



*Emerging Pollutants: Protecting Water Quality for the Health of People and the Environment*

# **Prioritization of Emerging Pollutants Used for Fingerprinting Specific Water Sources**

**Piero R. Gardinali, Milena Ceccopieri, Kassidy Troxell, Stefanie Landweeer**

Florida International University, Department of Chemistry & Biochemistry, Institute of Environment (InWE)

*January 19, 2023, 12:45 pm CET*



## What is water quality? – A traditional definition

---

- Water quality refers to the *chemical, physical, biological, and radiological* characteristics of water.
- It is a measure of the *condition* of water relative to the *requirements* of one or more biotic species and or to any human need or purpose.
- It is most frequently used by reference to a set of *standards* against which compliance can be assessed.

## Must let contaminants “emerge” – Standards are not widely available

---

There are *known knowns*. These are things we know that we know.  
There are *known unknowns*. That is to say, there are things that we know we don't know.

But there are also *unknown unknowns*. There are things we don't know we don't know.

**Donald Rumsfeld**

We need to move from *target* to *non-target* analysis for “*relevant*” things to “*emerge*”

We can only *manage* what we *measure*

## Things that we know - *Target analysis*

---



Associated Press

## Things that we don't know - Non-target analysis(NTA)



## Prioritizing an “emergent” contaminant- Non-target analysis(NTA)



# Why high-resolution and accurate mass?



Orbitrap



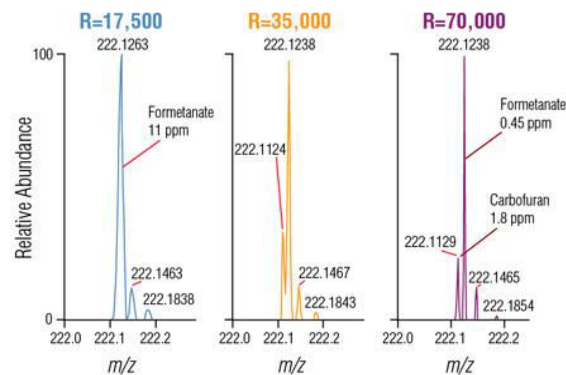
FT-ICR



qTOF

Investigate elemental composition of organic molecules

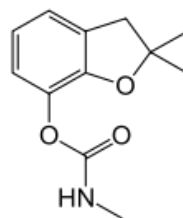
## Importance of Resolution in Compound ID



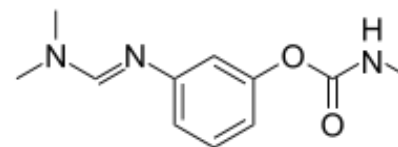
Carbofuran  
Formetanate

C<sub>12</sub>H<sub>15</sub>NO<sub>3</sub>  
C<sub>11</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>

