

Cody Henderson
Research Mentor: Piero Gardinali

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

- ❖ Characterization of bulk water parameters via fluorometry.
- ❖ 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

- ❖ Traditional water parameters were collected on site via YSI Exo 2 probe.
- ❖ Fluorometric analysis of bulk organics was accomplished via a Horiba Aqualog.
- ❖ Sediment and water samples were acquired at six sites from Everglades City.
- ❖ Sediment samples were extracted via sequential extractions with water, methanol, and acetonitrile via a Dionex ASE 200.
- ❖ Surface water samples were analyzed via Online SPE HPLC-HRMS.
- ❖ Sediment extracts were analyzed via direct injection HPLC-HRMS.

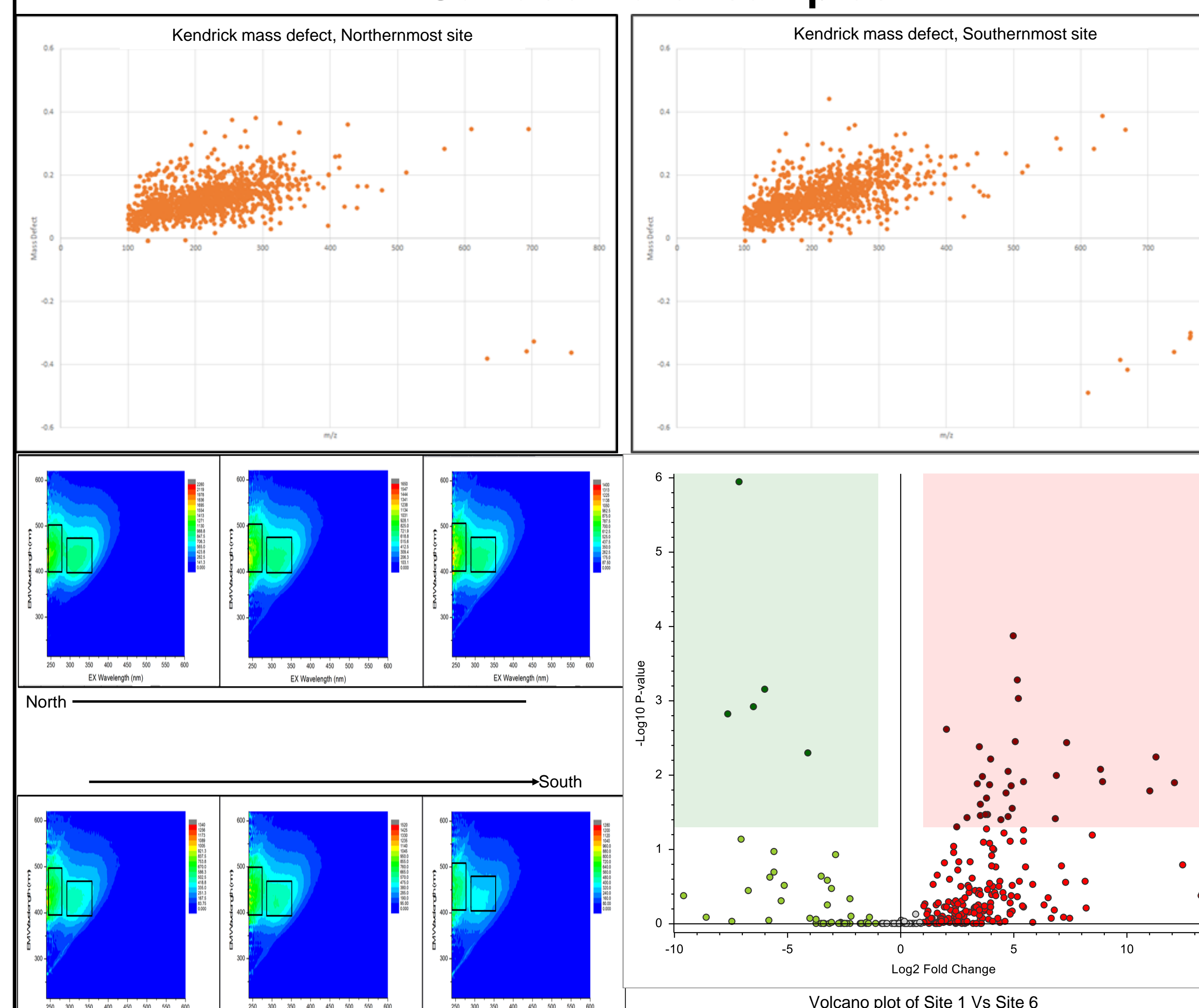
Online SPE HPLC-HRMS parameters:



- ❖ Heated Electrospray Ionization source
- ❖ Resolution of 140,000
- ❖ Scan range from 100-800 m/z.
- ❖ Positive and negative modes
- ❖ Four aliquots per sample
- ❖ MS¹, MS² 30 NCE
- ❖ Mass tolerance <5ppm
- ❖ Spray Voltage 5000 V
- ❖ Capillary temp 350 °C
- ❖ S-Lens RF Level 50

