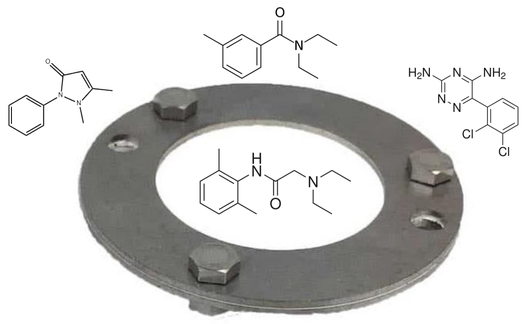
Investigation of pesticides, pharmaceuticals and personal care products in small water bodies using polar organic chemical integrative samplers (POCIS) and non-target screening

NIBIO
NORWEGIAN INSTITUTE OF BIOECONOMY RESEARCH

Ivo Havranek[1], Marit Almvik[1], Marianne Stenrød[1], Roger Holten[1]

BACKGROUND

Employing the different circular-economy strategies such as the usage of biosolids (i.e., sewage sludge or biogas digestates) in agriculture increases the risk for introduction of organic pollutants in the environment. On the other hand, the current surveillance programs for monitoring the water quality usually only focus on target analysis of chosen compounds such as pesticides. Using passive samplers combined with nontarget screening can therefore help disclose otherwise undetected, potentially harmful compounds, including their transformation products.



In this study, we employed polar organic samplers (POCIS) known for their ease of setup and post-treatment. The sorbent in the sampler can absorb a wide range of polar organic compounds, including pesticides, pharmaceuticals, personal care products (PPCPs), industrial pollutants, and more. These samplers can be deployed for specific time periods, making them ideal for qualitative and semi-quantitative water sample analysis. The three sampling sites are connected by a small stream originating in an agricultural area (1), passing under a waste-collection site (with leachate; 2) and finally flowing into a lake (3).

METHOD

Sampling, extraction and analysis

Sampling sites (following the stream)

Samples collected in 3-weeks intervals

SPE (MeOH) and reconstitution (ACN + internal standard)

Analysis on Thermo Q-exactive (HRAM Q-Orbitrap)

Screening using Thermo's (EFS) HRAM compound database (TraceFinder™)

- The compound database and spectral library are constantly extended (currently over 850 parent compounds and their transformation products, mainly pesticides)
- Compounds with known RT were acquired by using targeted data-dependent MS2 (FMS-ddMS2)
- Compounds with unknown RT were acquired in Data Independent Acquisition (FMS-DIA) mode

Screening and tentative identification by MassBank Europe-database (Compound Discoverer™ 3.3.)

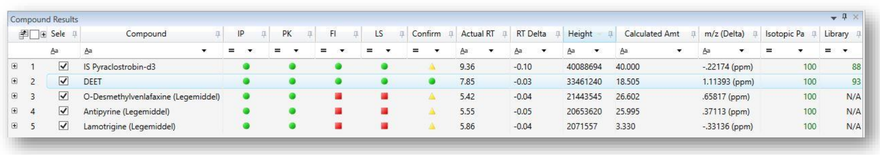
- We used a modified Environmental unknown ID workflow with search in the MassBank Europe-spectral library (currently over 96 449 spectra)

Identification requirements for high-resolution accurate mass MS

- m/z mass match of parent ion (mass error ≤ 5 ppm)
- m/z match of at least 1 fragment ion (mass error ≤ 5 ppm)
- RT-match (±0.1 min) to reference standard
- The peak of the fragment ion overlaps with the peak of the parent ion
- MS2 fragment spectra match
- Isotopic pattern match
- we have RT of over 400 compounds