M+H<sup>+</sup> = 222.1125  
M+H<sup>+</sup> = 222.1237



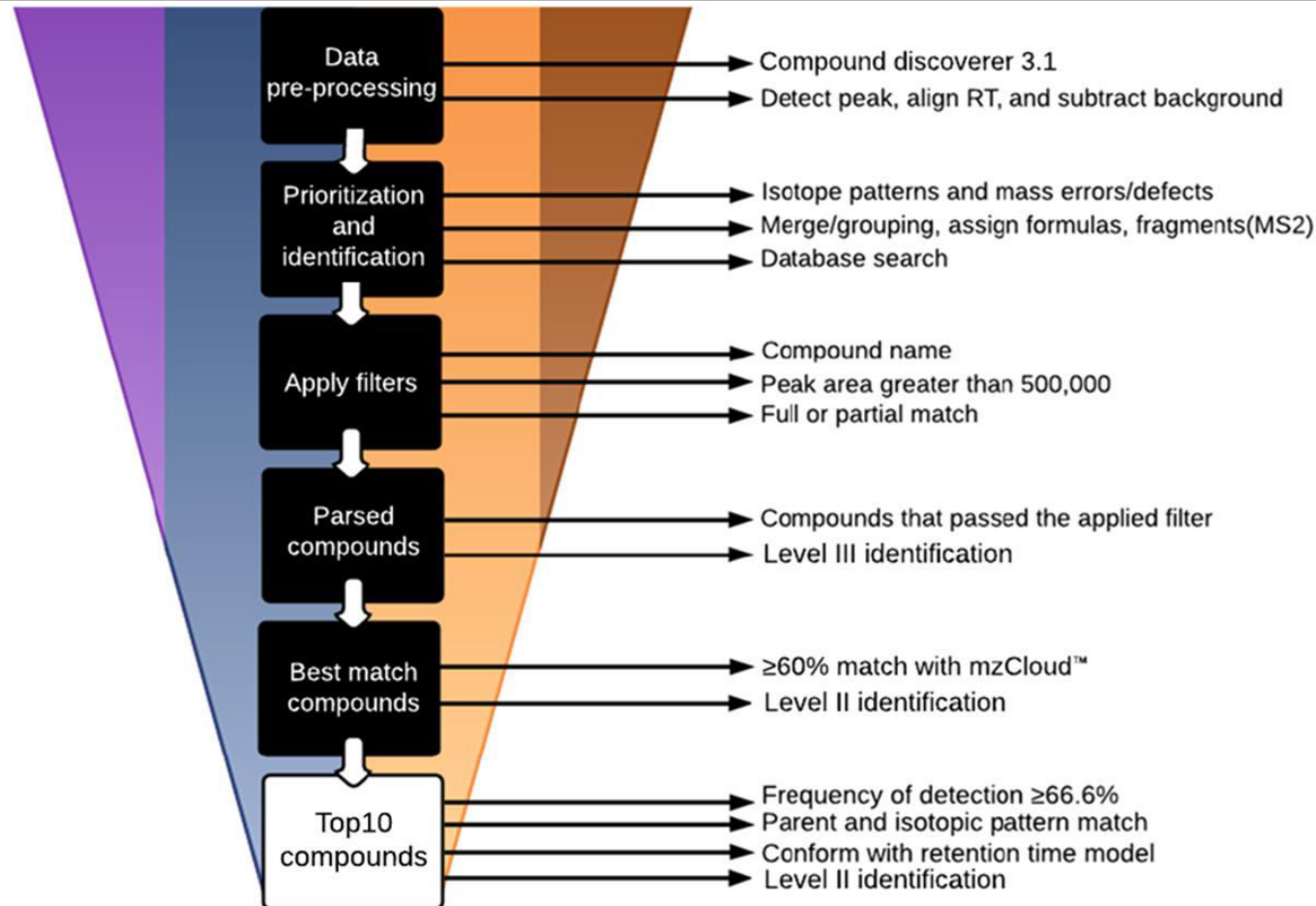
C<sub>12</sub>H<sub>15</sub>NO<sub>3</sub>  
221.1052



C<sub>11</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>  
221.1164

[M+H]<sup>+</sup> 222.1237

# Non-target Analysis Processing “workflow” - Objective, unattended



Yes, each feature could be identified to a degree of confidence.

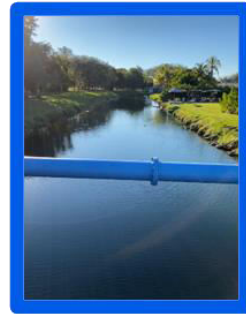
Unknown to tentatively identified compound.



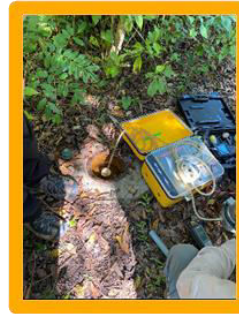
## Environmental application – Influence of septic tanks Southeast Florida



**PB Well**  
 septic tank influenced



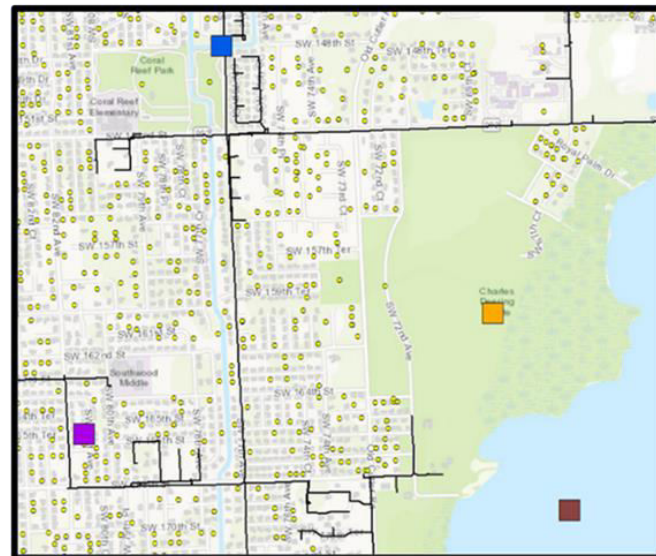
**C100E**  
 C100 freshwater canal



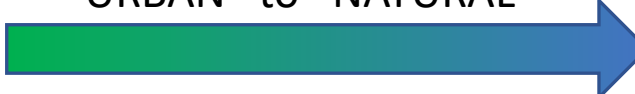
**GWW3**  
 non-septic influenced groundwater well



