Examination of trends and variations in contaminants via non-targeted mass spectrometry: An Everglades case study

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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

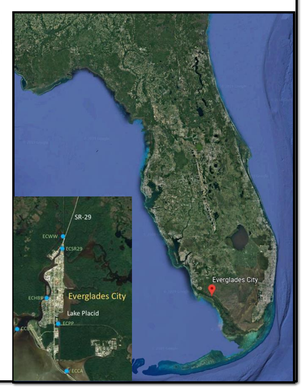
- Development of a sequential extraction method for nontarget mass spectrometric analysis of sediment samples.
- Analyze surface water samples and sediment extracts from waters near Everglades City, FL.

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.
- Detected features were required to show 1) meet a minimum ionization threshold above any potential presence in the blank, 2) have a databased matched name, and 3) have supporting ms2 fragmentation.

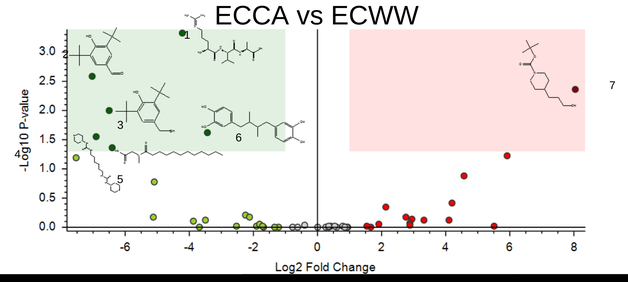
Online SPE HPLC-HRMS parameters:

- 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



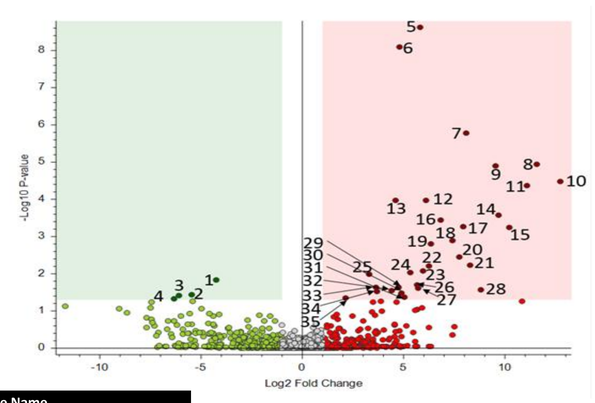
RESULTS

Surface water samples
ECCA vs ECWW



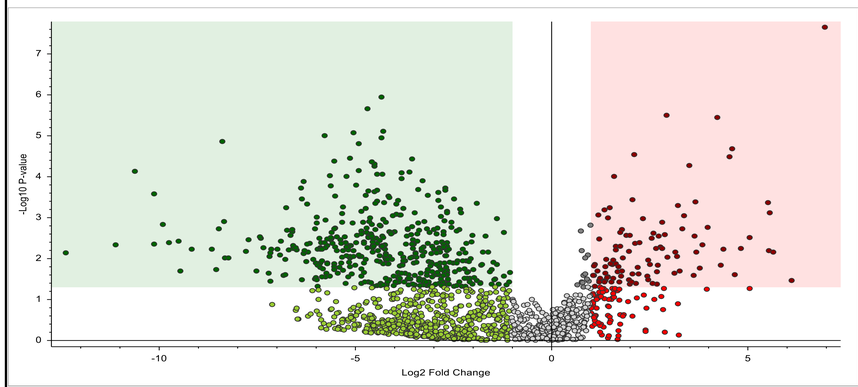
#	Feature Name	Compound of interest	Use	Sites detected
1	N~5~-(Diaminomethylene)-L-ornithyl-L-valyl-L-alanine*	Atrazine	Pesticide	All sites
2	3,5-Di-tert-butyl-4-hydroxybenzaldehyde	DEET	Insect repellant	1,2,3,5,6
3	2,6-Bis(2-methyl-2-propanyl)-4-(sulfanylmethyl)phenol*	Oxyphenolol	Pharmaceutical	3,4
4	1,1'-(1,6-Hexanediyl)bis[3-(4-morpholinyl)urea]	Diisopropyl Phosphate	Pharmaceutical	5,6
5	N-Dodecanoyl-N-methylglycin	Ethofumesate	Herbicide	4,5,6
6	Nordihydroguaiareticacid	Tetrahydrofurfuryl methacrolate	Plasticizer	5
7	Tert-Butyl 4-(3-Hydroxypropyl)Piperidine-1-Carboxylate	Ancymidol	Plant growth inhibitor	6

Sediment extracts
ECSR29 vs ECCA



#	Feature Name				
1	6,7-Dimethylpterin	14	Isopropyl dimethyl phosphorotetrathioate	27	Azelaic acid*
2	2-cyanopyridine	15	Undecylbenzene sulfonic acid*	28	4-Dodecylbenzene sulfonic acid
3	6-Phenyl-1,3,5-triazine-2,4-diamine	16	2,5-Bis(chlorocarbonyl)thiophene	29	Myristyl sulfate
4	Dodecyl sulfate	17	Lauryl hydrogen sulfate*	30	dodecyl 4-methylbenzenesulfonate
5	3-(Decyloxy)tetrahydrothiophene 1,1-dioxide	18	Lauryl hydrogen sulfate*	31	4-Dodecylbenzenesulfonic acid
6	4-Tetradecylbenzenesulfonic acid	19	Juniperic acid	32	3-Amino-1H-[1,3]dithiolo[4,5-c]pyrazole-5-thione
7	Bis[4-(vinyloxy)butyl] succinate	20	dodecyl 4-methylbenzenesulfonate	33	Hexadecanedioic acid
8	Dodecyl p-toluene sulfonate	21	3,6,9,12,15,18,21-Heptaoxatricosane-1,23-diamine	34	Lauryl hydrogen sulfate*
9	Methyl phenkapton*	22	Lauryl hydrogen sulfate*	35	1-Pyrrolidinecarboximidamide
10	4-Dodecylbenzenesulfonic acid	23	Suberic acid*		
11	Undecylbenzenesulfonic acid*	24	4-Decylbenzenesulfonic acid		
12	6-Dodecyl-1,2-oxathiane 2,2-dioxide	25	Dihydroxyethyl lauramine oxide		
13	5-(Di-tert-butylphosphino)-1-(naphthalen-1-yl)-1H-pyrazole	26	Undecylbenzenesulfonic acid*		

Seasonal variation in surface water
January vs April



CONCLUSIONS and FUTURE WORK

- Surface water samples show an increasing variety of compounds, with more anthropogenic compounds, denoted with asterisks, such as pharmaceuticals and plasticizers appearing in the southern sites.
- Features in surface water were far more abundant in January (Dry Season) as opposed to April (Wet Season).
- Features in sediment extracts from southern sites show far more complexity and contain more anthropogenic compounds than the northern sites.
- Features in sediments contained far less seasonal variation when compared to surface water samples.
- Duplicate features occurred in sediment extracts occurred due to analysis in three different solvents, however most can be removed from differential analysis by adjusting the P-Value.
- Future work will include development of a method for nontarget extraction of biological samples for complete characterization of sites.

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