RESULTS

Surface water samples

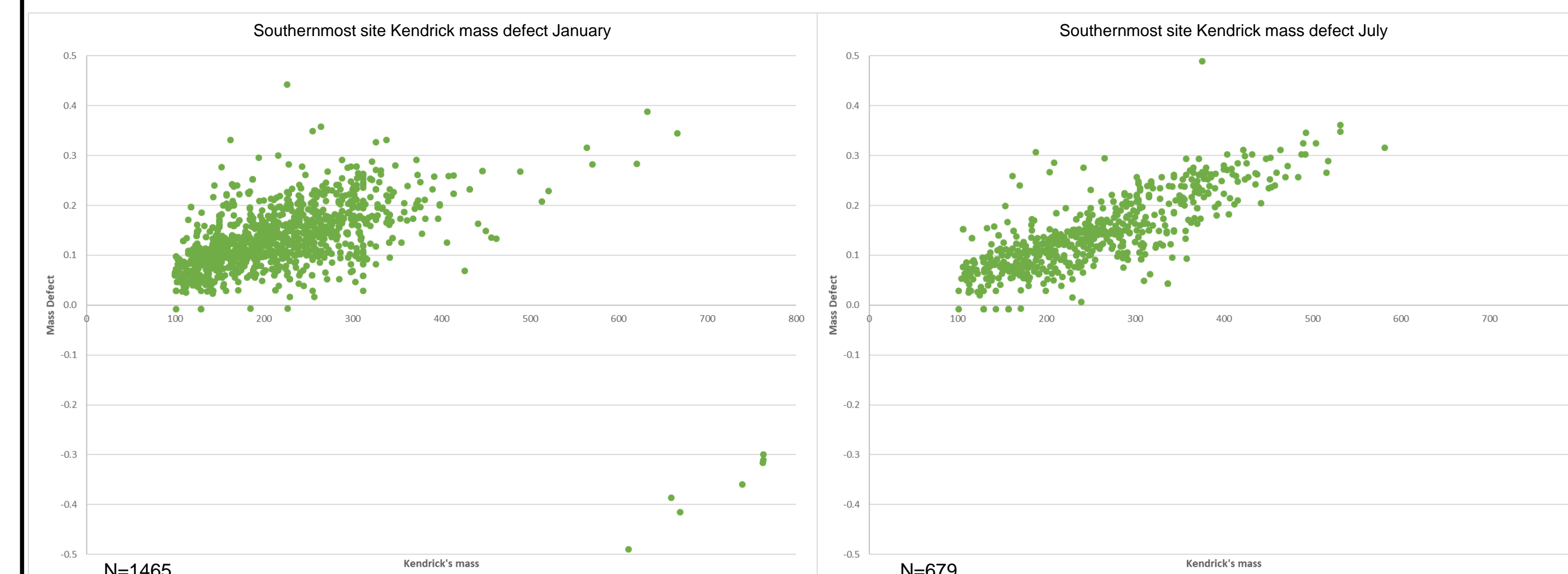


Features of interest	Purpose	Sites Present
Atrazine	Pesticide	All sites
DEET	Insect repellent	1,2,3,5,6
Oxyphenolol	Pharmaceutical	3,4
Diisopropyl Phosphate	Pharmaceutical	5,6
Ethofumesate	Herbicide	4,5,6
Tetrahydrofurfuryl methacrolate	Plasticizer	5
Ancymidol	Plant growth inhibitor	6

Sediment extracts



Seasonal variation



CONCLUSIONS and FUTURE WORK

- ❖ Fluorometry shows a consistent type of DOM, with decreasing intensity from North to South.
- ❖ DOM fluctuated seasonally, with significantly lower intensity emission peaks in May, and significantly higher intensity in both January and July.
- ❖ Surface water samples show an increasing variety of compounds, with more anthropogenic compounds such as pharmaceuticals and plasticizers appearing in the southern sites.
- ❖ Features in surface water from were far more abundant during the peak of the dry season (January), and far less abundant in the peak of the rainy season.
- ❖ Sediment extracts from northern sites show statistically significantly lower H:C ratios (mean 1.52, n=404), while southern sites showed higher H:C ratios (mean 1.65, n=452), however little seasonal variation was observed.
- ❖ The sediment extraction method developed was successful in extracting a wide variety of compounds and elucidating the differences between sites.
- ❖ Future work may include analysis via APCI ionization.
- ❖ Future work will include development of a method for nontarget extraction of biological samples for complete characterization of sites.

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. doi:10.1016/j.trac.2014.11.009
- ❖ Gardinali P, Quinete N, Henderson C, Castro J. (2017). Screening for water quality degradation along Everglades National Park's West Coast: A holistic 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](https://doi.org/10.1016/S0160-4120(02)00080-6)
- ❖ 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 Bioanalytical Chemistry*, 400(9), 3141-3149. <http://doi.org/10.1007/s00216-011-4939-x>

ACKNOWLEDGEMENTS

- ❖ Cody Henderson was supported by the National Science Foundation under Grant No. HRD-1547798. This NSF Grant was awarded to Florida International University as part of the Centers of Research Excellence in Science and Technology (CREST) Program.
- ❖ Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

