Analysis of Targeted and Non-Targeted Identified Contaminants in Storm Water Retention Ponds Using LC-HRMS With Online Solid Phase Extraction

Gordon Getzinger,[1] P. Lee Ferguson,[1] Jonathan Beck,[2] Charles Yang,[2] Frans Schoutsen,[3]
[1]Duke University, Durham, NC USA, [2]Thermo Scientific, San Jose, CA USA,
[3]Thermo Scientific, Breda, The Netherlands

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Introduction

This poster demonstrates the implementation of a data-driven environmental monitoring approach to examine the occurrence and distribution of wastewater-derived and turf grass management organic compounds in storm water retention ponds located on a coastal golf course community at Kiawah Island, SC. Water samples were collected and screened for the presence of trace organic contaminants by a non-targeted HPLC-high-resolution/accurate-mass (HR/AM) mass spectrometry workflow. The occurrence of identified and confirmed contaminants was then quantitatively assessed by a high-throughput online-SPE-LC-MS method.

Site description and Sampling

Surface water, groundwater and wastewater effluent samples were collected from Kiawah Island, SC **(Figure 1),** a costal golf-course community where turf grass management chemicals are extensively applied and reclaimed wastewater is used for irrigation. Golf course and storm-water runoff is collected in a series of ponds (blue area) which are connected (red lines) in series and communicate tidally with a neighboring estuary.

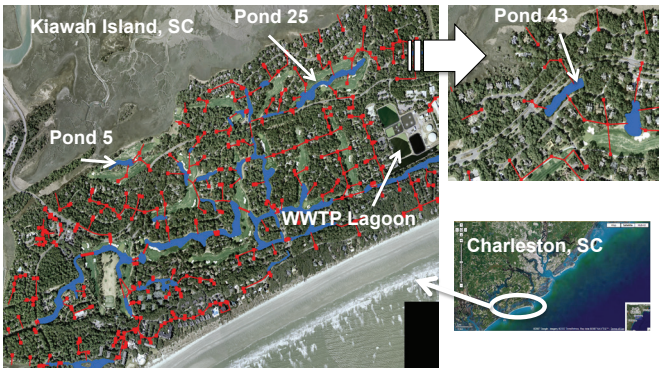


FIGURE 1. Aerial view of Kiawah Island, SC.

Initial sampling for non-targeted screening consisted of 0.5 L grab samples collected and field extracted by SPE (Oasis® HLB, Waters Corporation) over two weeks in May 2010. Similarly, 10 mL grab samples were collected in May 2011 for quantitative analysis.

Sample sites were chosen to represent various routes of micropollutant loading into the aquatic environment and potential routes of chemical exposure as detailed in **Table 1**.

TABLE 1. Sites samples and description of potential sources of micropollutants to those sites. Golf course runoff consists of both turf-grass management chemicals applied to the course and wastewater derived contaminants introduced through irrigation.

Sample Site	Inputs
Pond 5	Golf course runoff
Pond 25	Golf course runoff
Pond 43	Residential stormwater
Wastewater lagoon	Treated municpal wastewater
Wastewater Composite	24 hr composite effluent
Well 1	Infiltration from pond 25
Well 7	Infiltration from pond 5

Data-driven Environmental Monitoring

- **Comprehensive assessment of the aquatic fate and effects of organic micropollutants is greatly hindered by the need to develop compound-specific methodologies prior to sampling and analysis.**
- **A data-driven workflow, coupling HR/AM mass spectrometry and highly sensitive Online SPE-MS analysis, will ensure complete characterization of organic pollutants in aquatic environments.**

Methods

1. Broad-spectrum HPLC-HR/AM MS Screening:

- Thermo Scientific™ LTQ Orbitrap Velos™ MS
- H-ESI positive ionization
- Full-scan (100-1000 *m/z*) at R=60k
- Data-dependent top 3 AM MS/MS with dynamic exclusion and peak apex detection

2. Non-targeted Compound Identification:

- ThermoScientific™ ExactFinder™ 2.0 software
- HR/AM data screened for ~1000 known contaminants (EFS database)
- Automated feature scoring and filtering based on chromatographic peak shape, mass error (ppm) and isotope pattern.
- Identification based on AM library searching (EFS Library).

