Fast and accurate screening of small polar organics in the water cycle with UHPLC-QTOF-MS

Vittorio Albergamo[a], Rick Helmus[a] and Pim de Voogt [a,b]

[a] *Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, The Netherlands*

[b] *KWR Watercycle Research Institute, The Netherlands*

UNIVERSITEIT VAN AMSTERDAM

Introduction

The ubiquitous occurrence of polar micropollutants (PMs) and their transformation products (TPs) in the aqueous environment and particularly in drinking water sources is cause of ecotoxicological and toxicological concern. PMs can be highly water soluble, highly mobile and can accumulate in the environment when they are not (completely) removed by conventional water treatment. Consequently, there is a demand for flexible and accurate analytical tools. In the present study we have explored the capabilities of a UHPLC-HRMS system to screen for PMs in samples from a Dutch drinking water treatment plant (DWTP) which will start production from riverbank filtrate by applying a standalone reverse osmosis treatment.

Materials & methods

UHPLC-HRMS

UHPLC

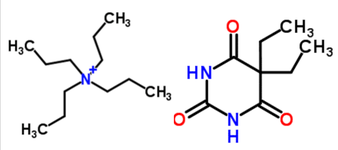
- Shimadzu Nexera UHPLC
- Stationary phase: core-shell biphenyl
- Mobile phases tested H_2O, ACN, MeOH (with modifiers)

HRMS

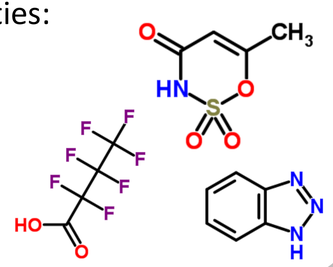
- Bruker maXis 4G Q-TOF HRMS with ESI
- RP 35000 – 80000 FWHM

Chemicals

- **30 analytes** including pharmaceutical, personal care products, biocides, industrial chemicals and TPs selected from scientific literature and covering a broad range of physicochemical properties:



i. **Found in DW sources**
ii. **Found in finished DW**
iii. **Not fully removed by RO**



- 15 isotope-labeled standards

Data processing

- Automated screening and quantitation with TASQ (Bruker Daltonics)

Batch Navigator | Analysis Result | Quantitation | Mass Calibration | Processing View | Batch Summary | Batch Result | TASQ Quick Start | Methods

Row	Analyte	ΔRT [min]	Area	MRSQ	Height	RT [min]	Score	Δm/z [ppm]	mSigma	mSigma Score	m/z Score	RT Score
1	Diglyme	-0.04	137212		27620	4.06	+++	-0.95	4.7	++	++	++
2	4-quinolol	-0.01	593659		117811	4.01	+++	0.03	0.9	++	++	++
3	5-methyl-1H-benzotriazole	0.10	548975		127941	4.90	+++	1.10	9.0	++	++	++
4	TEP	-0.01	814944		187739	5.09	+++	-0.07	4.2	++	++	++
5	Paracetamol-D4	0.01	524555		105044	3.31	+++	0.69	2.8	++	++	++
6	2-quinolol	-0.01	372460		88475	5.02	+++	0.55	6.6	++	++	++
7	Carbamazepine-13C6	0.05	241933		59092	5.75	+++	-0.45	5.7	++	++	++

- Analytes scored by t_R, m/z, isotopic fit and MS/MS data
- Identification with high certainty from full scan HRMS data

Samples

- RBF and RO permeate enriched with 50 ng/L 12C and isotope-labeled spike mix and:

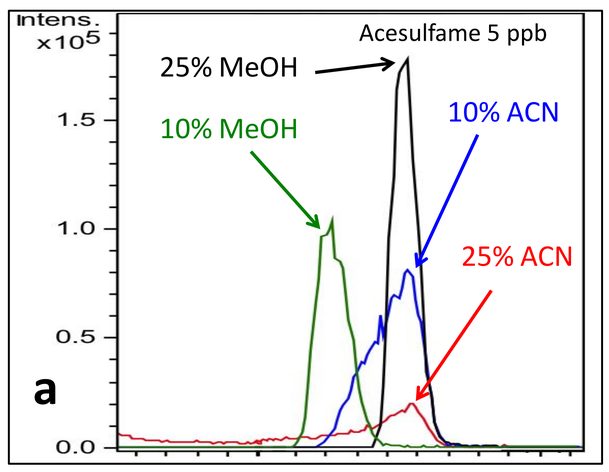
① **Extracted with Oasis HLB** (150 mg)
- Sample V= 100 mL
- Conc. factor: 40x

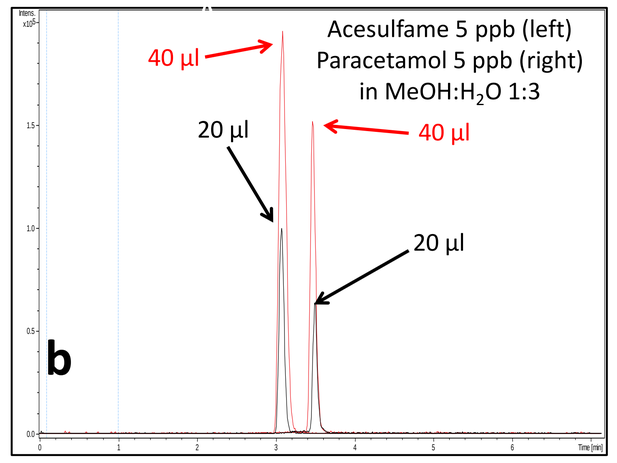
② **Filtered (ø 0.22) µm and directly injected**

