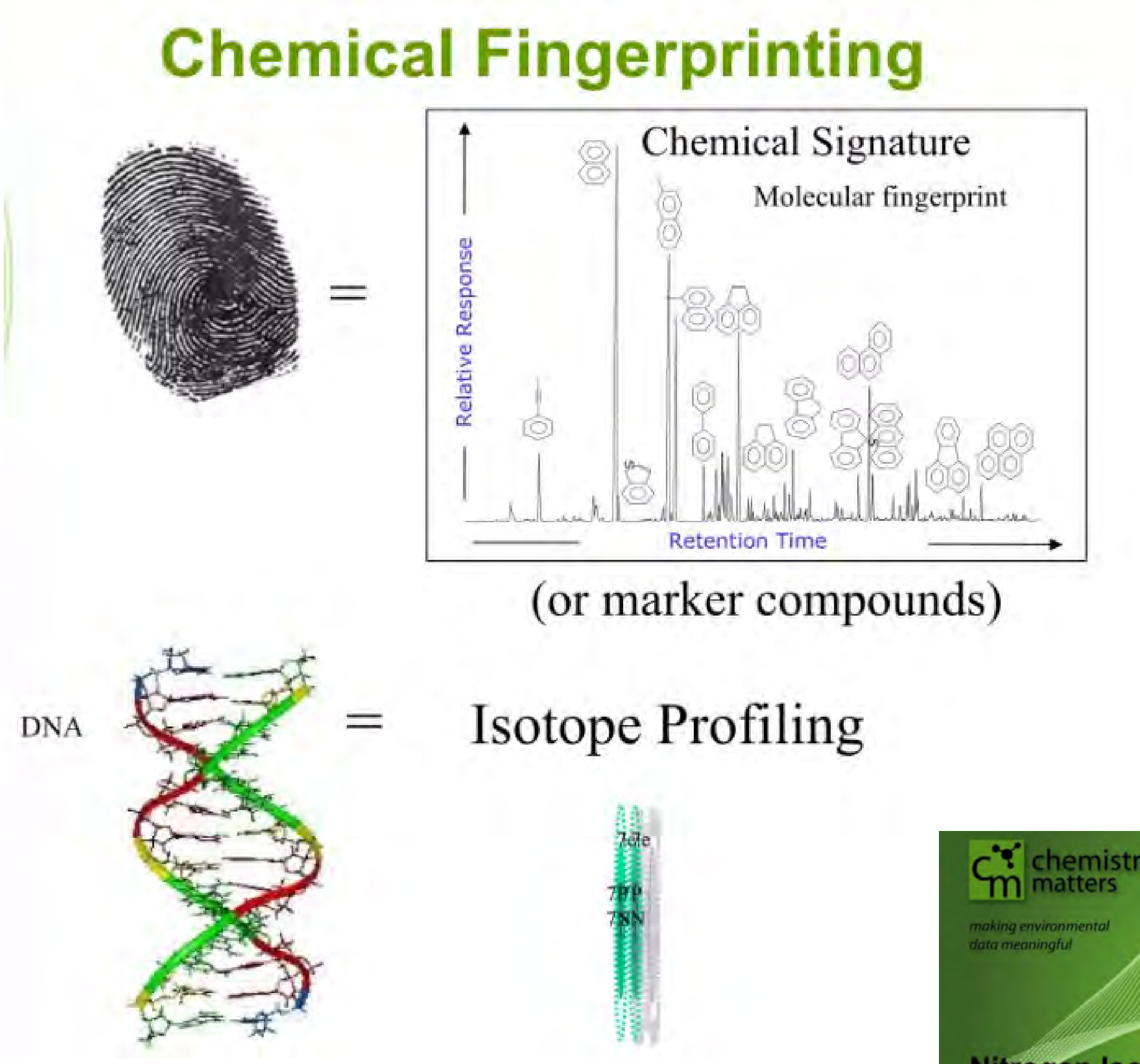
Differentiating sources of anthropogenic loading to impaired water bodies utilizing ratios of sucralose and other microconstituents

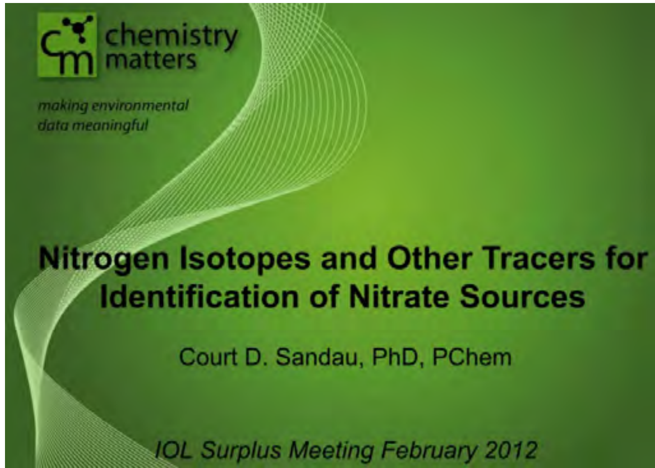
Joan A. Oppenheimer [a,*], *Mohammad Badruzzaman* [a], *Joseph G. Jacangelo* [b,c]

[a] *MWH, 618 Michillinda Avenue, Suite 200, Arcadia, CA 91007, USA*
[b] *The Johns Hopkins University, Bloomberg School of Public Health, 615 N. Wolfe Street, Baltimore, MD, USA*
[c] *MWH, 40814 Stoneburner Mill Lane, Lovettsville, VA 20180, USA*

