Screening for Emerging Persistent and Mobile Organic Water Contaminants by LC and SFC Coupled to MS

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Introduction

The release of **persistent** and **mobile** organic chemicals (PMOCs) into the aquatic environment is a risk to the quality of water resources. As a consequence of their aquatic mobility, PMOCs can pass through wastewater treatment plants, natural barriers and drinking water purification processes and are thus of concern for human health (Fig. 1).

The aim of this study was to screen for potential PMOCs of concern in European water samples.

Fig. 1

Summary & Next Steps

- Extraction and determination of **novel** and **known industrial PMOCs** in surface water, groundwater, bank filtrate, reversed osmosis permeate and concentrate
- Detection of **41 PMOCs** in environmental water samples with the selected methods
- Estimated concentrations of detected PMOCs in ng/L - µg/L range
- **Currently ongoing:**
  - Validation of methods for quantification of PMOCs
  - Quantify PMOCs in raw water and in drinking water treatment
- **Visions of the future:**
  - Investigation of sources of environmentally relevant PMOCs
  - Toxicology data for quantified PMOCs
  - Recommend problematic PMOCs for regulatory actions

Approach

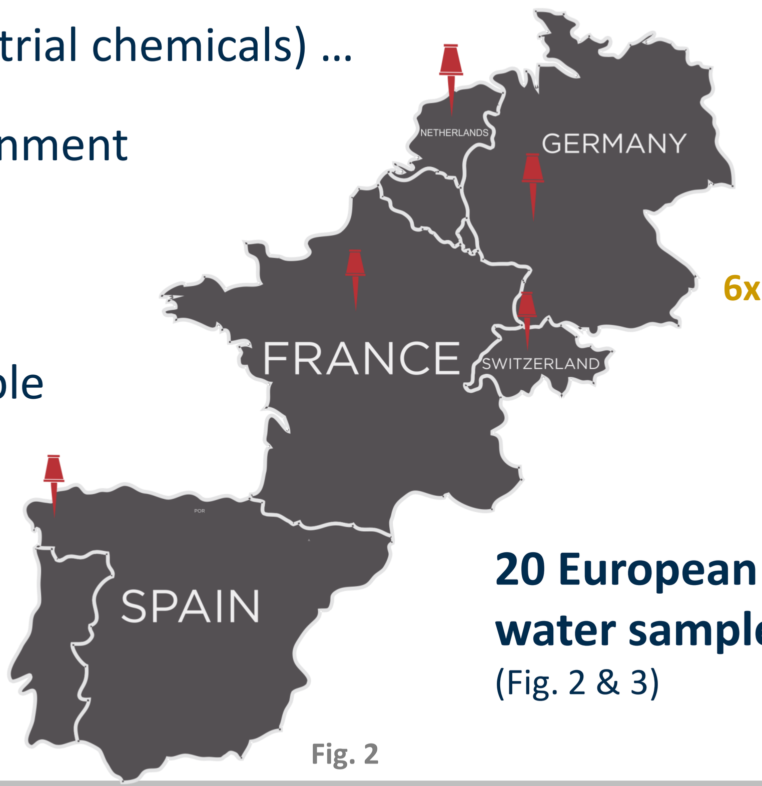
1. Selection of the compounds

REACH registered organic chemicals (industrial chemicals) ...

- with a potential **emission** into the environment
- that are **persistent** and **mobile** in the aquatic environment
- for which analytical **standards** are available
- that are amenable to analysis by chromatography/mass spectrometry