Method optimization

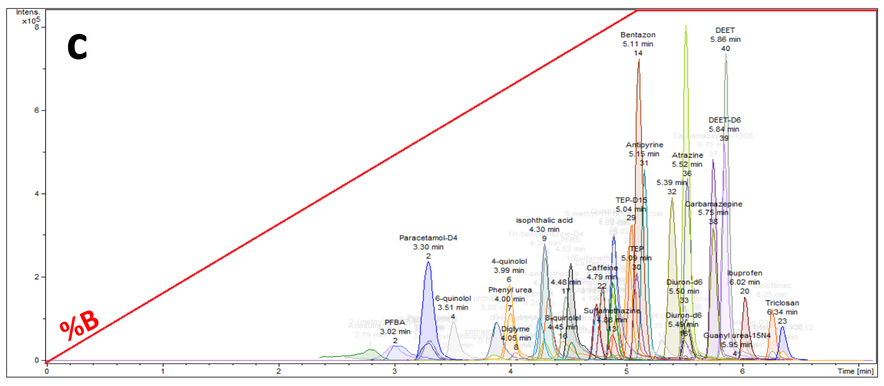
Influence of vial composition and injection volume

- Peaks scored by area/intensity ratio
- Best chromatography with A: H2O (0.05% acetic acid); B: MeOH
- Effect of vial organic composition (a) and injection volume (b)



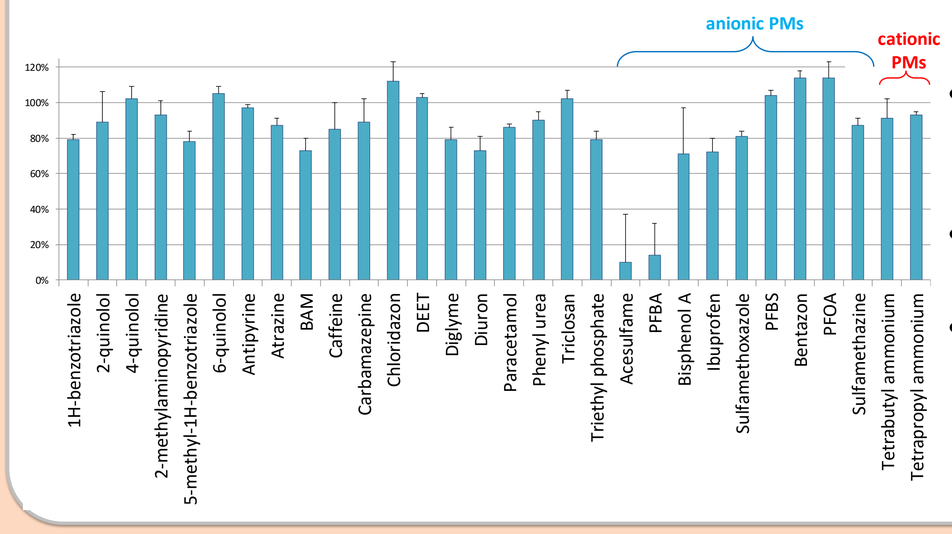


Results & discussion



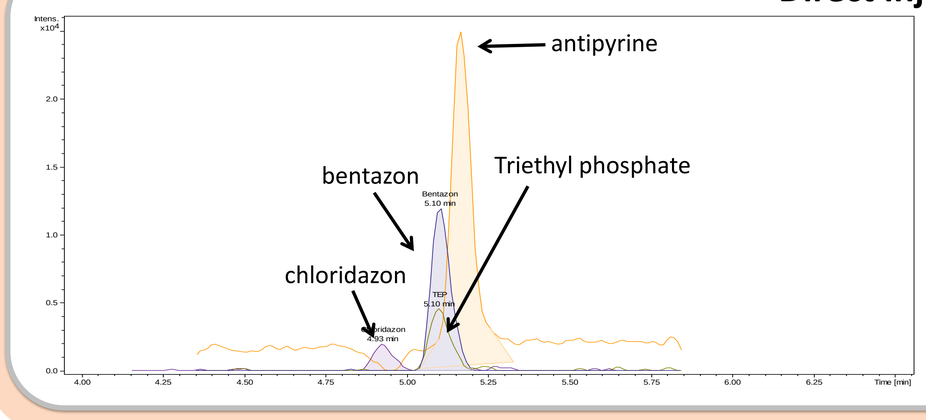
- Optimum peak shape with vial ≤25% MeOH
- Separation and detection of all target analytes with UHPLC-ESI-Q-TOF/MS**.** Fast elution within 7 min. (c).
- Good linear regressions for all PMs (R^2>0.99)

SPE recovery from RO permeate (n=4)



- Satisfactory SPE recoveries for most target analytes from different water matrices.
- LOQs from 0.6 to 8 ng/L
- Acesulfame and PFBA lost during sample preparation possibly due to their high hydrophilicity

Direct injection



- Antipyrine (64 ng/L), bentazon (68 ng/L), chloridazon (<LOQ) and triethyl phosphate (<LOQ) detected in RBF.
- These peaks are absent from RO permeate
- Most LOQs from 32 to 250 ng/L

Conclusions

- SPE-UHPLC-HRMS can lead to quantification of PMs down to sub-ng/L range, particularly relevant for DW samples.
- Direct injection analysis offers environmentally relevant LOQs and saves sample prep time
- Automated screening with TASQ leads to PMs identification based on HRMS data with high degree of certainty and proved to be an excellent tool for the processing of large batches
- Our approach can contribute to the characterization of toxic and ecotoxic profiles in the water cycle

Contact
Vittorio Albergamo
Institute for Biodiversity and Ecosystem Dynamics
Science Park 904, 1098 XH Amsterdam, the Netherlands

email: v.albergamo@uva.nl
phone: +31 20 525 6578

This study is financially supported by OASEN, Gouda, The Netherlands