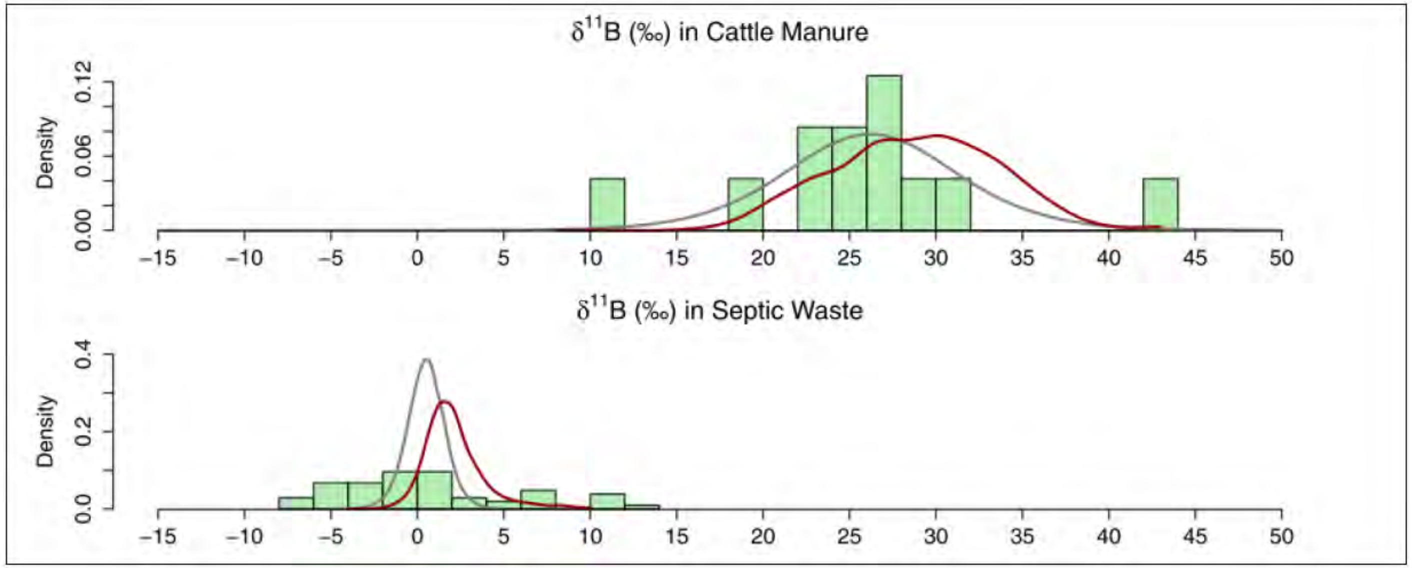
Isotopes

Isotopes

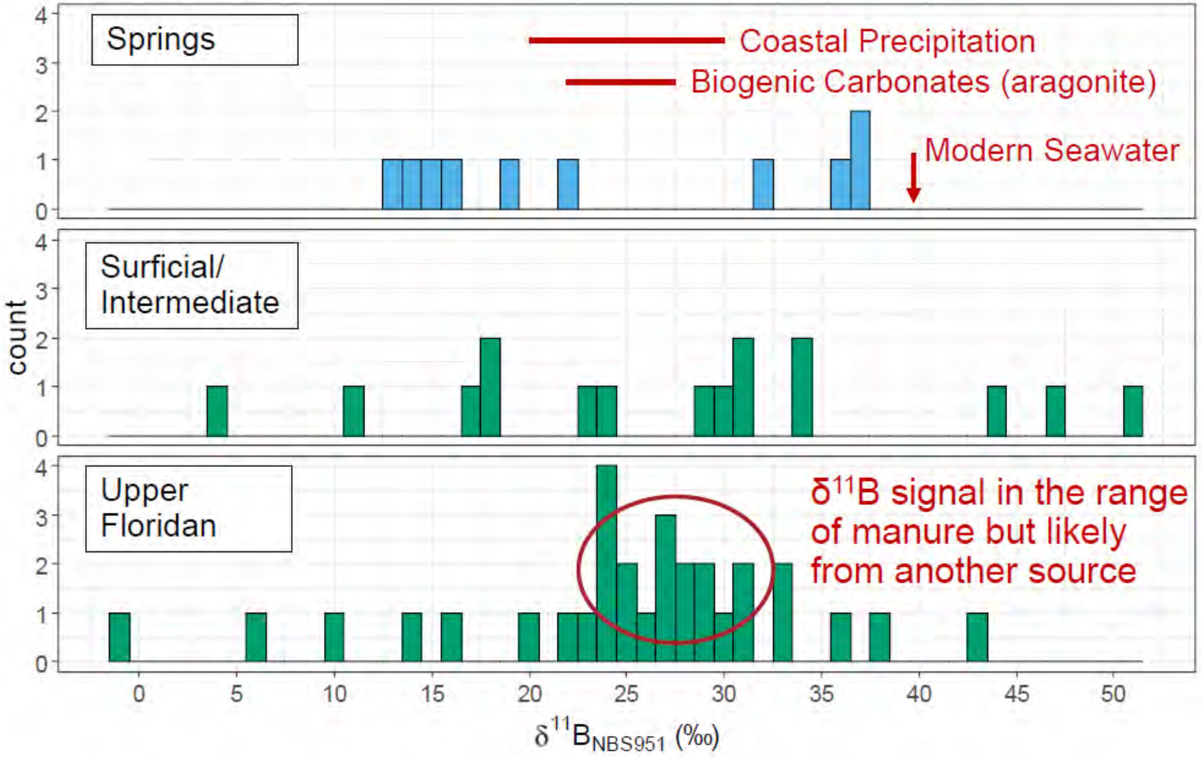

Chemical Fingerprinting
=
Chemical Signature
Molecular fingerprint
Relative Response
Retention Time
(or marker compounds)
DNA
=
Isotope Profiling


chemistry matters
making environmental data meaningful
Nitrogen Isotopes and Other Tracers for Identification of Nitrate Sources
Court D. Sandau, PhD, PChem
IOL Surplus Meeting February 2012

δ^{11}Boron Isotopes



Modified after Ransom et al. 2016



From: Canion et al 2020, UF Water Symposium

Stable Isotopes of Nitrate

Definition: $\delta^{15}N$ and $\delta^{18}O$ isotopes of nitrate

Reported as: Ratios of $\delta^{14}N$ to $\delta^{15}N$ and $\delta^{18}O$ to $\delta^{16}O$ relative to standard ratios

$\delta^{15}N$ vs $\delta^{18}O$ Isotope Biplots

- “Gold Standard” for nitrate source identification
- Extensive published research using this relationship to infer sources
- Clearer results in areas with single (high concentration) nitrate sources

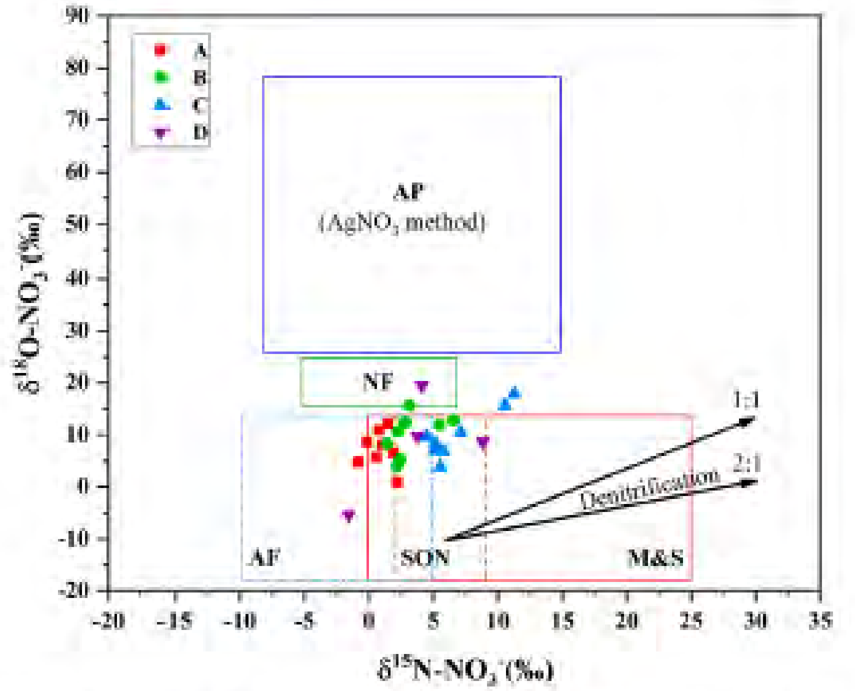


Fig. 7. Scatterplot of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ for groundwater in the QRB. The $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values of the sources (NF: NO_3^- fertilizer; AP: NH_4^+ fertilizer; AP: atmospheric NO_3^-; SON: soil organic nitrogen; M&S: manure and sewage) were summarized by (Kendall and McDonnell, 1998).

Huang et al, 2022

Isotopes in Environmental and Health Studies
Vol. 43, No. 3, September 2007, 237–247

Taylor & Francis
Taylor & Francis Group

Fertilizer nitrogen isotope signatures

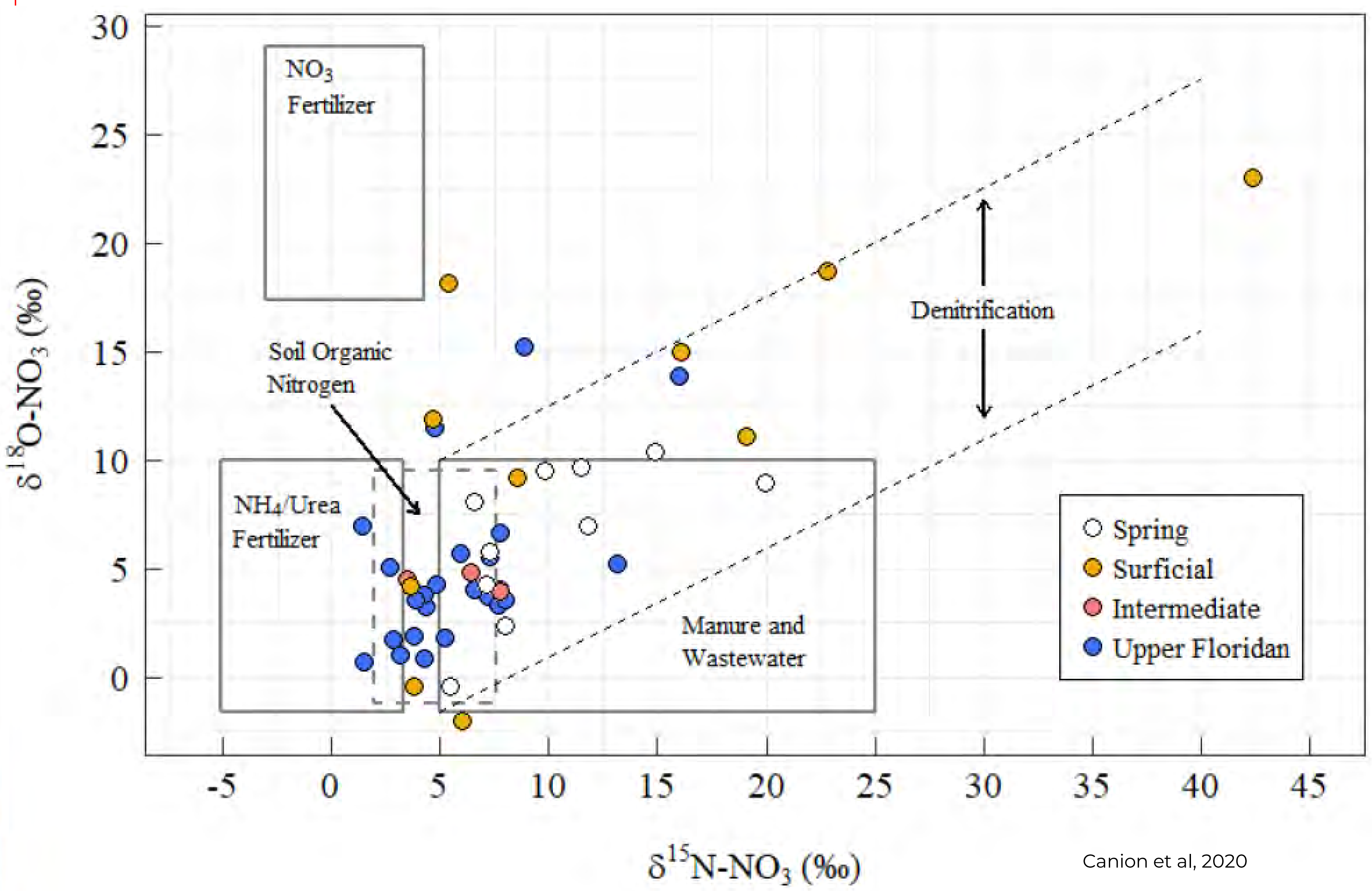
ALISON S. BATEMAN† and SIMON D. KELLY*†‡

†School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK
‡Institute of Food Research, Norwich Research Park, Colney, Norwich NR4 7UA, UK

(Received 12 March 2007; in final form 30 May 2007)

