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Filling the knowledge gap: Suspect Screening for over 1400 PM(T)-substances in German surface waters

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Introduction

Persistent, mobile chemicals (PM-substances) are particularly difficult to remove in partially closed water cycles and thus can reach drinking water (Fig.1) [1]. This is of special concern for PM-substances that are also toxic (PMT-substances). However, for screening routinely applied reversed phase liquid chromatography coupled to high resolution mass spectrometry (HRMS) does not fully cover this class of substances («analytical gap»). Hence, only very limited knowledge is available on the extend to which PM-substances occur in the water cycle. In the present study hydrophilic interaction liquid chromatography (HILIC) [2] and supercritical fluid chromatography (SFC) [3] were applied to extent the analytical window to highly polar substances. An extensive suspect screening for over 1400 potential PM(T)-substances (REACH chemicals, pharmaceuticals, plant protection chemicals, sweeteners) was carried out. The list of PM(T)-suspects was compiled from previous prioritization and identification studies [4, 5].

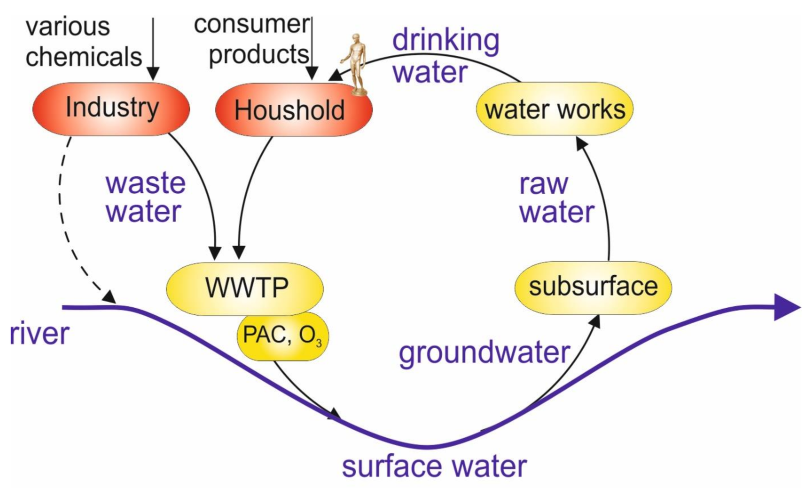


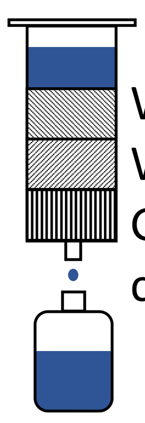
Fig.1 Distribution of PM(T)-substances in the water cycle

Experimental

12 German surface water samples (Rhein/Main and Mulde/Saale)

↓ concentration

(I) mlSPE [6]



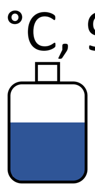
Weak Anion eXchange
Weak Cation eXchange
Graphitised black carbon

ACN/H_2O (95/5)

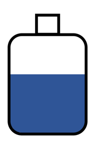
200fold enrichmet

(II) Evaporation (EVAP) [6]

45 °C, 9mbar


Surface water

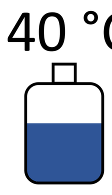
↓ Reconstitution


ACN/H_2O 95/5

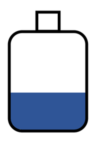
20fold enrichment

(III) Azeotropic EVAP

40 °C, nitrogen

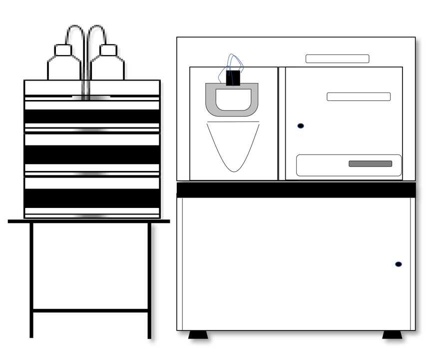

ACN + Surface water

↓ Reconstitution


ACN/H_2O 95/5

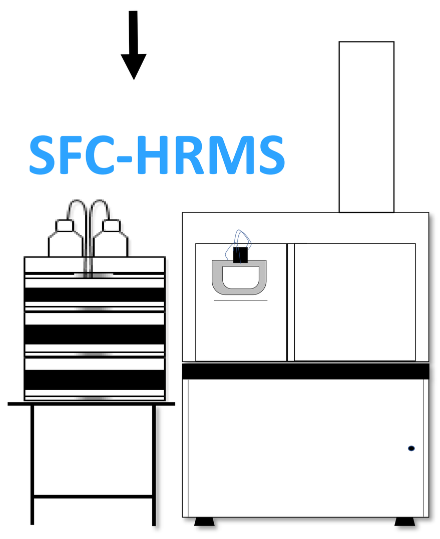
20fold enrichment

HILIC-HRMS



Eluent A: 5mM NH_4HCOO in ACN/H_2O (95/5)
Eluent B: 5mM NH_4HCOO in ACN/H_2O (5/95)
MS: Orbitrap Velos Pro (Thermo)

