Screening persistent polar contaminants in present drinking water sources and future drinking water with UHPLC-QTOF: focus on reverse osmosis applied to riverbank filtrate

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Background

The ubiquitous occurrence of polar micropollutants (PMs) and their transformation products (TPs) in the aqueous environment has increased the demand to accurately screen for polar organics, particularly in drinking water sources. We study the occurrence of PMs in a riverbank filtrate (RBF) from the Dutch Rhine basin area and their removal by reverse osmosis (RO) for potable use by screening with HRMS. Our semi-automated identification strategy is successfully applied to samples from a Dutch drinking water treatment plant which will start production from RBF by applying a standalone RO treatment.

Analytical tools: UHPLC-ESI-Q-TOF/MS

- Shimadzu Nexera UHPLC
- Stationary phase: core-shell biphenyl
- Mobile phase:
  A (H2O 0.05% AA); B (MeOH)

- Bruker maXis 4G Q-TOF
- HD collision cell upgrade
- RP 35000 – 80000 FWHM
- Auto mass calibration
- ESI (+/- mode)

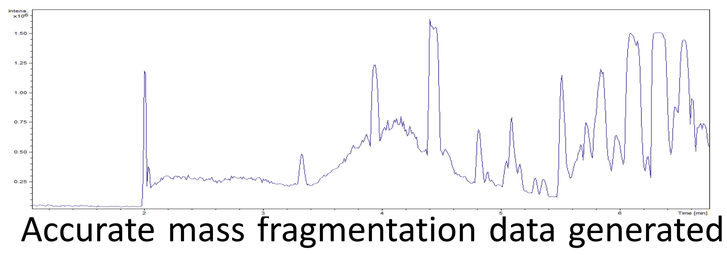
RBF and RO permeate samples

- 100 mL enriched with 50 ng/L isotope-labeled standards → SPE (40x conc.)

- 1 mL enriched with 2 µg/L isotope-labeled standards, filtered and analysed by direct injection

Identification strategy

① Acquisition of HRMS data



Accurate mass fragmentation data generated in bbCID MS/MS in full scan mode

② Preliminary list screening with TASQ (Bruker)

Row	Analyte	Area	MRSQ	Height	RT [min]	Score	Δm/z [ppm]	mSigma	mSigma Score
1	2-Aminobenzimidazole	695571		192835	4.90	+	1.38	13.8	+
2	2,6-dichloro-1,4-benzenediamine	3124289		774327	5.07	---	1.58	27.4	---
3	Tramadol met 1 -234	99349		18099	5.99	---	-1.34	170.1	---
4	(4-chlorophenyl)hydrazine	1612390		379141	3.67	---	1.66	26.4	---
5	O-Desmethyl Tramadol	60894		14309	5.71	+	-6.91	12.5	+
6	Tramadol met 3 - 249	60894		14309	5.71	+	-6.91	12.5	+
7	N,N-Didesvenlafaxine	60894		14309	5.71	+	-6.91	12.5	+
8	Venlafaxine met 3 -249	60894		14309	5.71	+	-6.91	12.5	+

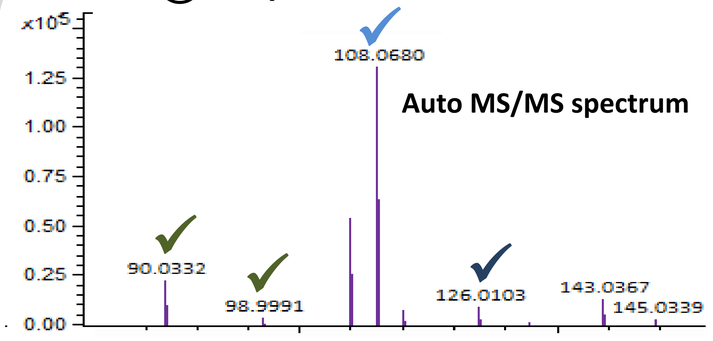
Suspects scored by t_R, m/z, isotopic fit and MS/MS data (when available).

③ Final candidate list

From preliminary screening:

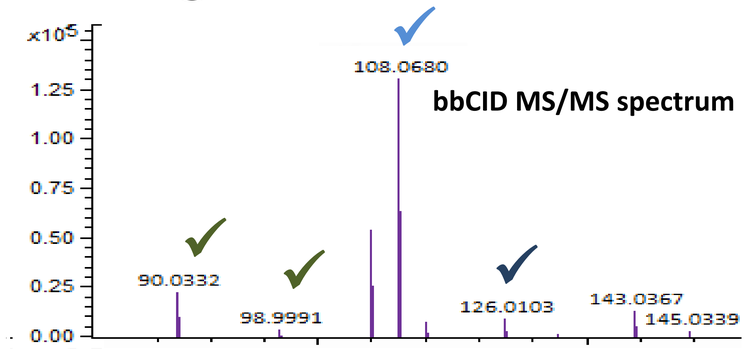
- ✓ m/z absent from procedural blank
- ✓ Typical adducts are present
- ✓ Δm/z < 5 ppm M and adducts
- ✓ mSigma < 100
- ✓ Consistent t_R
- ✓ MS/MS data (if available)