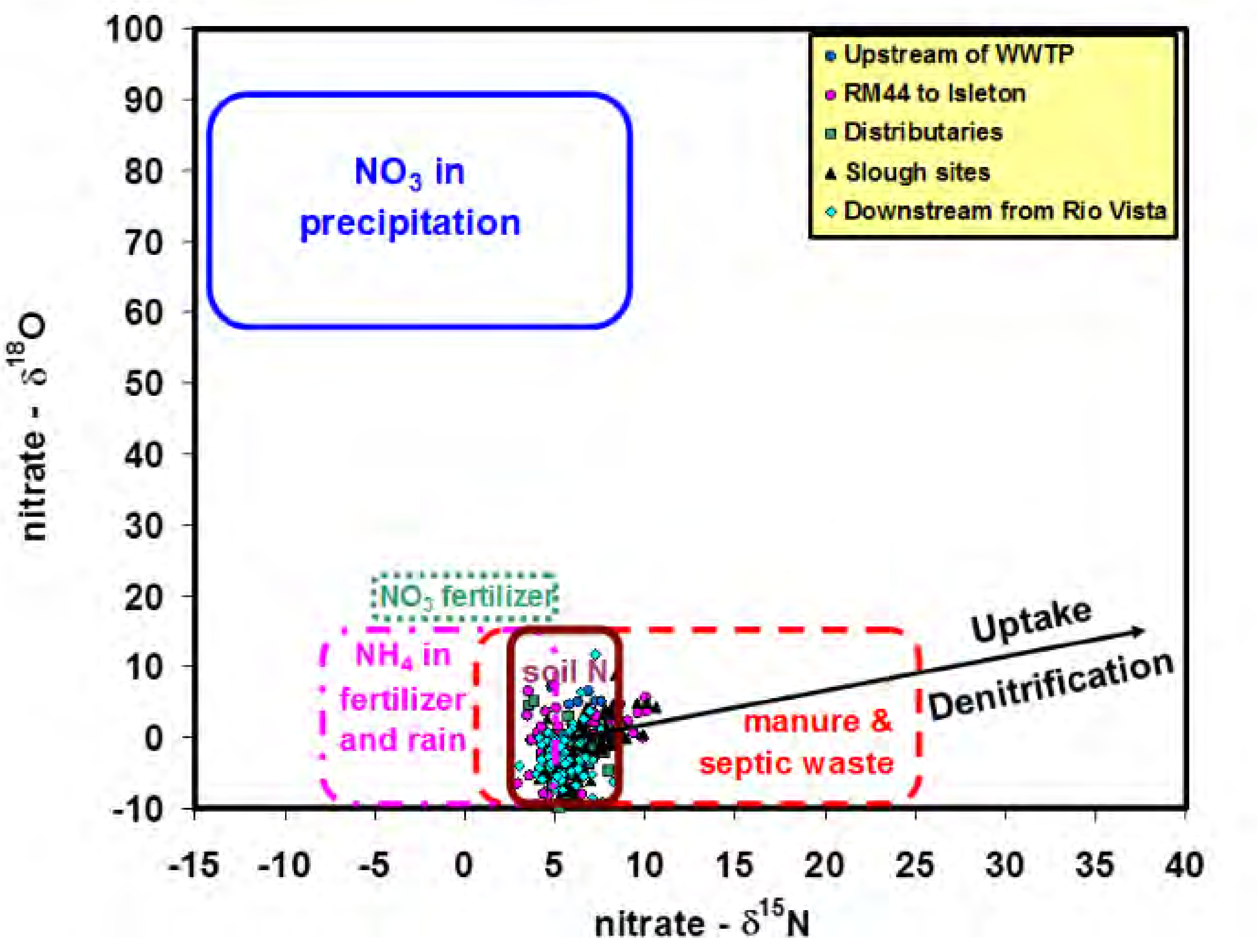
	Fertilizer type	Manufacturer	$\delta^{15}N(‰)_{air}$
Synthetic	$(NH_4)_2SO_4$	W.L Dingley	0.8
	$(NH_4)_2SO_4$	Gem	6.6
	$(NH_4)_2SO_4$	Terra	−1.2
	$(NH_4)_2SO_4$	Bunn	0.7
	KNO_3	W.L Dingley	−1.5
	KNO_3	Gem	−1.1
	KNO_3	Yara	−1.0
	Urea	Gem	−2.4
	Urea	Unknown	−1.1
	Urea	Bunn	−0.8
	Urea	W.L Dingley	−1.6
	Urea	Yara	−5.9
	NH_4NO_3	Unknown	2.6
	NH_4NO_3	Bunn	0.5
	NH_4NO_3	Kemira	2.2
	NH_4NO_3	Terra	−1.3
	NH_4NO_3	Yara	−1.4
	NH_4NO_3	Unknown	−0.9
	$(NH_4)H_2PO_4$	Gem	−0.9
	$(NH_4)H_2PO_4$	Terra	−0.3
	NPK 20-10-10	Kemira	1.9
	NP 27-10	Kemira	0.8
	NPK 28-5-5	Kemira	1.1
	$Ca(NO_3)_2$	Yara	−0.3
	NPK 16-16-16	Yara	−0.6
	NPK 21-8-11	Yara	−0.7
	NPK 12-12-12	Unknown	0.4
	Hydroponic solution NH_4NO_3 and $Ca(NO_3)_2$	Unknown	0.2
	Hydroponic solution KNO_3 and $Ca(NO_3)_2$	Unknown	0.7

The fertilizer manufacturer is shown where known.



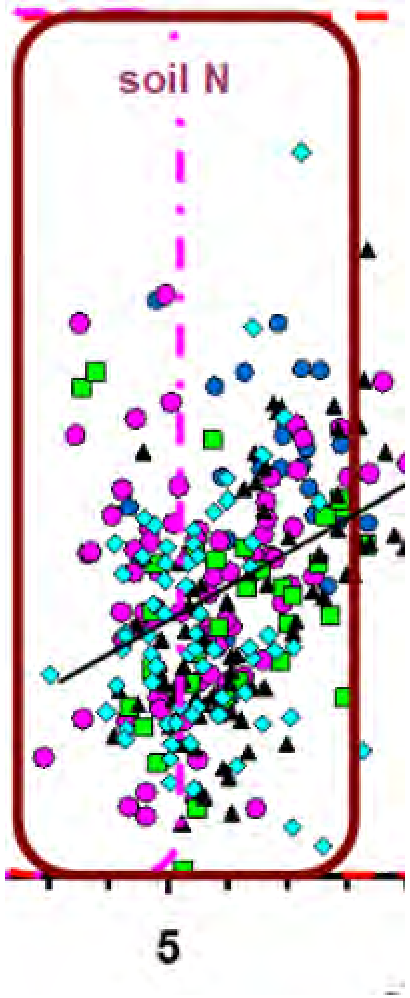
Canion et al, 2020

Stable Isotopes of Nitrate—Biplot—Many samples land in the “mud zone”



Kendall et al 2015, modified from Kendall et al 2018

Pattern?



How do we increase our confidence in source differentiation?

wsp

Isotopes in Environmental and Health Studies
Vol. 43, No. 3, September 2007, 237–247

Taylor & Francis
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Fertilizer nitrogen isotope signatures

