

# Comprehensive nontarget analysis of sediment and aqueous environmental samples via SPE LC-ESI-HRMS: A case study for the Florida Everglades.

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# BACKGROUND

The Contaminant Assessment and Risk Evaluation (CARE) Project was an extensive study that aimed to assess and inform resource managers about risks to the ecosystems of Everglades National Park, Biscayne National Park, and Big Cypress National Preserve. Previous analyses included organochlorine pesticides, trace metals, and contaminants of emerging concern, such as pharmaceuticals and personal care products. Recently, citizen complaints and public reports of potential contamination from poorly treated wastewater and repeated fish and seagrass die offs near Everglades City and Chokoloskee Bay have renewed the interest in assessing the current conditions in the bay and nearby coastal basins. Due to the lack of certainty of the source of potential contaminants, this area forms an ideal test bed for nontarget mass spectrometric screening methods.

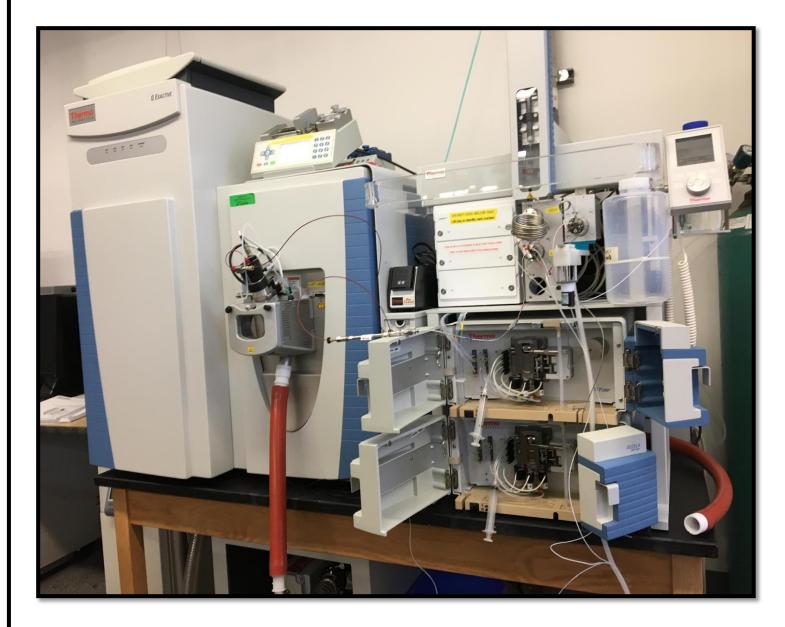
## GOALS

- Development of a sequential extraction method for nontarget mass spectrometric analysis of sediment samples.
- Analyze surface water samples and sediment extracts from waters near Everglades City Fl.