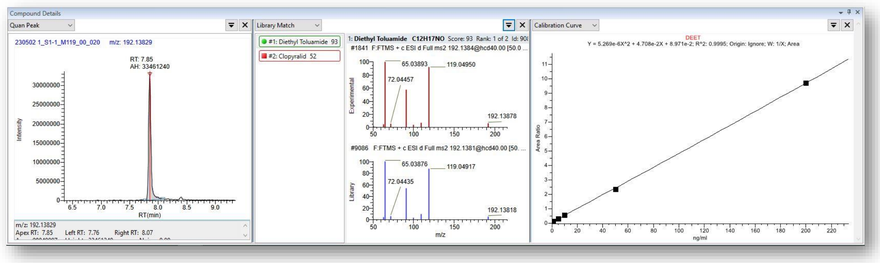
RESULTS

1. Suspect screening using (EFS) HRAM compound database



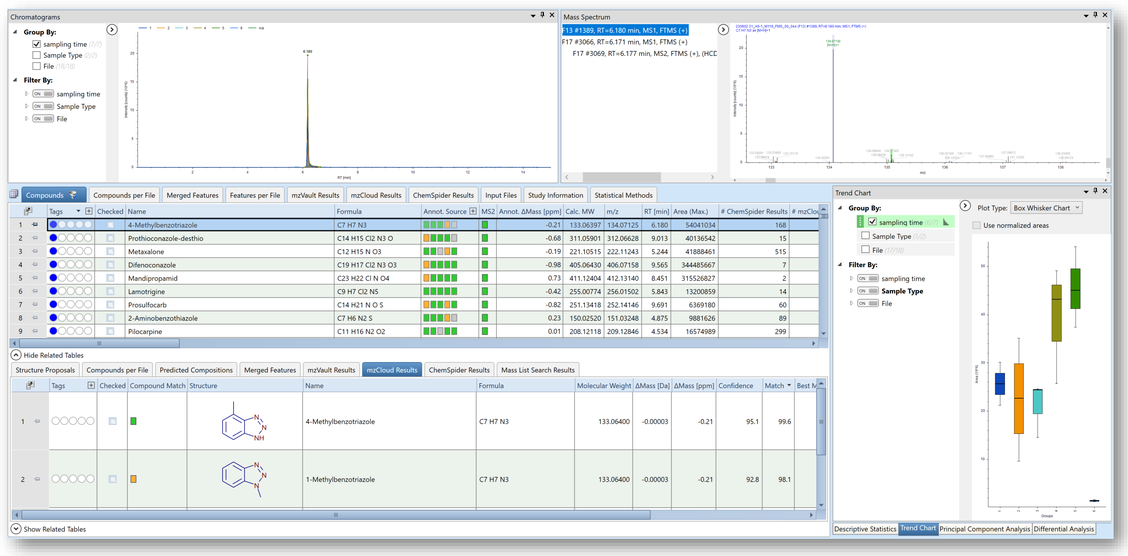
	Sele	Compound	IP	PK	FI	LS	Confirm	Actual RT	RT Delta	Height	Calculated Amt	m/z (Delta)	Isotopic Pa	Library
1	☑	IS Pyraclostrobin-d3	●	●	●	●	▲	9.36	-0.10	40088694	40.000	-.22174 (ppm)	100	88
2	☑	DEET	●	●	●	●	●	7.85	-0.03	33461240	18.505	1.11393 (ppm)	100	93
3	☑	O-Desmethylvenlafaxine (Legemiddel)	●	●	■	■	▲	5.42	-0.04	21443545	26.602	.65817 (ppm)	100	N/A
4	☑	Antipyrine (Legemiddel)	●	●	■	■	▲	5.55	-0.05	20653620	25.995	.37113 (ppm)	100	N/A
5	☑	Lamotrigine (Legemiddel)	●	●	■	■	▲	5.86	-0.04	2071557	3.330	-.33136 (ppm)	100	N/A

In addition to 19 confirmed pesticides, the Environmental and Food Safety (EFS) HRAM database search detected 14 PPCPs of which 6 have been confirmed by reference standards so far (1 false positive).



Compounds were confirmed by comparing the mass, MS2-spectra and RT.

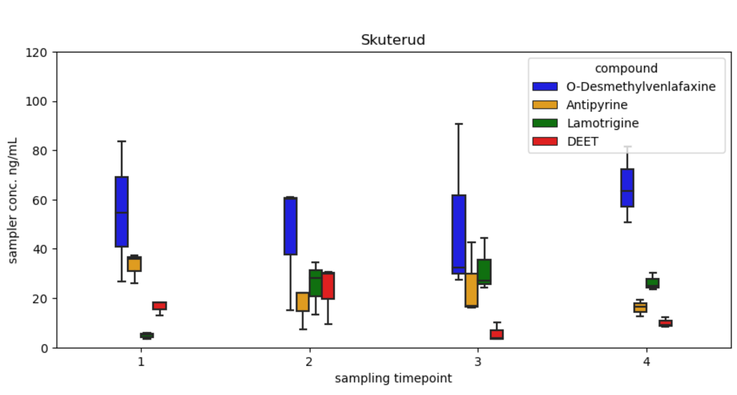
2. Non-targeted screening using MassBank Europe spectral library