ALISON S. BATEMAN† and SIMON D. KELLY*†‡

†School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK
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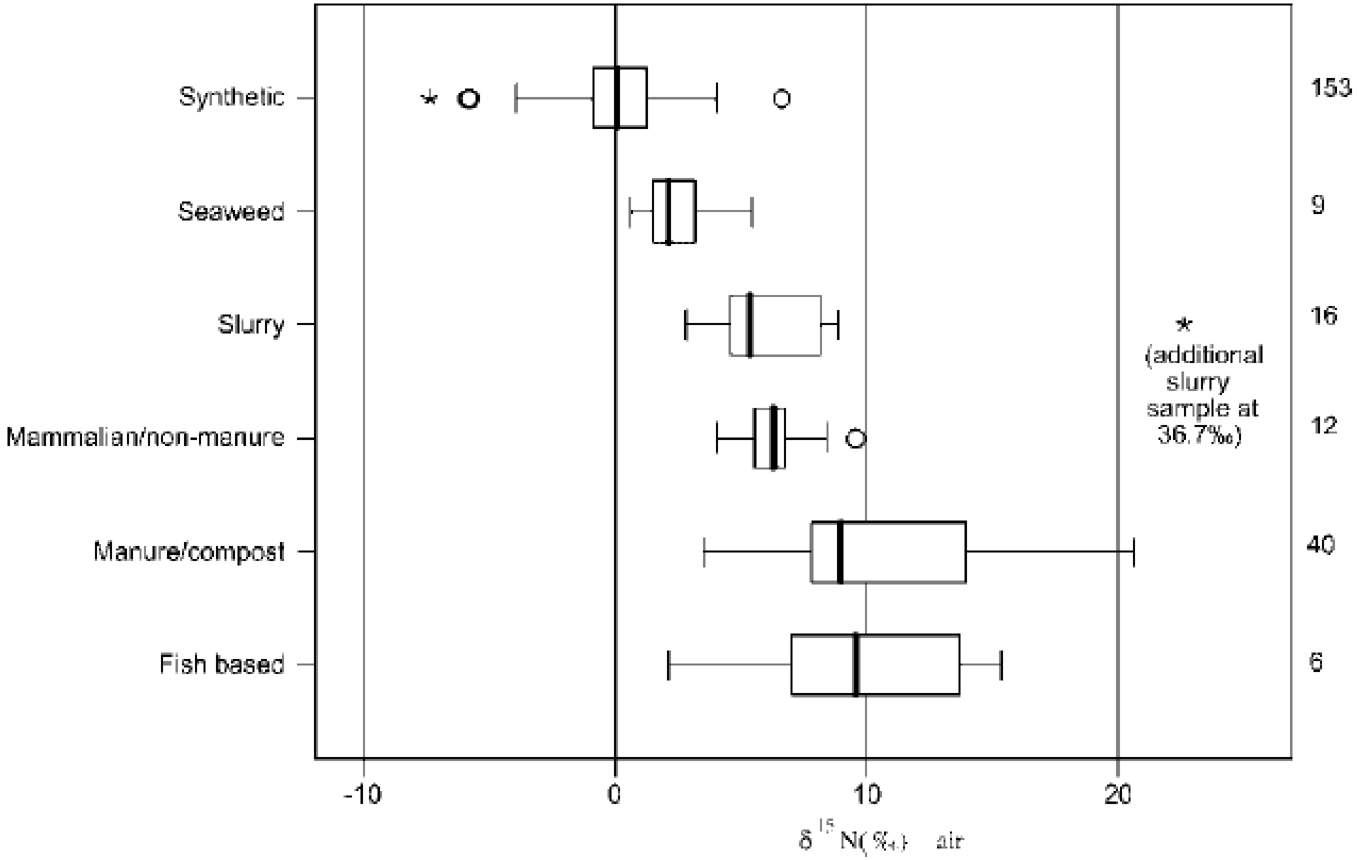
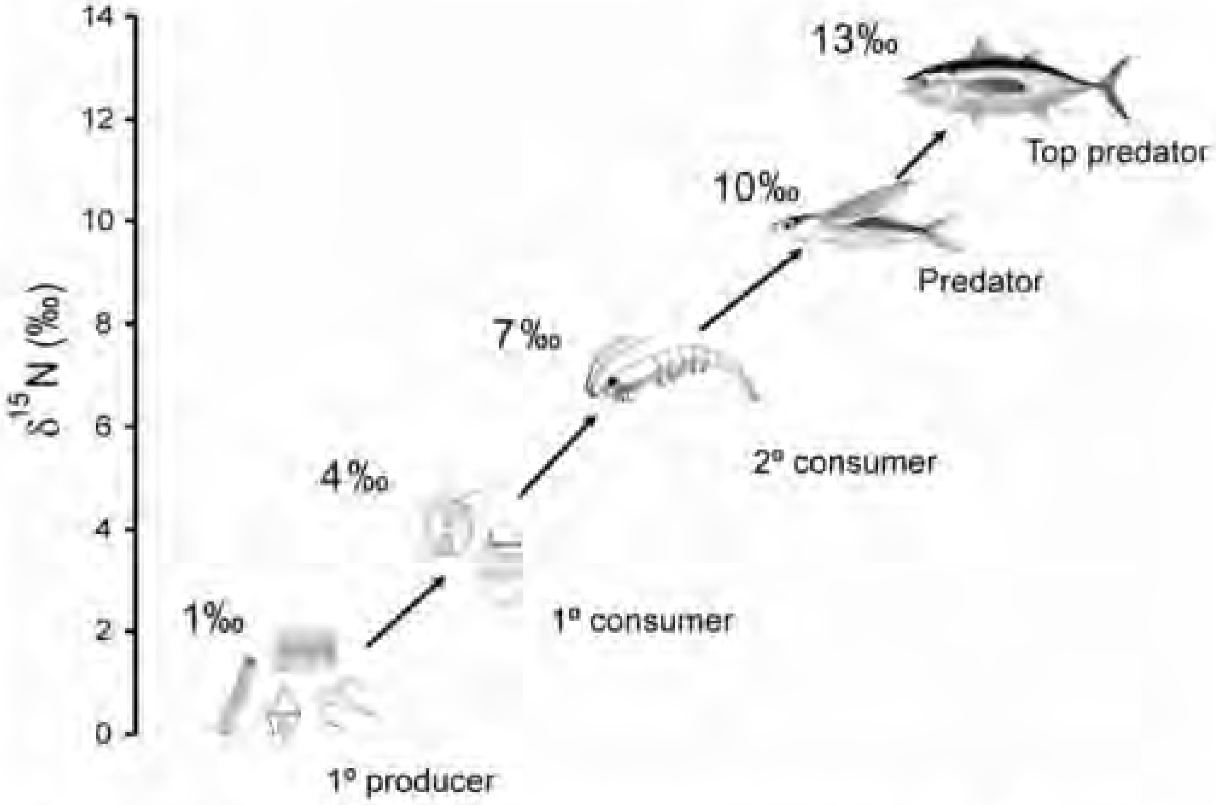


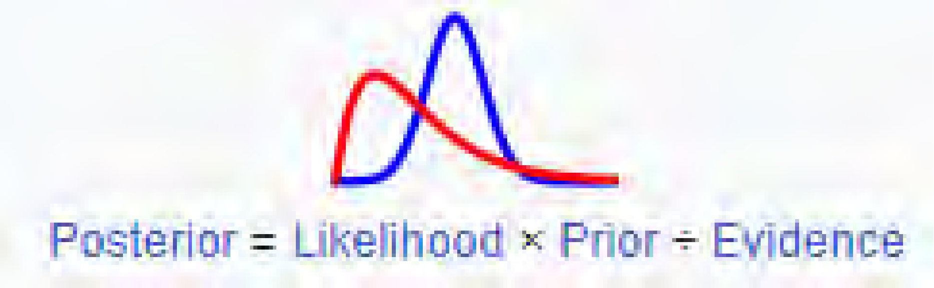
Bayesian Mixing Models

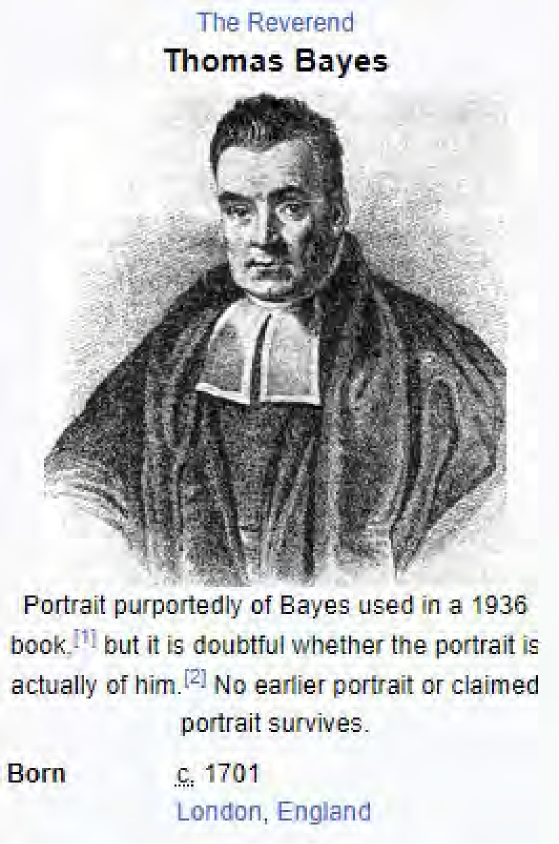


General trophic positions and approximate bulk delta nitrogen isotopes ratios for organisms in the Pacific Ocean. Source: http://www.spc.int/oceanfish/en/ofpsection/ema/biological-research/trophic-dynamic-sampling

Bayesian Statistics

Probability based on **prior** knowledge of an event





Source: Wikipedia

Bayesian Mixing Models

PLOS ONE

OPEN ACCESS PEER-REVIEWED

RESEARCH ARTICLE

Source Partitioning Using Stable Isotopes: Coping with Too Much Variation

Andrew C. Parnell, Richard Inger, Stuart Bearhop, Andrew L. Jackson

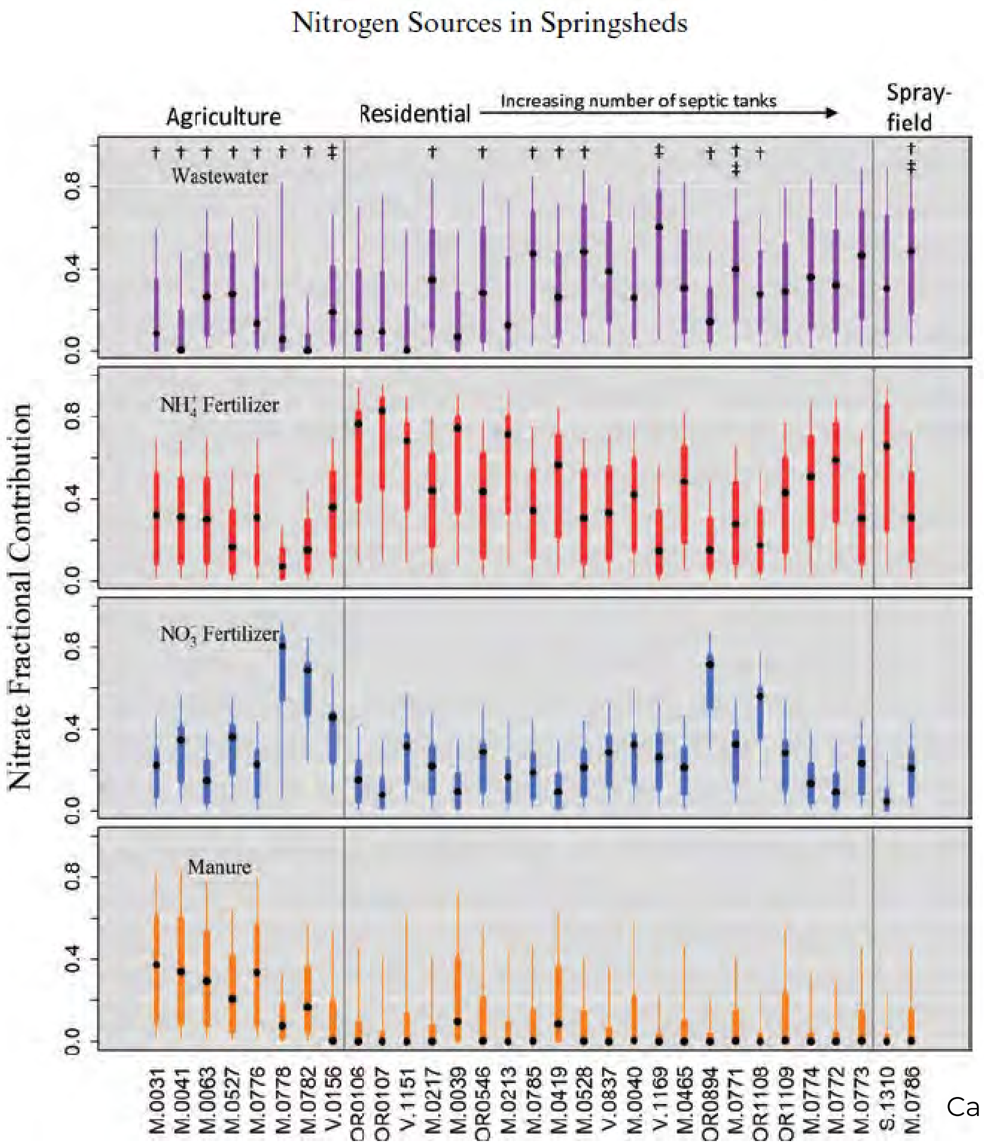
Published: March 12, 2010 • https://doi.org/10.1371/journal.pone.0009672