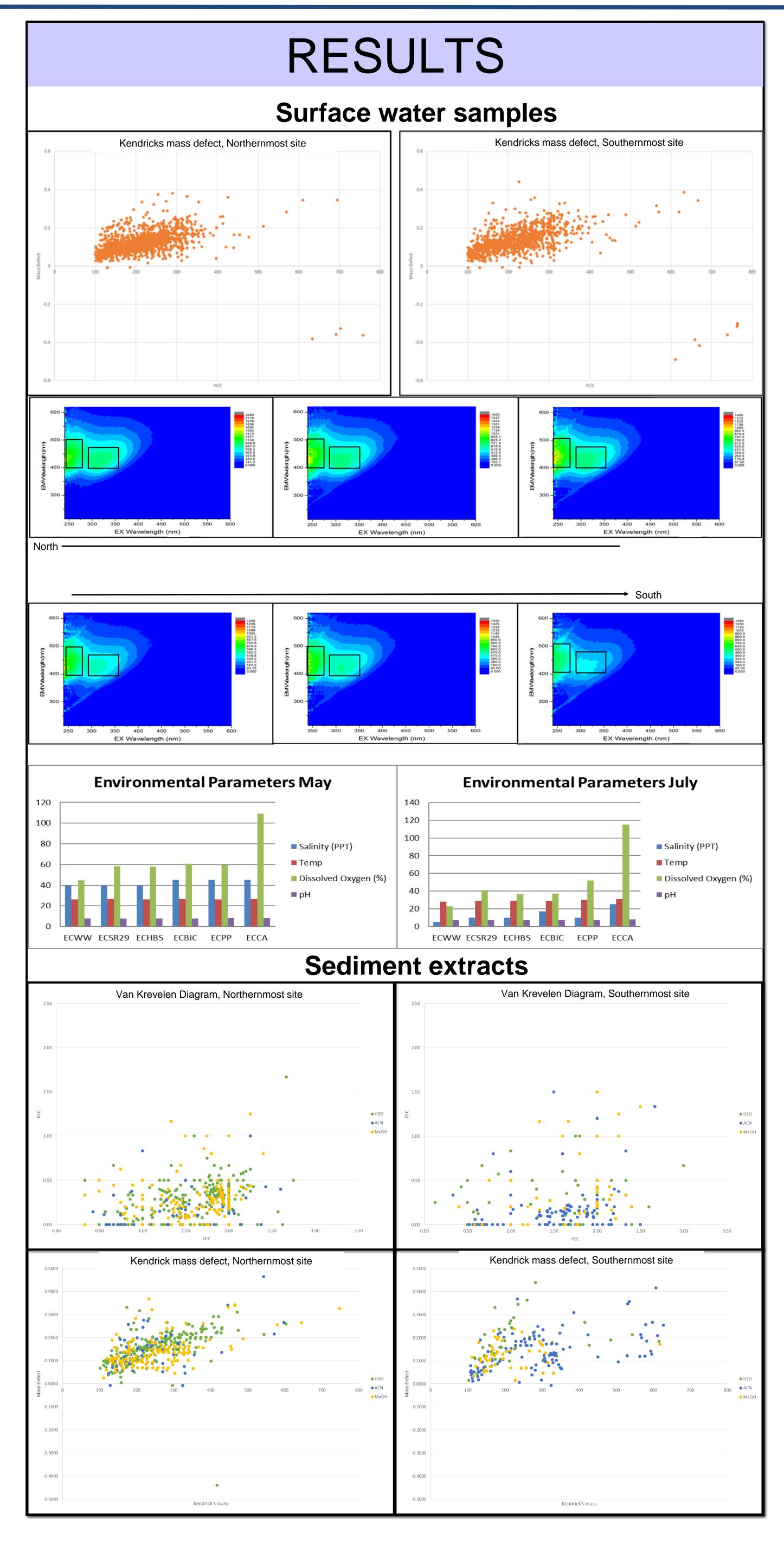
#### METHODS

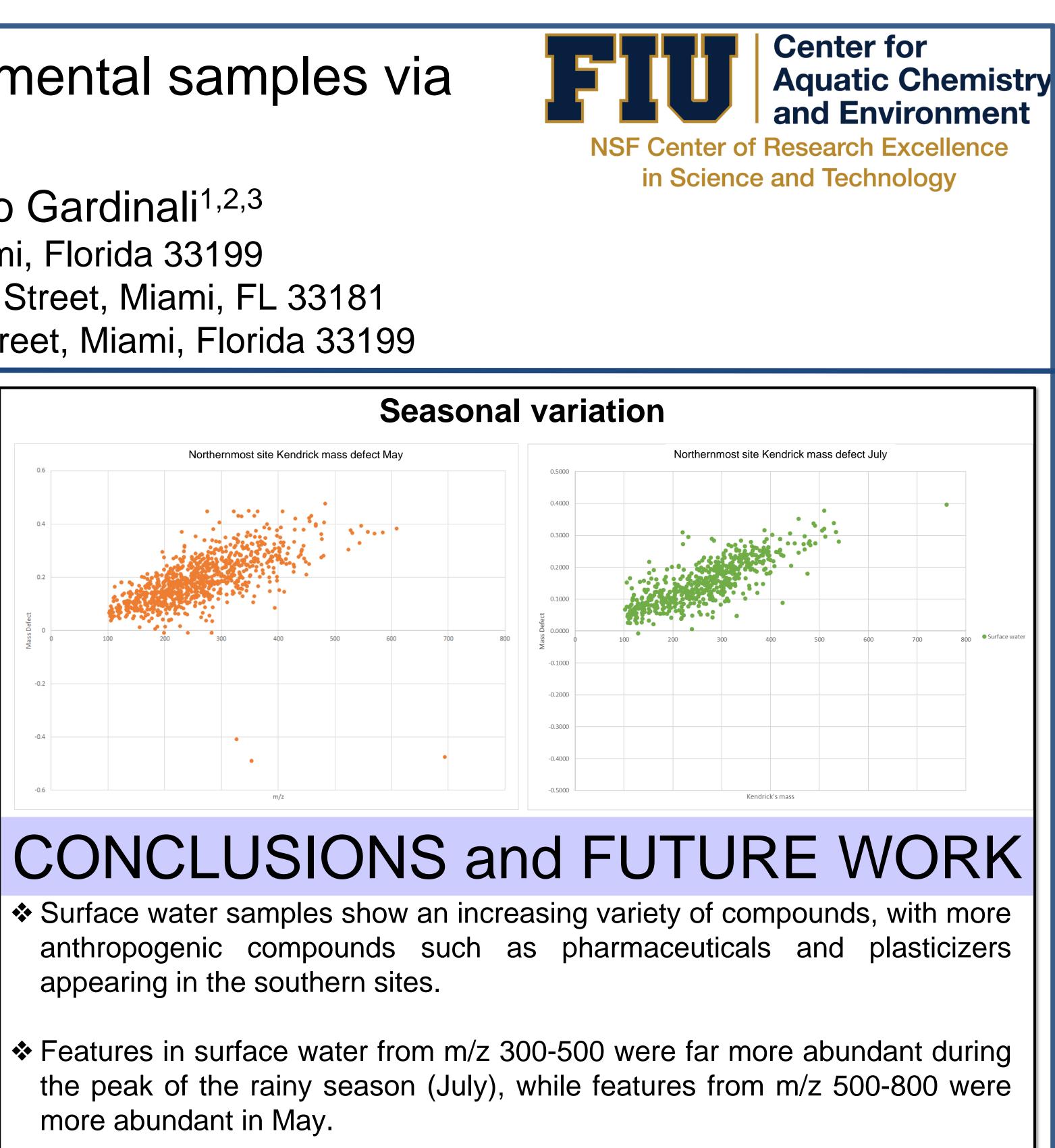
- Sediment and water samples were acquired at six sites from Everglades City.
- Sediment samples were extracted via sequential extractions with water, methanol, and acetonitrile
- Surface water samples were analyzed via Online SPE HPLC-HRMS, while sediment extracts were analyzed via direct injection with the same parameters.
- Sediment extracts were diluted and analyzed via direct injection HPLC-HESI-HRMS.
- Sediments were digested and analyzed for metals via ICP-QqQ-MS

#### **Online SPE HPLC-HRMS parameters:**



- Heated Electrospray Ionization \* source
- Resolution of 140,000
- Scan range from 100-800 m/z.
- Positive and negative scans
- ✤ MS/MS confirmation: 30 NCE
- ✤ Mass tolerance <5ppm</p>





- contain far more natural products.
- to surface water samples.
- Volcano plots:
- Musselwatch data from nearby stations.
- biological samples for complete characterization of sites.



- doi:10.1016/j.trac.2014.11.009
- unattended chemical analysis approach. National Parks Service, FIU, (2016) Contaminant assessment and risk evaluation project summary report.
- https://www.nps.gov/ever/learn/nature/upload/CARE\_merged\_final.pdf https://doi.org/10.1016/S0160-4120(02)00080-6 Bioanalytical Chemistry, 400(9), 3141–3149. http://doi.org/10.1007/s00216-011-4939-x



- Program.
- necessarily reflect the views of the National Science Foundation.

Features in sediment extracts from southern sites show far more complexity and contain more anthropogenic compounds than the northern sites, which

Features in sediments contained far less seasonal variation when compared

Metal analysis largely revealed concentrations consistent with NOAA's

Future work will include development of a method for nontarget extraction of

## REFERENCES

Bletsou, A. A., Jeon, J., Hollender, J., Archontaki, E., & Thomaidis, N. S. (2015). Targeted and non-targeted liquid chromatography-mass spectrometric workflows for identification of transformation products of emerging pollutants in the aquatic environment. TrAC Trends in Analytical Chemistry, 66, 32-44.

Gardinali P, Quinete N, Henderson C, Castro J. (2017). Screening for water quality degradation along Everglades National Park's West Coast: A holistic

Weiss, J. M., Simon, E., Stroomberg, G. J., de Boer, R., de Boer, J., van der Linden, S. C., ... Lamoree, M. H. (2011). Identification strategy for unknown pollutants using high-resolution mass spectrometry: Androgen-disrupting compounds identified through effect-directed analysis. Analytical and

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