→ **60 PMOCs** were selected according to the above-mentioned criteria

2. Sampling



20 European water samples (Fig. 2 & 3)

Fig. 2

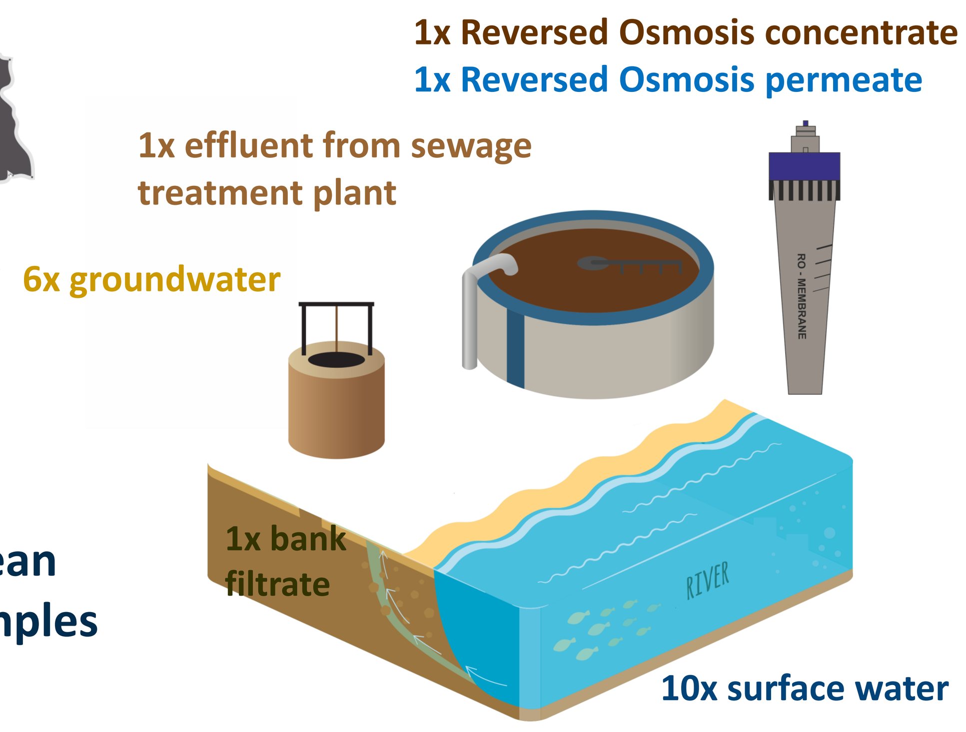


Fig. 3

3. Extraction

Solid phase extraction (Fig. 4)

- Graphitzed carbon black
- Weak anion exchanger
- Moderate cation exchanger
- Hydroxylated polystyrene-divinylbenzene

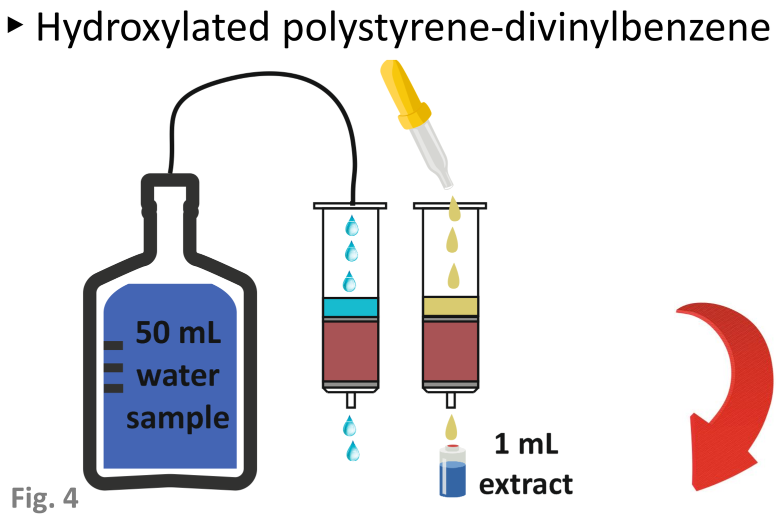


Fig. 4

4. Chromatographic & Detection Methods

a) Liquid Chromatography – MS/MS

Columns:
- Waters **HSST3**, 2.1x50 mm, 1.8 µm
- Thermo **Hypercarb**, 2.1x100 mm, 3 µm

Gradient:
- H_2O / MeOH with NH_4HCOO
- H_2O / ACN with diethylamine

ESI - MS/MS:
- MRM mode

b) Supercritical Fluid Chromatography – HRMS

Columns:
- Waters UPC² **BEH**, 3x100 mm, 1.7 µm
- Waters UPC² **Torus Diol**, 3x100 mm, 1.7 µm

Gradient (both columns):
- CO_2 / MeOH / H_2O with NH_4OH

Make Up Flow:
- MeOH / H_2O with HCOOH

ESI - q-TOF-MS:
- Exact mass (mass window: 5 ppm)