Stable Isotope Mixing Models in R with simmr

Andrew Parnell and Richard Inger

2021-02-27

Examples of *simmr* Bayesian Model Outputs



Canion et al, 2020

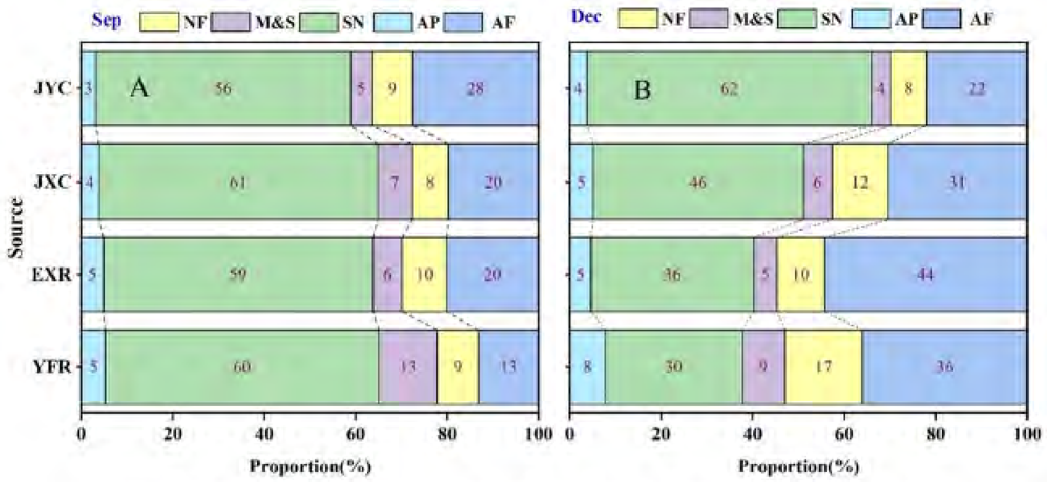
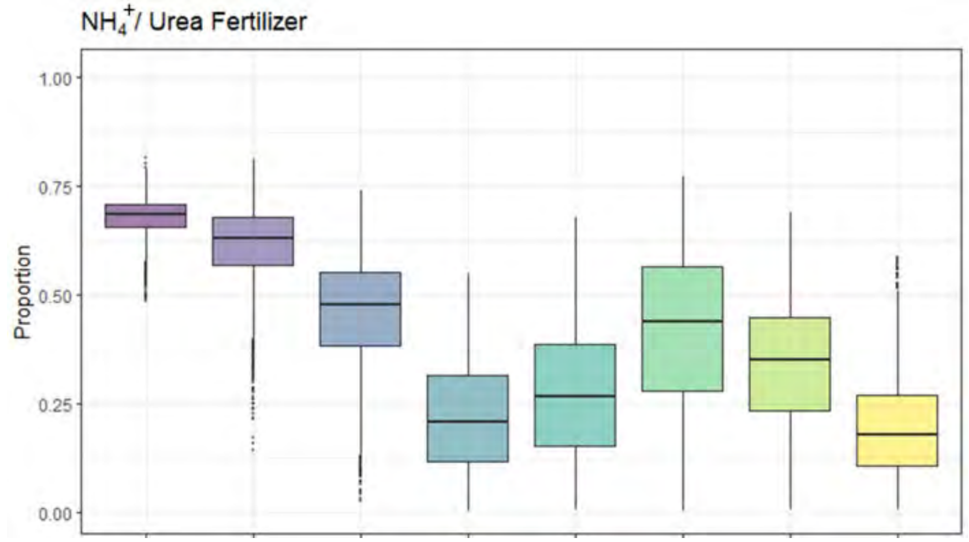


Fig. 8. Fractional contributions of five potential NO_3^- sources estimated by Simmr in the JYR watershed.

NF: nitrate fertilizer;, M&S: manure and sewage; SN: soil nitrogen; AP: atmospheric precipitation; AF: ammonium fertilizer (Zhang et al., 2022)



WSP, 2022

Stormwater?

Science of the Total Environment 750 (2021) 142320

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Sources and concentrations of nutrients in surface runoff from waterfront homes with different landscape practices

Lisa S. Krimsky [a,*], Mary G. Lusk [b], Holly Abeels [c], Linda Seals [c,1]

[a] University of Florida/Institute of Food and Agricultural Sciences, Indian River Research and Education Center, 2199 South Rock Road, Fort Pierce, FL 34945, United States
[b] University of Florida/Institute of Food and Agricultural Sciences, Gulf Coast Research and Education Center, 14625 Co Rd 672, Wimauma, FL 33598, United States
[c] University of Florida/Institute of Food and Agricultural Sciences, Brevard County, 3695 Lake Drive, Cocoa, FL 32926, United States

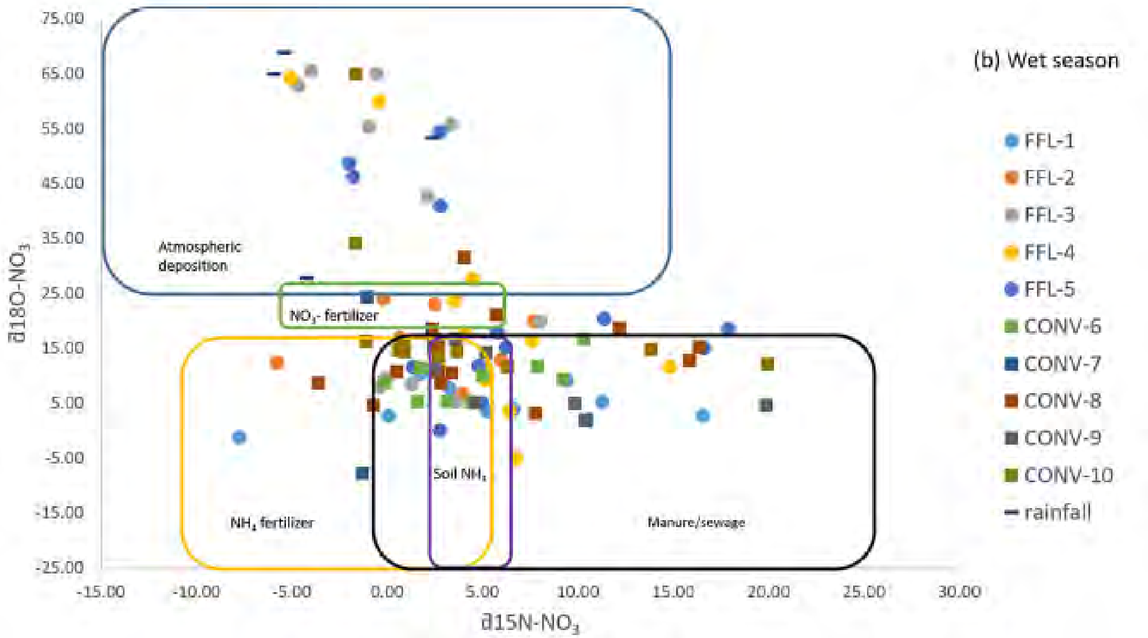


Table 3
Mixing model results showing mean relative percent contributions of various sources of NO_3^- in lawn runoff.

Nitrate source	Seasonal comparison		Landscape comparison	
	Dry season	Wet season	FFL	Conventional
Atmospheric deposition	15	30.6	30.4	15.7
NH_4^+-fertilizer	15.8	7.7	10.6	12.4
NO_3^--fertilizer	28.6	23.1	20.8	27.0
Soil and organic N	37.5	36.5	34.5	36.8
Manure/sewage	3.2	3.1	3.8	8.1

MixSIAR Model

Stormwater?

Environmental Science & Technology
Article
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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