④ MS/MS elucidation



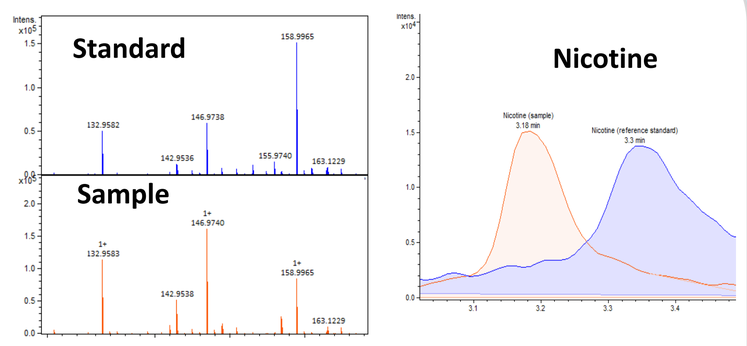
A subset of samples is re-analysed in auto MS/MS to collect fragmentation data

⑤ Tentative identification



Auto MS/MS fragments used as qualifiers in a retrospective screening of the bbCID data

⑥ Confirmation with reference standard

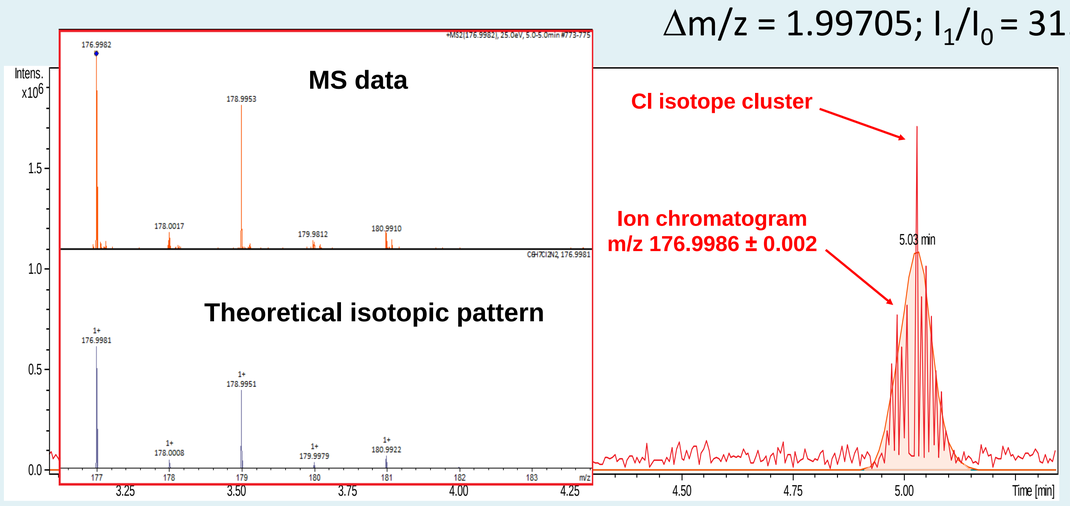


When possible, unequivocal identity is confirmed with reference standards

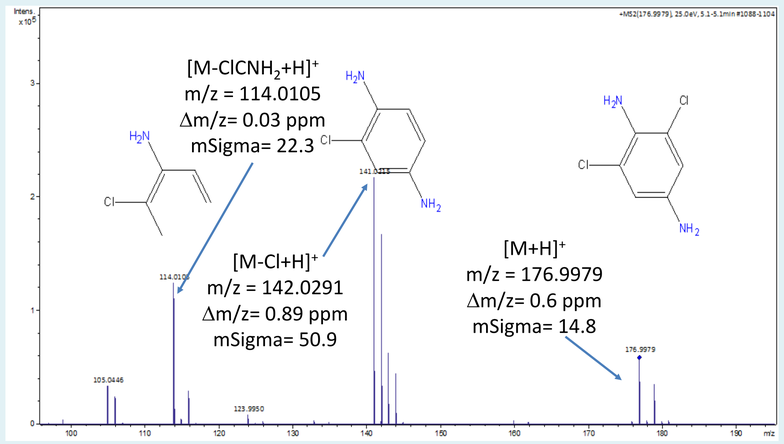
Additional tools: isotope cluster analysis

- Chromatograms of specified Δm/z and intensity ratios between peak pairs can highlight the presence of characteristic isotopic patterns. When screening for chlorinated compounds:

  $\Delta m/z = 1.99705$; $I_1/I_0 = 31.996\%$



- Unequivocal formula with SmartFormula 3D
- Fragments elucidation by analysis of a subset of samples in auto MS/MS full scan mode
- Tentative identification by retrospective analysis of bbCID data and with *in silico* fragmentation (MetFrag and Metfusion)



- MS2 spectrum and proposed fragmentation pattern of 2,6-dichloro-1,4-benzenediamine ($C_6H_6Cl_2N_2$)
- Peak found in RBF and RO permeate

Conclusion

- Q-TOF HRMS/MS is a powerful analytical tool to screen for PMs and TPs which can impair drinking water quality and threaten aquatic biota
- Analysis of HRMS data for the qualitative assessment of chemical removal by RO: m/z>200 observed in RBF are not present in RO permeate samples
- Automated screening with TASQ allows the efficient processing of large batches and building personal analyte database from HRMS data

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