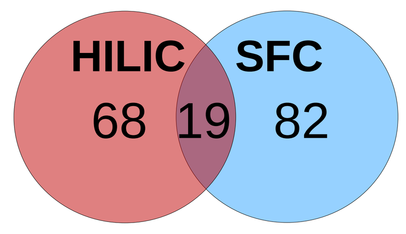
SFC-HRMS



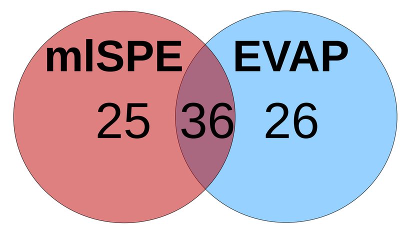
Eluent A: CO2
Eluent B: 95% MeOH, 5% H_2O, 10 mM NH_4HCOO
MS: TOF (Synapt G2-S, Waters)

Results

- Extensive suspect screening for 1444 PM(T)-substances
- 169 tentatively identified compounds:

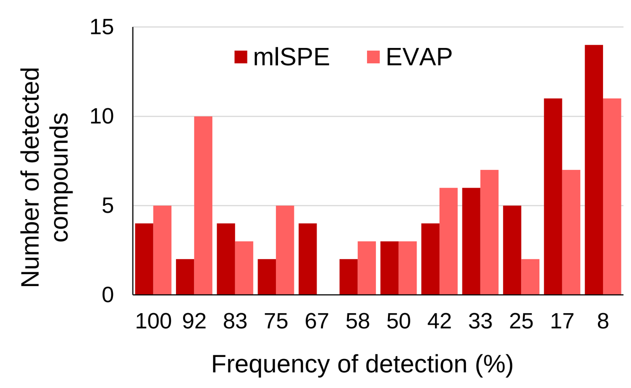


- Strong influence of sample preparation to HILIC-HRMS:

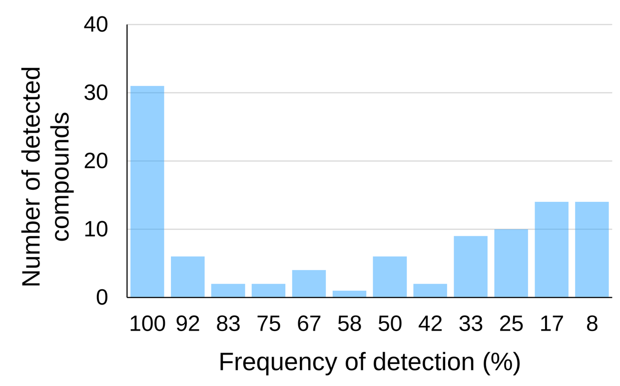


- 68 compounds tentatively identified using HILIC- and 82 using SFC-HRMS underlining the complementarity of both methods
- Frequency of detection (FOD) indicates on the presence of site-specific and ubiquitous chemicals:

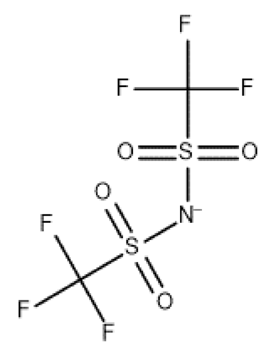
HILIC-HRMS



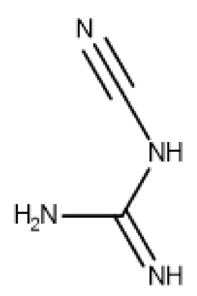
SFC-HRMS



- Examples of identified compounds:

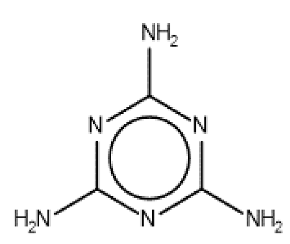


- Bis(trifluor-methansulfonyl)amid
- Ionic Liquid; alternative solvent for extraction of aromatic compounds (« green chemistry»)
- FOD: 83%
- (Eco)toxicological hazard potential demonstrated by test battery [7]

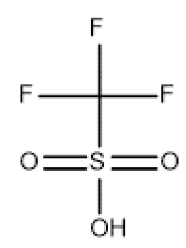


- Cyanoguanidine
- Industrial use as processing aid, manufacture of textiles, etc.
- FOD: 100%

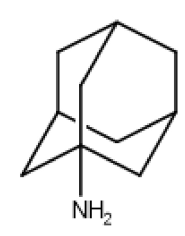
Melamine



Trifluormethansulfonic acid



Adamantan-1-amine



Conclusions

In respect to PM(T)-substances HILIC and SFC significantly contribute to:

- Improved detection in environmental samples
- Learn more about their occurence in the aquatic environment
- Prioritize PM(T)-substances for future activities aiming at (a) the reduction of their discharge or at (b) the development of novel methods for their removal from the water cycle

[1] Reemtsma et al. (2016) ES&T. 50, 10308.
[2] Zahn et al. (2019) Water Research 150, 86.
[3] Schulze et al. (2019) Water Research 153, 80.
[4] Schulze et al.; STOTEN 2018, 625, 1122.
[5] Zahn et al. (2016) Water Research 101, 292
[6] Köke et al. (2018) ABC 410(9), 2403.
[7] Matzke et al. (2007) Green Chemistry, 9(11), 1198.

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