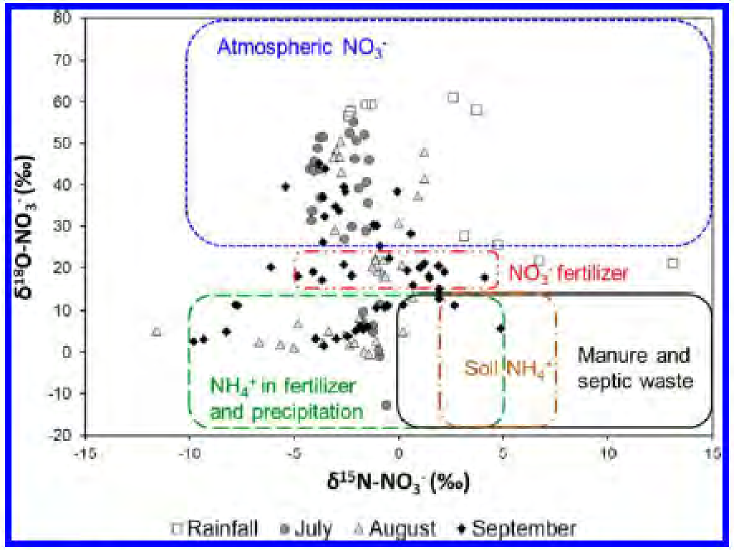
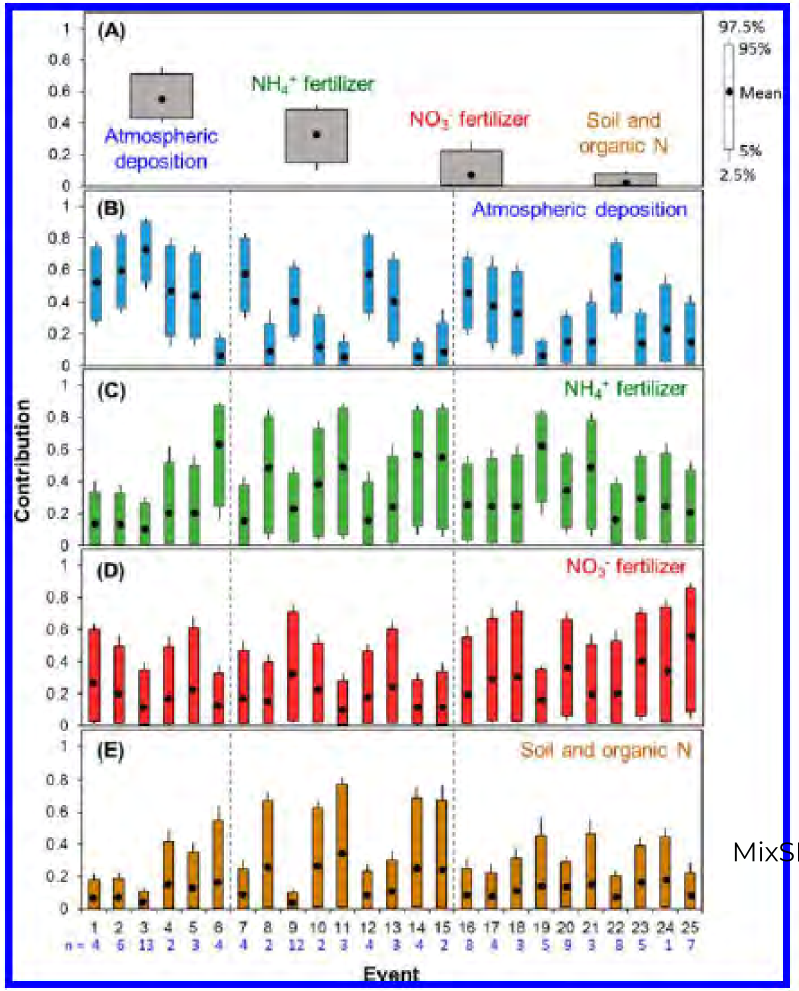
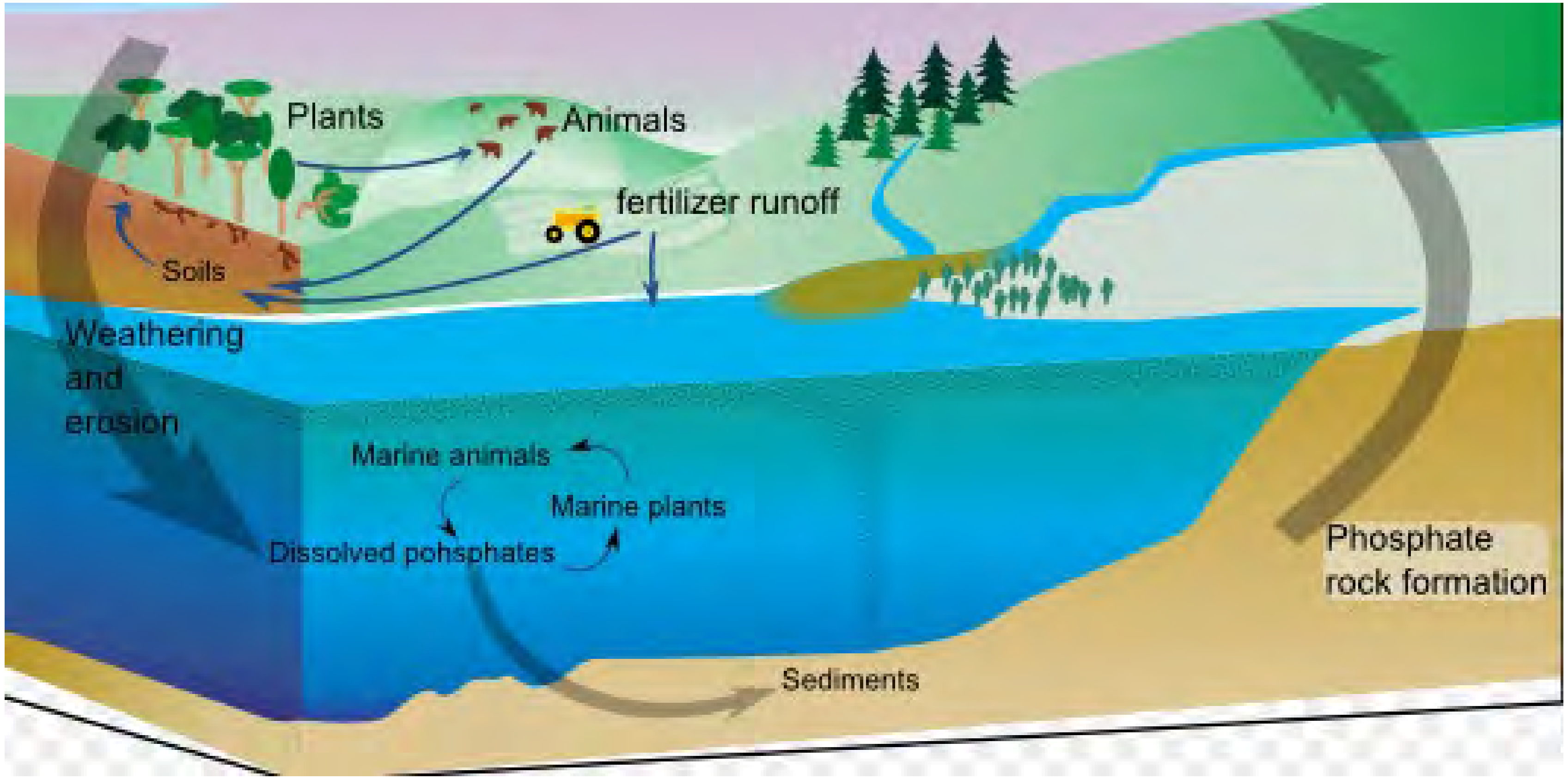


Figure 3. Dual δ^{15}N-NO_3^- and δ^{18}O-NO_3^- in rainfall and stormwater runoff during the wet season in 2014. Area shows the range of the δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values from Kendall et al. (2007)[10]



MixSIAR Model

Phosphorus Isotopes



Methods (From: Musser, 2020)

- Extraction
  - Water— centrifuge to obtain a colloidal sample
    - Two step centrifuge
  - Soils or sediments—freeze dried, homogenized, sieved
  - Sequential P-extraction of solid material
- Precipitation
  - Concentrate P using a silver phosphate precipitation method
- Measure in Elemental Analyzer

Results (Musser, 2020)

Appears that farm soils more depleted in P isotope, but more enriched in C and N isotopes

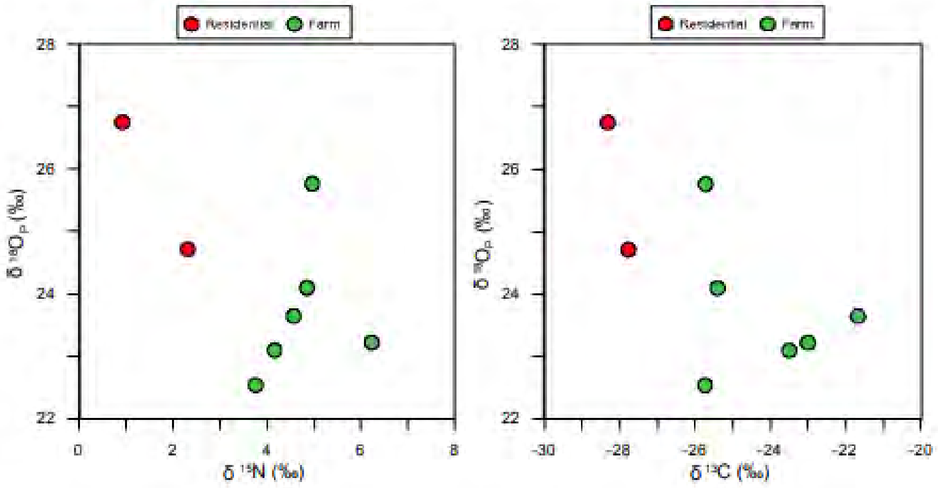


Figure 19. Phosphate-oxygen vs. nitrogen (left) and carbon (right) isotopic compositions of two different soil land use types from Murderkill watershed: residential (red circles) and farm (green circles).