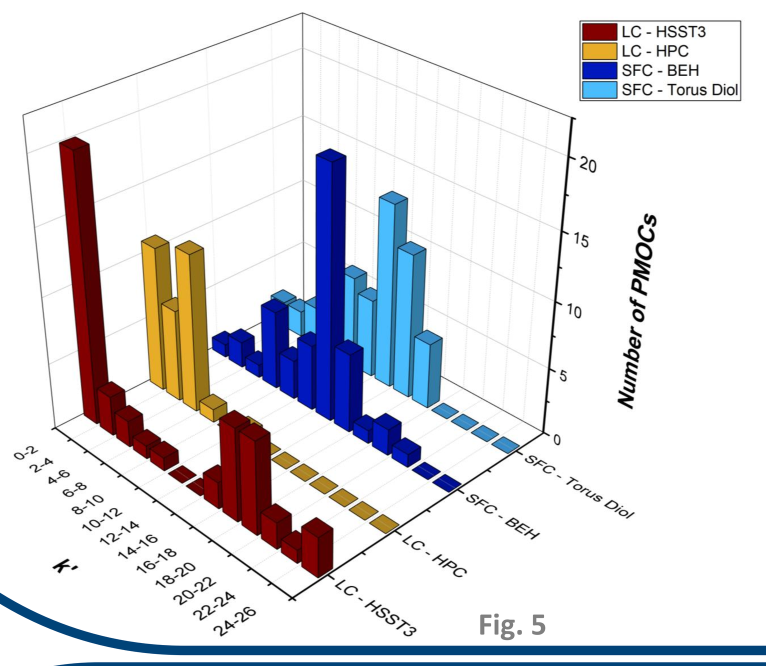


Fig. 5

The performance of the chromatographic methods was tested to choose the best method for the analysed PMOCs

- With **LC** (**HSST3** and **Hypercarb)** more PMOCs elute in the **void volume** / have smaller retention factors (k') in comparison to SFC (**BEH** and **Torus Diol**) (Fig. 5)
- Bravais-Pearson correlation coefficients k' of all the methods show linear correlation to logD (LC: positive, SFC: negative) (Fig. 6)
- SFC is better suited than LC for the analysis of polar and mobile chemicals.

Retention factor k' for a substance i:

$$k' = \frac{t_{R,i} - t_0}{t_0}$$

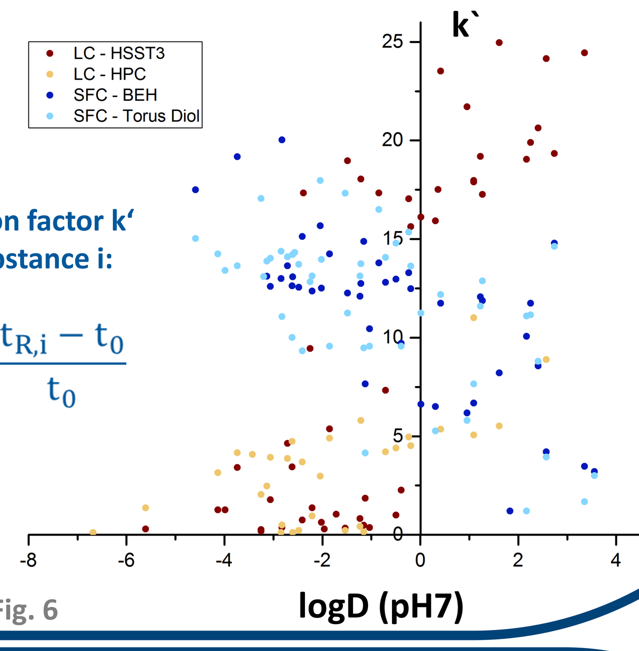


Fig. 6

Screening Results

Tab. 1

PMOC No.	CAS	PMOC No.	CAS
1	51410-72-1	22	81-07-2
2	7365-45-9	23	105-60-2
3	1704-62-7	24	121-57-3 / 121-47-1
4	622-40-2	25	80-09-1
5	6331-96-0	26	85-47-2
6	80-08-0	27	56-93-9
7	104-23-4	28	542-02-9
8	19715-19-6	29	13674-84-5
9	140-31-8	30	461-58-5
10	101-72-4	31	834-12-8
11	5205-93-6	32	768-94-5
12	52722-86-8	33	102-06-7
13	3965-55-7	34	5165-97-9
14	342573-75-5	35	70-55-3 / 88-19-7
15	512-42-5	36	25321-41-9 / 1300-72-7
16	81-04-9	37	1493-13-6
17	108-80-5	38	104-15-4
18	7529-22-8	39	55589-62-3
19	23386-52-9	40	97-39-2
20	1561-92-8	41	108-78-1
21	101-77-9		