3. Targeted Quantitation:

- Thermo Scientific™ EQuan MAX Plus™ online SPE and HPLC system.
- 1mL injection loaded onto a Thermo Scientific™ Hypersil™ GOLD aQ column (20x2.1 mm) followed by separation on an Accucore aQ analytical column (100x2.1) by gradient elution with methanol/water mobile phase.
- MS data was acquired in SRM mode on a Thermo Scientific™ TSQ Quantiva™ MS equipped with a H-ESI interface. Quantitative analysis was performed in Thermo Scientific™ TraceFinder™ 3.1. Software

Results: HR/AM Screening and Non-target Identification

FIGURE 2. Representative HR/AM chromatograms of SPE extracts subjected to non-targeted screening for the identification of organic pollutants relevant to the systems under investigation on Kiawah Island and selection of target compounds for quantitative analysis.

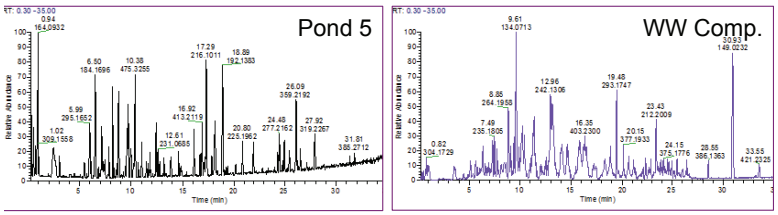
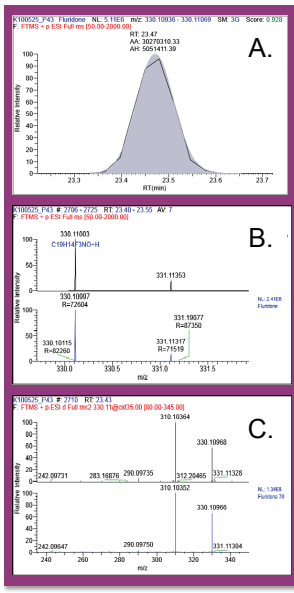


FIGURE 3. Example of non-targeted identification of Fluridone in Pond 43 by EFS database screening and spectral library searching in ExactFinder.



A. EFS database match for Fluridone showing the goodness of fit (score=0.93) between a modeled chromatographic peak (gray area) and the observed peak (black trace).

B. Comparison of a modeled mass spectrum for the proposed pseudo-molecular ion $[C_{19}H_{14}F_3NO]^{M+H}$ (blue) and avg. full-scan obs. data (black) reveals excellent mass accuracy (-0.31ppm) at the mono-isotopic peak and 100% isotope pattern score.

C. Library searching of the observed AM CID MS^2 spectrum (black) returns a match to the EFS library entry for Fluridone (blue) with a score of 70%.

TABLE 2. Compounds identified by non-target screening.

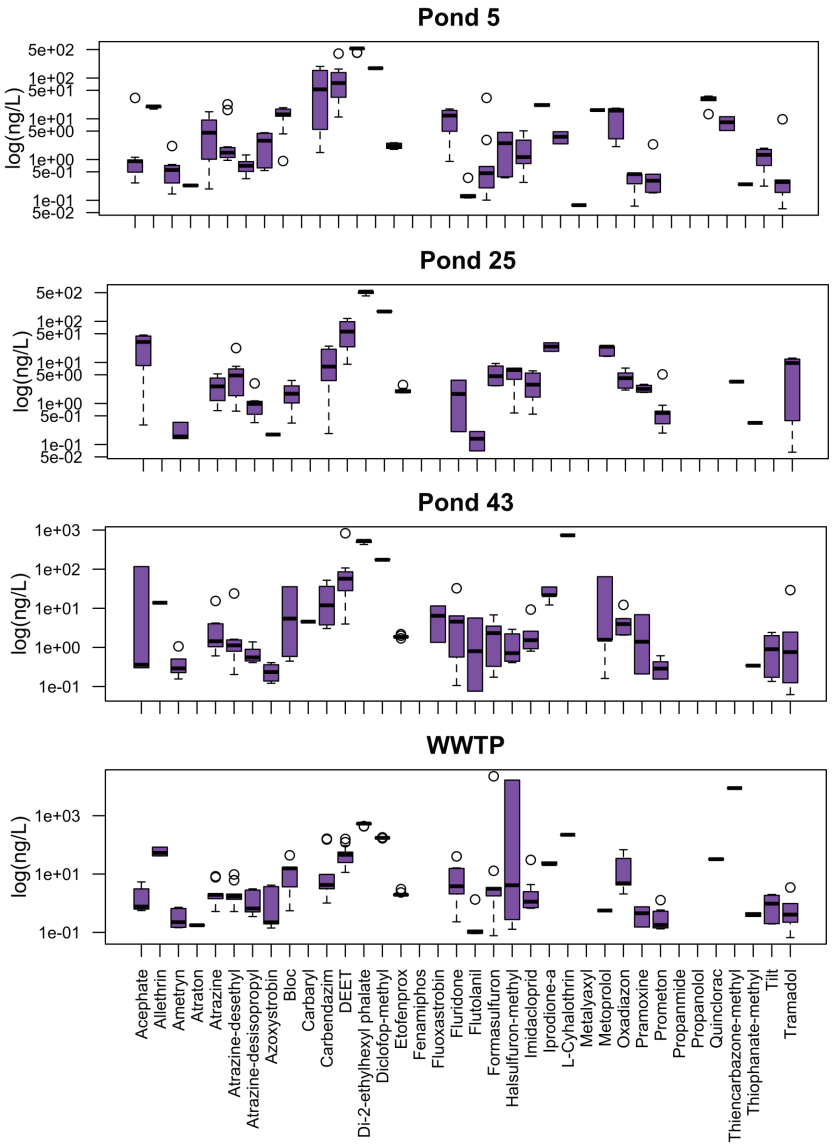
Compound	Sample(s)
Atraton	25, 43
Atrazine	5, 25, 43, WWTP, WW Comp.
Atrazine-2-hydroxy	25
Carbamazepin	WWTP, WW Comp.
Carbendazim	WWTP
DEET	5, 25, 43, WWTP, WW Comp.
Fluridone	25, 43
Hydrocortisone	WWTP, WW. Comp.
Mefluidide	5, 25
Metolcarb	WWTP
Metoprolol	WWTP, WW Comp.
Promecarb	WW Comp.
Propanolol	WWTP, WW Comp.
Pyroquilon	5, 25, WWTP, WW Comp.
Sulfamethoxazole	WW Comp.
Temeazepam	WW Comp.
Trimethoprim	WWTP, WW Comp.