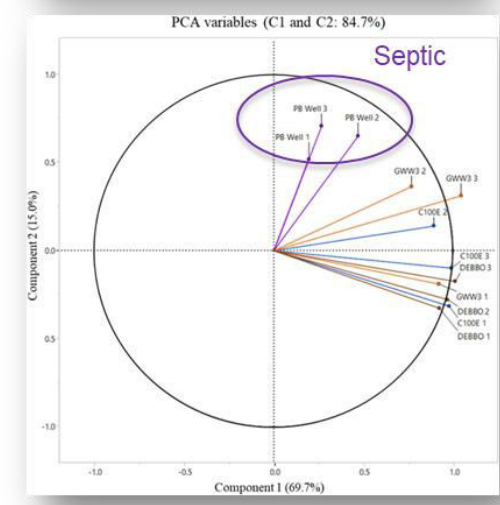
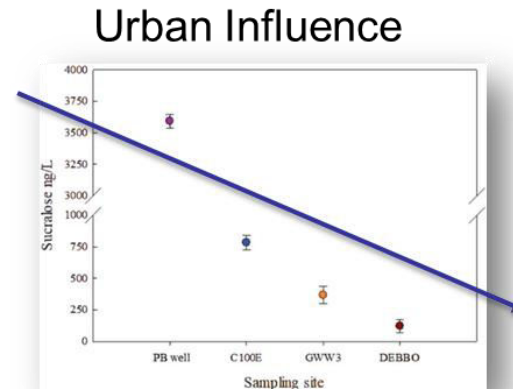
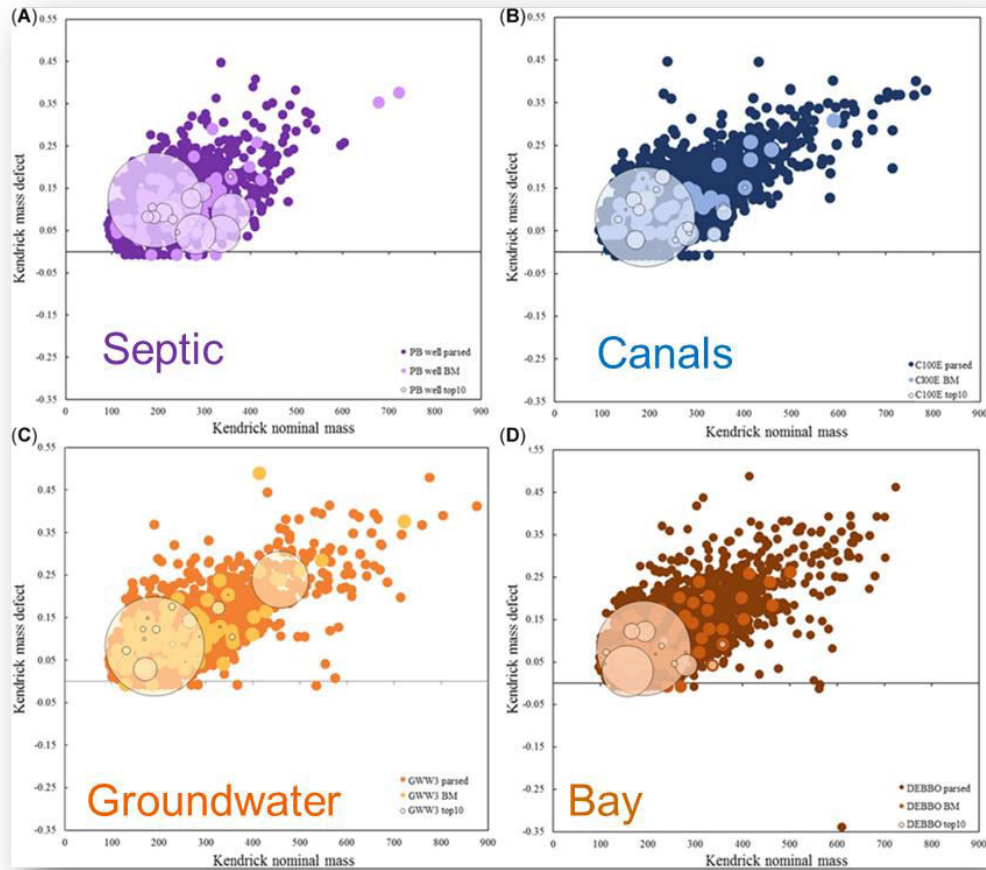
**DEBBO**  
 saltwater Biscayne Bay