- With **LC – MS/MS** / **SFC – qTOF** methods detection of **41** PMOCs in the extracted water samples (Tab. 1)

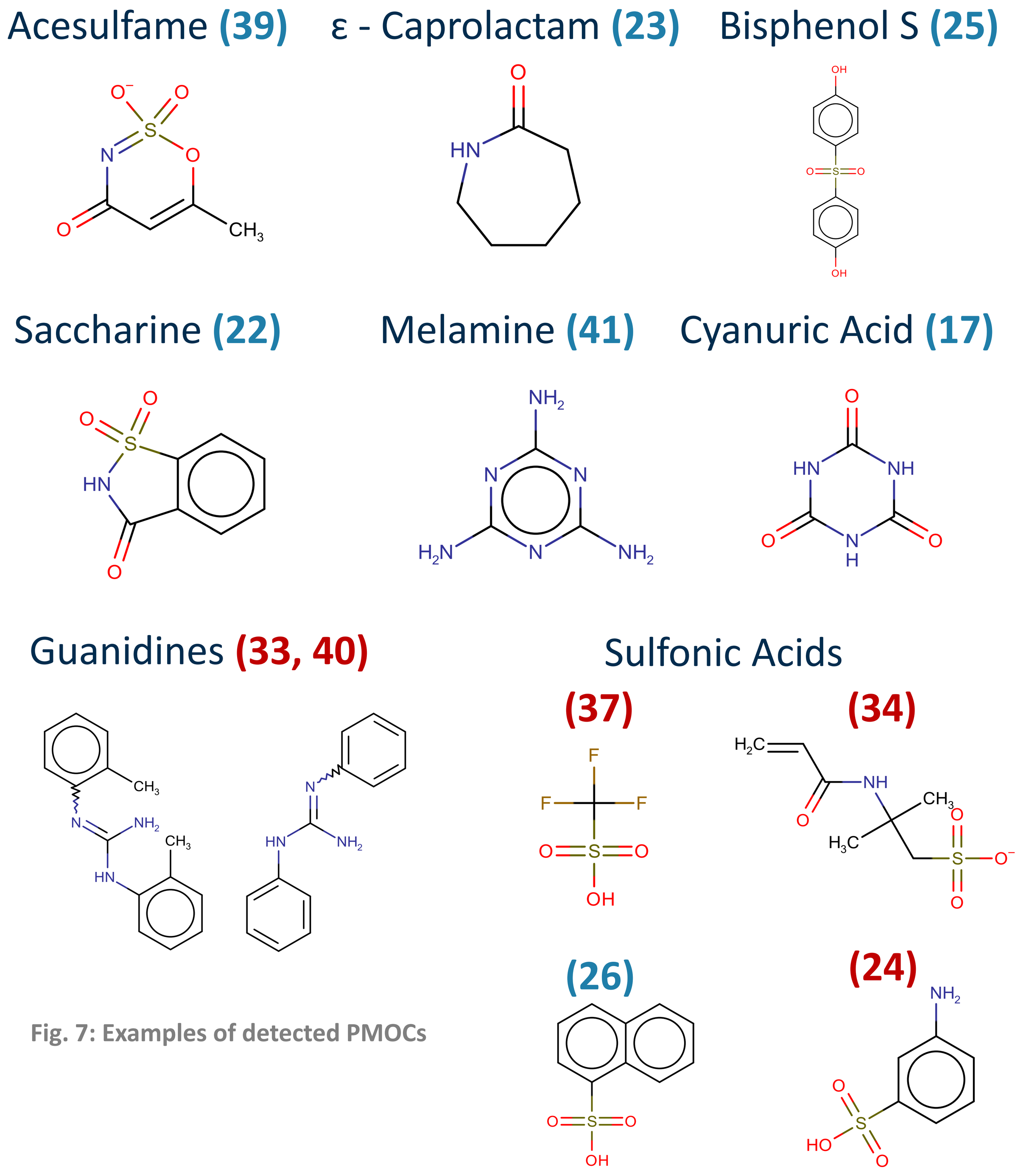


Fig. 7: Examples of detected PMOCs

- Some PMOCs were frequently detected in water samples and other ones were rarely detected (Fig. 8).
- Detection of **known** water contaminants as well as **novel PMOCs** (Fig. 7 + 8)