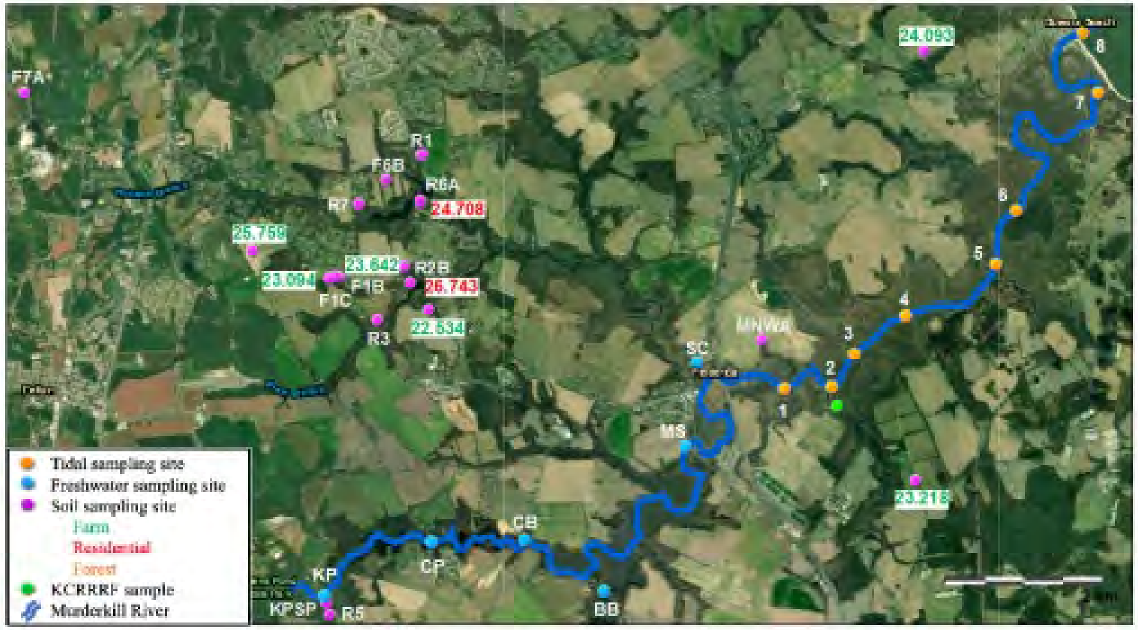


Figure 20. Phosphate-oxygen isotopic values of soil (farm in green text and residential in red text) plotted in their Murderkill watershed location.

Agriculture vs Forest (Li et al, 2021)

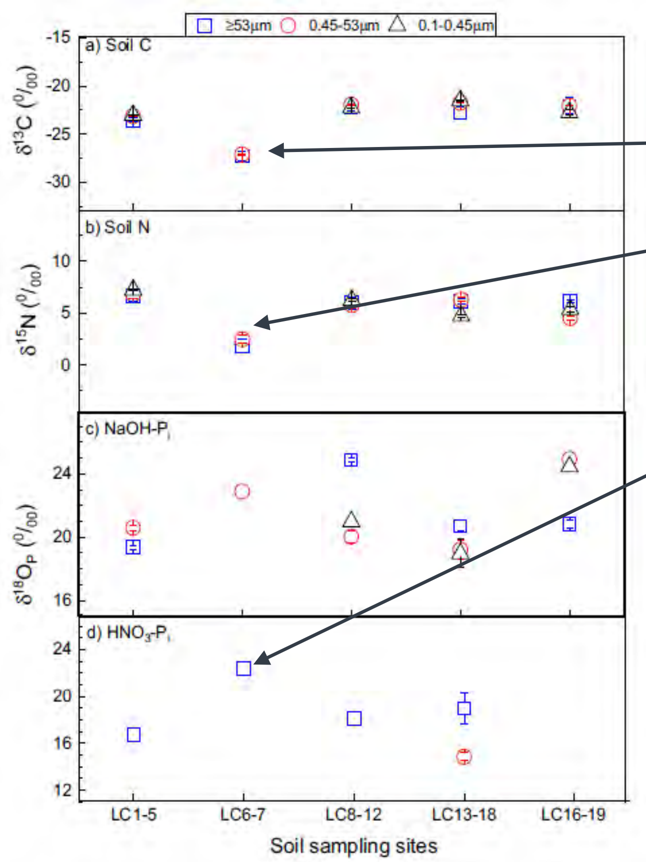
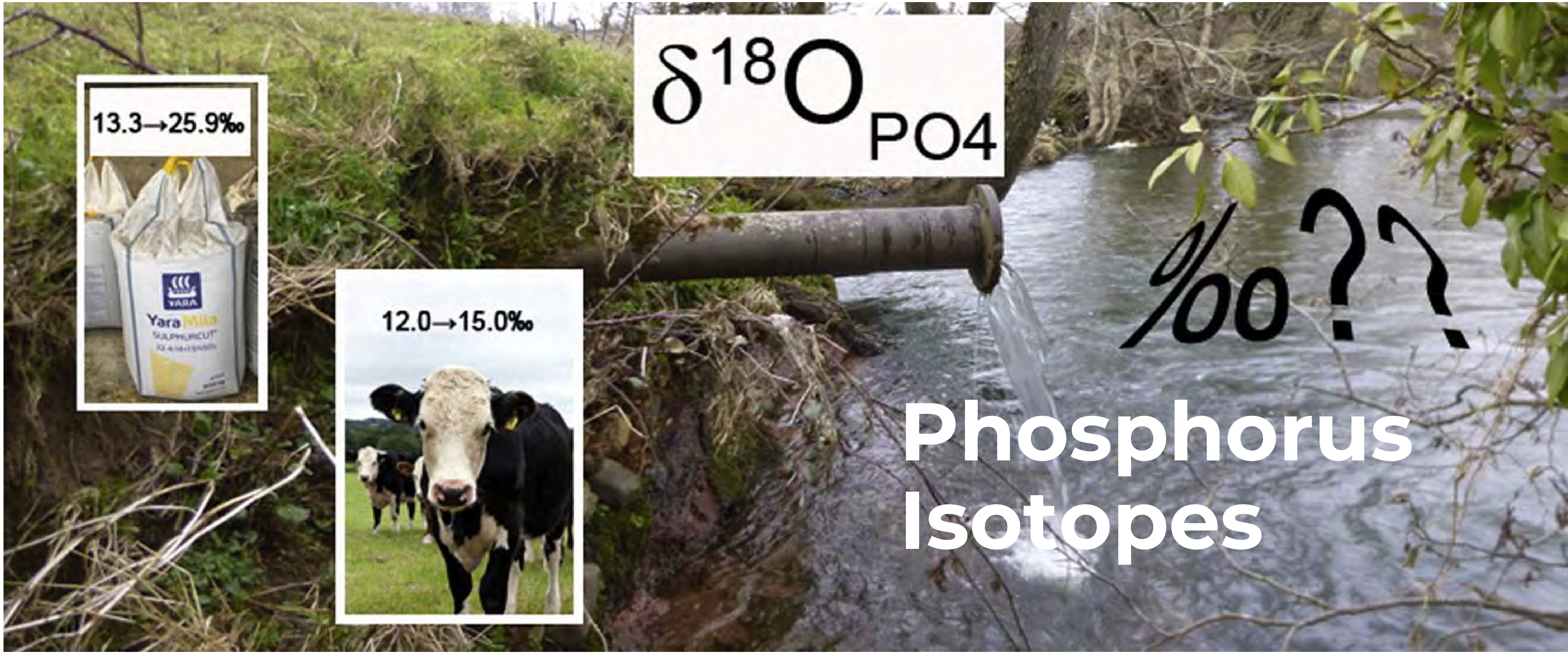


Fig. 6. Measured isotope values of a) soil carbon ($\delta^{13}C$), b) soil nitrogen ($\delta^{15}N$), c) soil NaOH-P pool, and d) soil HNO_3-P pool of surface soils.

(Li et al., 2021)

Forest (LC6-7) vs. Agriculture (All other sites)

- Lighter ^{13}C and ^{15}N
- Heavier $^{18}O_P$ values than the farms



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Science of The Total Environment
Volume 574, 1 January 2017, Pages 680-690

The oxygen isotopic composition of phosphate in river water and its potential sources in the Upper River Taw catchment, UK

Steven J. Granger [a], Tim H.E. Heaton [b], Verena Pfahler [a], Martin S.A. Blackwell [a], Huimin Yuan [c], Adrian L. Collins [a]

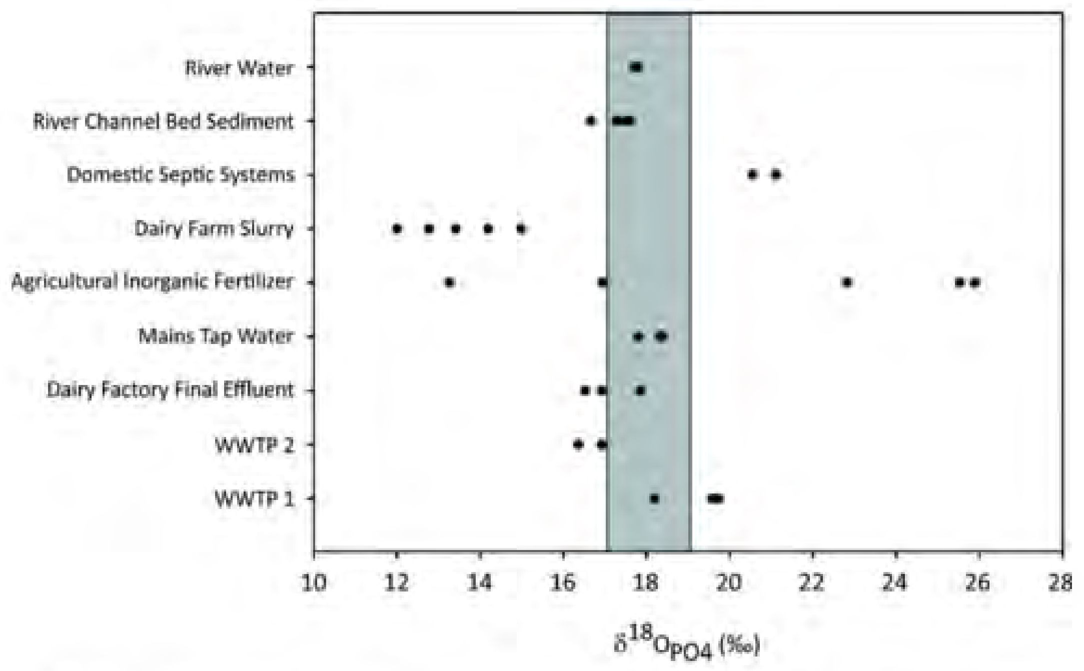


Fig. 3. Summary of $\delta^{18}O_{PO4}$ values for various PO_4 sources within the Upper Taw catchment and the values measured within the river itself. All values are for water soluble/extractable TRP except for the River Channel Bed Sediment which is a 1 M HCL extraction. Range of $E\delta^{18}O_{PO4}$ for the river is indicated by the grey area.