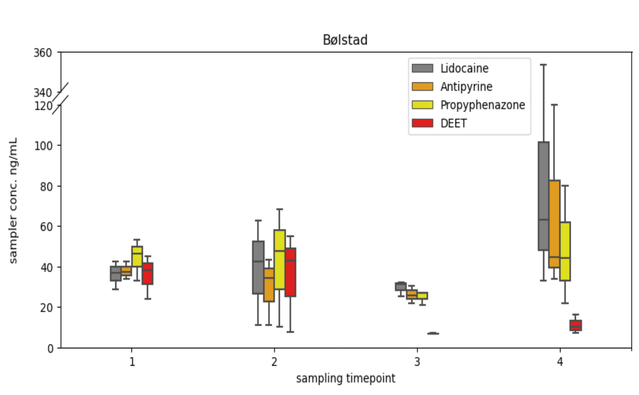


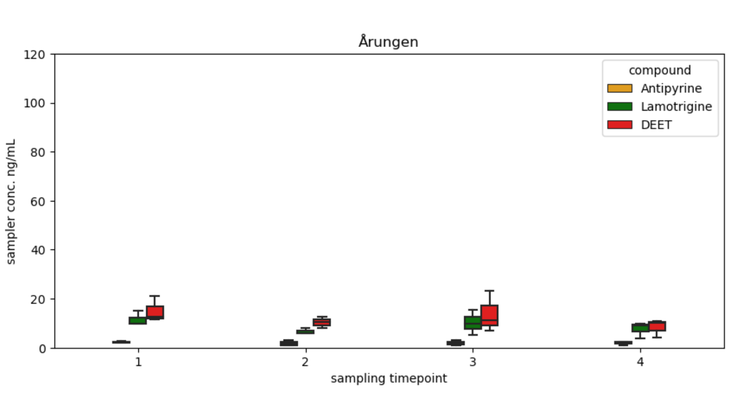
Tags	Checked	Name	Formula	Annot. Source	MS2	Annot. ΔMass [ppm]	Calc. MW	m/z	RT [min]	Area (Max.)	# ChemSpider Results
1		4-Methylbenzotriazole	C7 H7 N3			-0.21	133.06397	134.07125	6.180	54041034	168
2		Prothioconazole-desthio	C14 H15 Cl2 N3 O			-0.68	311.05901	312.06628	9.013	40136542	15
3		Metaxalone	C12 H15 N O3			-0.19	221.10515	222.11243	5.244	41888461	515
4		Difenoconazole	C19 H17 Cl2 N3 O3			-0.98	405.06430	406.07158	9.565	344485667	7
5		Mandipropamid	C23 H22 Cl N O4			0.73	411.12404	412.13140	8.451	315526827	2
6		Lamotrigine	C9 H7 Cl2 N5			-0.42	255.00774	256.01502	5.843	13200859	14
7		Prosulfocarb	C14 H21 N O S			-0.82	251.13418	252.14146	9.691	6369180	60
8		2-Aminobenzothiazole	C7 H6 N2 S			0.23	150.02520	151.03248	4.875	9881626	89
9		Pilocarpine	C11 H16 N2 O2			0.01	208.12118	209.12846	4.534	16574989	299

Tags	Checked	Compound Match	Structure	Name	Formula	Molecular Weight	ΔMass [Da]	ΔMass [ppm]	Confidence	Match	Best M
1				4-Methylbenzotriazole	C7 H7 N3	133.06400	-0.00003	-0.21	95.1	99.6	
2				1-Methylbenzotriazole	C7 H7 N3	133.06400	-0.00003	-0.21	92.8	98.1	

Processing the samples in Compound Discoverer with search in the MassBank spectral library provided 1700-2500 results per sampling site. The best matching compounds will be compared with the reference standards.







- POCIS samplers have successfully been used for semi-quantitative HRAM-screening of pesticides, pharmaceuticals and personal care products in small water streams.
- The results revealed varying, but stable concentration levels of individual compounds across the three sampling sites during the 12-weeks campaign.
- The concentrations were lowest at the last site along the stream (lake Årungen), while for some compounds they were nearly three times higher near the waste-collection site (Bølstad).

compound	site	conc. ng/sampler (min; max)	compound	site	conc. ng/sampler (min; max)
Cyprodinil	Årungen	0.02-0.33	Diuron	Skuterud	0.58-6.17
Isoproturon	all	0.14-5.17	2,6-dichlorbenzamid (BAM)	all	0.72-14.98
Fenpropimorph	Bølstad	0.18-0.66	DMST	all	0.72-87.73
Carbendazim	all	0.26-5.61	Cyprodinil met CGA	all	1.47-13.47
Azoxystrobin	all	0.27-1.46	Triadimenol	Bølstad	1.69-6.00
Isoxaben	Årungen	0.31-0.93	Bixafen	all	1.89-11.35
Clomazone	Årungen	0.34-3.68	Protioconazole-desthio	all	3.87-83.5
Tebuconazole	alle	0.46-2.61	Boscalid	Årungen	4.86-32.25
Fluopyram	all	0.49-89.00	Trifloxystrobin acid	all	5.24-78.2
Fluopyram-7-hydroxy	all	0.56-26.49			

Measured concentrations of pesticides on the same samplers

The work has been funded by NIBIO (project FS-pilot 52788)

[1]NIBIO Department of pesticides and natural products chemistry. Contact person: ivo.havranek@nibio.no, Tel: +47 95789734. Pictures: Ivo Havranek and Affinisep