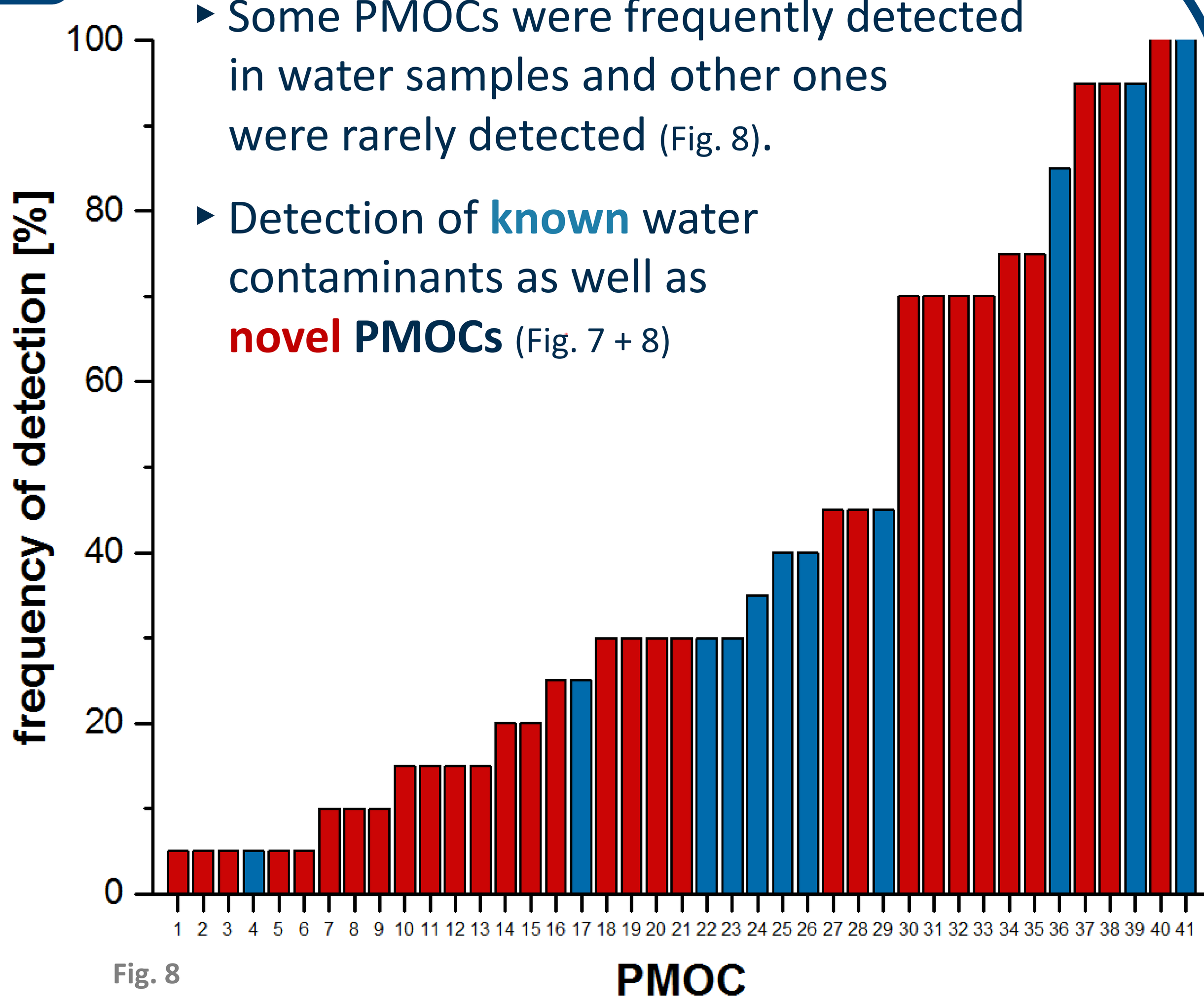


Fig. 8

References:

Reemtsma, T., et al., Mind the Gap: Persistent and Mobile Organic Compounds – Water Contaminants That Slip Through, *Environ. Sci. Technol.*, 2016, 50: 10308-10315

Zahn, D., et al., Halogenated methanesulfonic acids: A new class of organic micro-pollutants in the water cycle, Water Research, 2016, 101: 292-299

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