● Septic system  
 — Sewage line

URBAN to NATURAL  


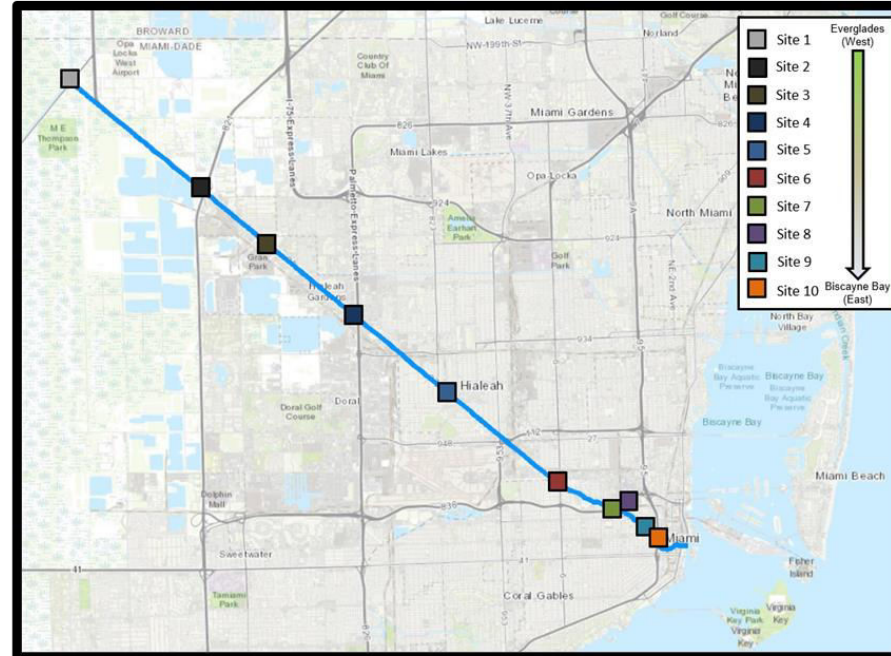
# Isolating sources and indicators from NTA?



Troxell, K., Ng, B., Zamora-Ley, I., & Gardinali, P. (2022). Detecting Water Constituents Unique to Septic Tanks as a Wastewater Source in the Environment by Nontarget Analysis: South Florida's Deering Estate Rehydration Project Case Study. *Environmental Toxicology and Chemistry*.