Results: Targeted quantitation by online-SPE-LC-MS

Based on the results of non-target screening, knowledge of chemical usage on the island and readily available reference standards, an online-SPE-LC-MS method was developed to quantify the occurrence and distribution of wastewater and turf grass management derived organic pollutants on Kiawah Island.

TABLE 3. Compounds monitored by online-SPE-LC-MS, method parameters and and instrument limits of detection.

Compound	Retention Time (min)	Precursor Mass	Product Mass 1	Product Mass 2	LOD (pg/mL)
Acephate	4.36	184	143	95	0.24
Allethrin	12.43	303.2	135	220	7.8
Ametryn	9.55	228.1	186	96	0.12
Atraton	8.22	212.2	170	100	0.12
Atrazine	9.72	216.1	174	104	0.12
Atrazine Desethyl	7.61	188.1	146	104	0.12
Atrazine-desisopropyl	6.52	174.1	132	104	0.24
Azoxystrobin	10.38	404.1	372	329	0.12
Benzotriazole	6.6	120.1	65	92	7.8
Bioresmethrin	13.24	339.2	171	293	62.5
Bloc (Fenarimol)	10.3	331.2	268	311	0.24
Carbaryl	9.32	202	145	127	0.12
Carbendazim	6.01	192.1	160	132	0.12
DEET	9.79	192.1	119	91	0.98
Etofenprox	13.55	394	177	135	3.9
Fenamiphos	11.25	304.1	217	234	0.12
Fluoxastrobin	10.95	459.1	427	188	0.5
Fluridone	10.31	330.1	309	310	0.12
Flutolanil	10.75	324	262	242	0.06
Formasulfuron	9.41	453.1	183	272	0.12
Halosulfuron-methyl	11.23	435.1	182	139	0.12
Imidacloprid	6.89	256	209	175	0.06
Iprodione_a	11.26	330	245	-	15.63
Iprodione_b	11.26	332	247	-	31.25
Metalaxyl	9.81	280.2	220	160	0.06
Metoprolol	7.34	268.2	116	191	0.24
Oxadiazon	12.44	345.1	303	220	3.9
Pramoxine	9.65	294.2	128	100	0.12
Prometron	9.11	226.1	142	170	0.12
Propanmide	10.81	256	173	209	0.12
Quinclorac	8.33	242	161	224	7.8
Thiencarbazone-methyl	8.67	391	359	230	3.9
Thiophanate-methyl	8.88	343	151	311	0.24
Tramadol	7.25	264.2	58	246	0.06



Conclusion

A multifaceted approach to identifying and quantifying non-targeted emerging compounds in environmental surface and ground water samples impacted by treated waste water has been demonstrated.

- HRAM can be used to identify environmental compounds in WWTP impacted environments.
- Online SPE coupled with a triple quadrupole can be used to quantitate samples down to the sub ppt (pg/mL) level.
- Future work will include studying the toxicological impact of these compounds on aquatic species.

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