- High degree of overlap among the sources
- Microbial activities can alter the isotopic ratio
- Not recommended

- (Granger et al, 2017)

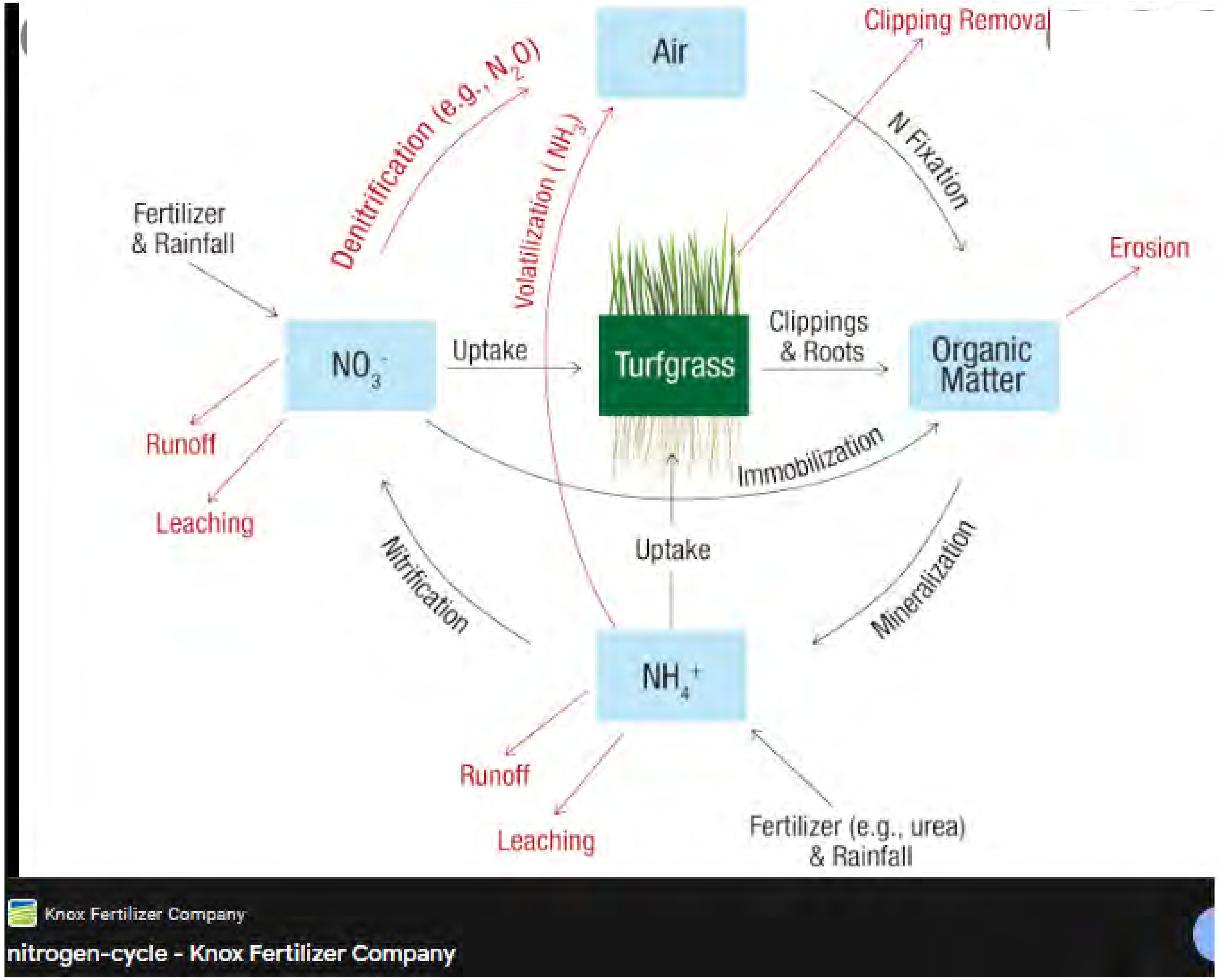
Phosphorus Isotopes

Summary

- Some promise for differentiating sources
- Specialized, and relatively complex analytical procedure
- Rapid microbial cycling can alter PO_4 isotopic ratios.
- Appears to be inappropriate for systems with rapid microbial cycling of PO_4
- Likely not practical

Challenges and Limitations

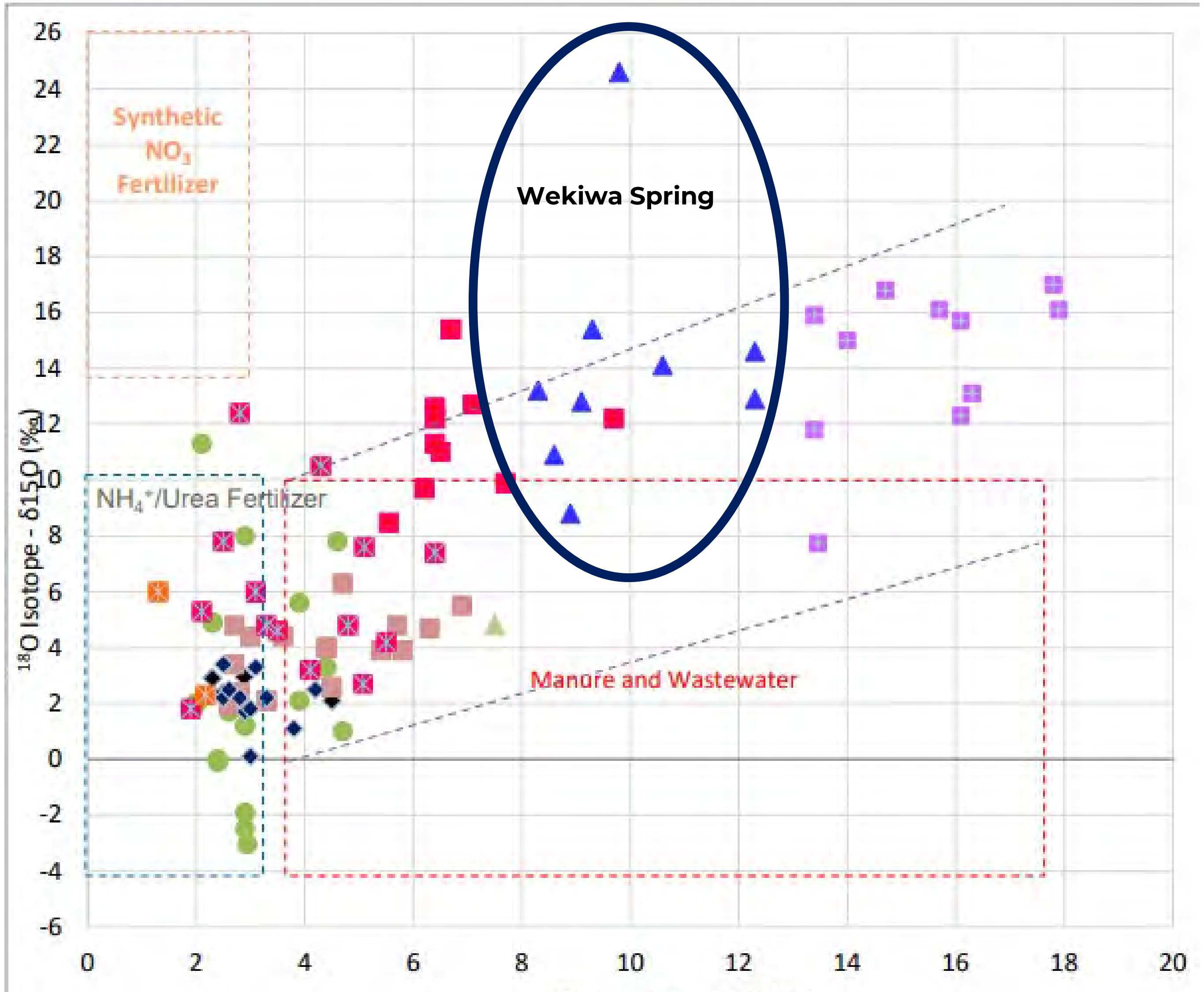
Biogeochemical Transformations



Overlap of Sources

Legacy Sources

Multiple Sources



Source: OCEPD, 2021

Challenges for differentiation

- Overlap among sources
- Biogeochemical transformations
- Legacy nutrient inputs
- Costs
- Collection
- Analytical processing

Practical Considerations

Sampling and Analyses

Sample design

- Minimize other potential sources

Collecting samples

- Minimize interference
- Stormwater vs groundwater

Laboratory selection

- Different detection limits, and preservation

Isotopes:

- Different methods, conduct split sampling if a new lab

Groundwater seepage into lakes

Groundwater Flux In Lakes

- Groundwater flux into lake is typically highest at the edges of lakes
- Nitrate concentrations have to be high enough; lab dependent generally >1 to > 3 mg/L nitrate-N
- Challenging: alligators, volume limitations, nitrate limitations, matrix interference, biogeochemical reactions
- Limit of detection issues with sucralose

Summary

Summary

Best Practices

- Develop a sampling plan based on your primary questions
- Select sampling sites based on minimizing potential confounding influences
- Use multiple lines of evidence approach

Evidence of Nutrients

- Examine species of nitrogen and phosphorus
- Boron isotopes appear to be of limited use in Florida
- Sucralose appears to be a robust indicator of human wastewater
- Stable isotopes of N, combined with Bayesian modeling can be used to differentiate sources, but frequently overlap among the sources
- Stable isotopes analyses can be used in groundwater, lake seepage, and surface water

Thank you

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