# Miami River: Urban Managed Influence and Mixed Sources

Florida Everglades

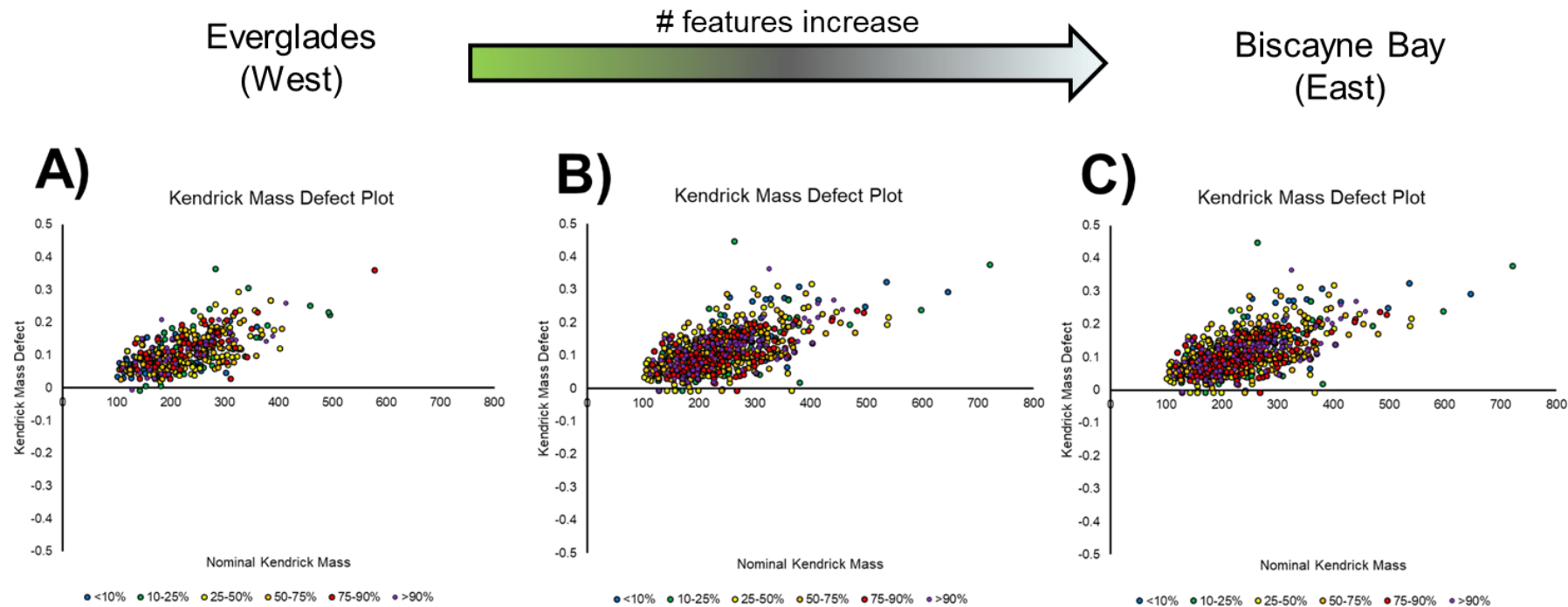


- Many tributaries
- Managed watershed
- Ailing infrastructure
- Long-term water quality issues
- Discharges to Biscayne Bay



Miami River

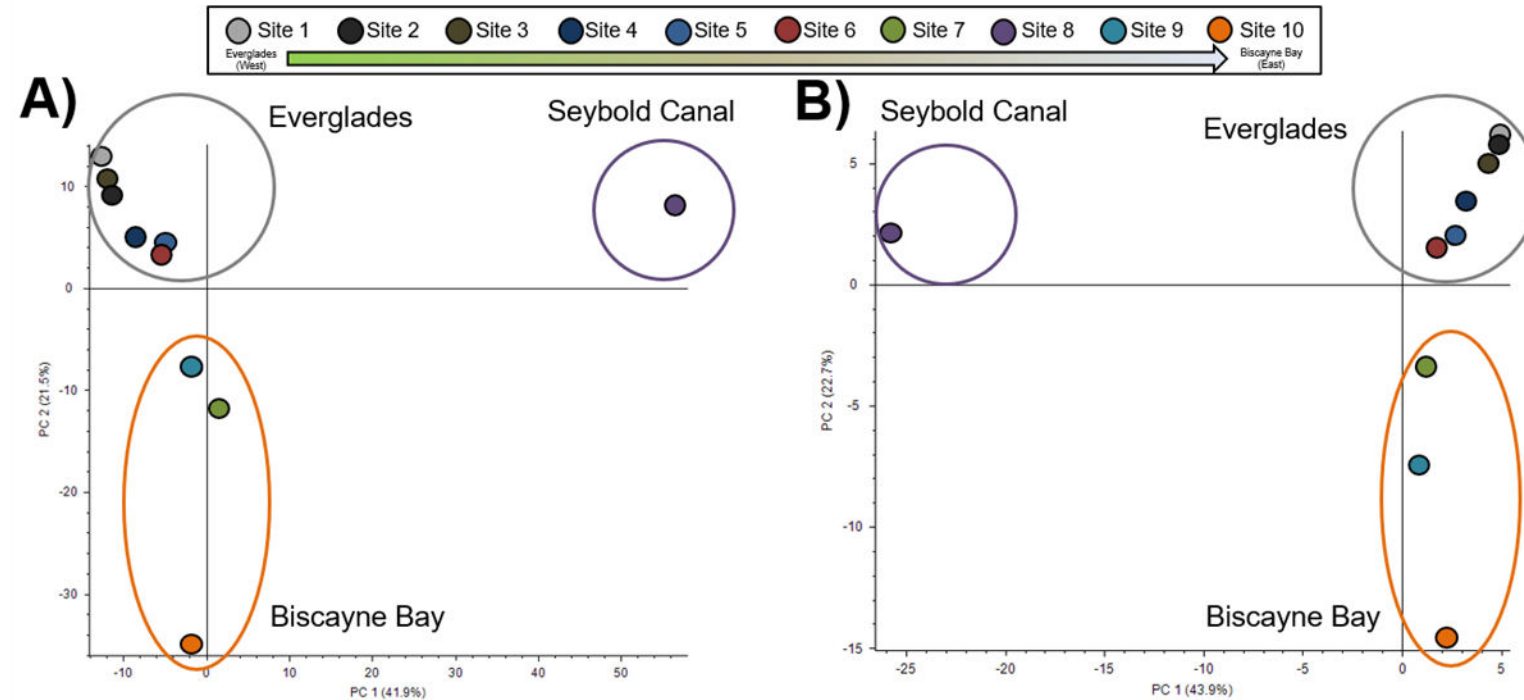
## First goal, define the chemical space in time and geographical scale



- Kendrick mass defect plots (KMD) of the three endmembers of the Miami River Site 1 (A), 8 (B), and 10 (C).

# Use statistical analysis to isolate sources

Florida Everglades

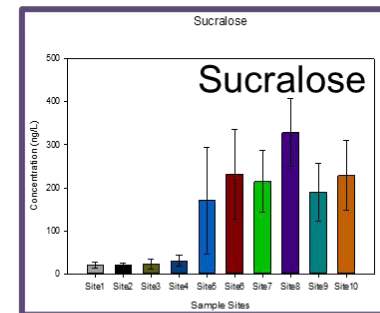
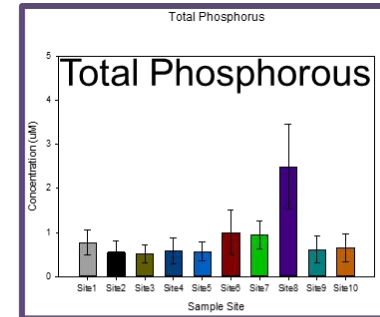
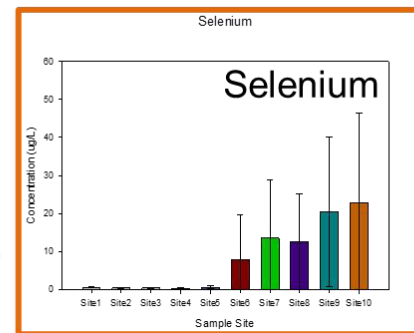
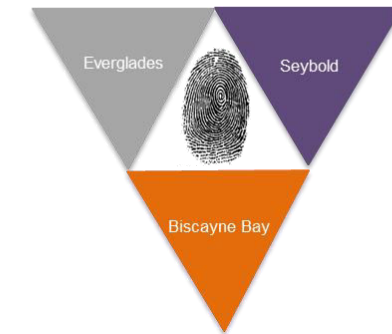
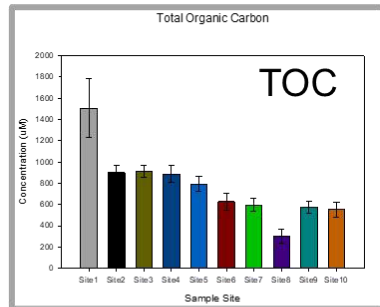
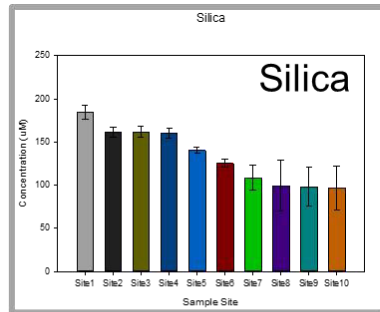


- Comparing all samples tentatively identified peaks and intensities throughout the Miami River. Positive (A) and negative (B) mode both showing three distinctive water sources from site 1, 8, and 10.



Miami River

# Identify unique features of sources and *prioritize* the target analysis



## Can we take a step forward? Yes, but we need guidance

- Yes, we can ***fingerprint*** water!
- Based on these fingerprints we can prioritize ***sites*** of interest as well as ***compounds*** of interest.
- NTA workflows ***are capable*** to differentiate water sources in a system and show how it is influenced by a managed urban environment.
- ***Both*** NTA and traditional analyses are needed to understand the sources of ***emergent contaminants***.

