Persistent and mobile organic chemicals – An emerging group of ubiquitous water pollutants

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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

- A total of **45 novel** and **known industrial PMOCs** detected in surface water, groundwater, bank filtrate, reversed osmosis permeate and concentrate
- 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
  - Potentially problematic PMOCs recommend for regulatory actions

Approach

1. Selection of 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

→ **70 PMOCs** were selected according to the above-mentioned criteria

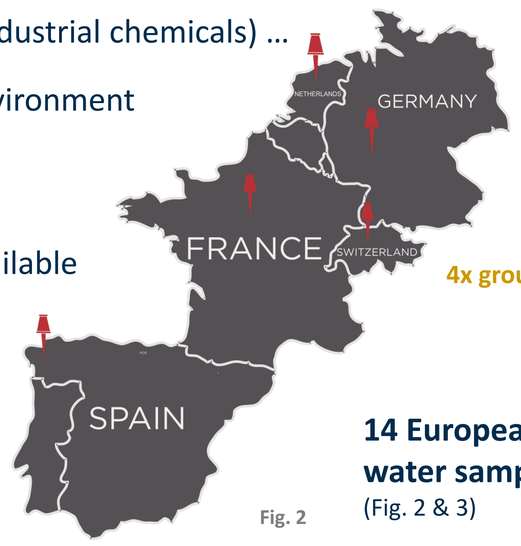


Fig. 2

2. Sampling

14 European water samples (Fig. 2 & 3)

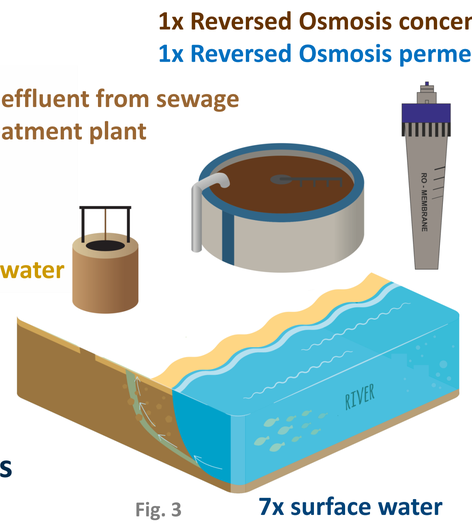


Fig. 3

3. Extraction

Solid phase extraction

- 1) Graphitzed carbon black
- 2) Weak anion exchanger
- 3) Weak cation exchanger
- 4) Moderate cation exchanger
- 5) Hydroxylated polystyrene-divinylbenzene
- 6) Multilayer solid phase extraction (Zahn et al.)

Evaporation

- 7) 9 mbar; 45° C

Enrichment factor 1:20 – 1:500

4. Chromatographic & Detection Methods

a) Reversed Phase Liquid Chromatography – MS/MS (after extraction 1, 2, 4, 5)

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 (after extraction 1, 2, 4, 5)

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)

c) Hydrophilic Interaction Liquid Chromatography – MS/MS (after extraction 6, 7)

Column:
- ACQUITY BEH Amide, 2.1x100 mm, 1.7 µm

Gradient:
- ACN / H_2O with NH_4HCOO at pH 3

ESI - QqQ:
- sMRM mode

d) Mixed Mode Liquid Chromatography – MS/MS (after extraction 2, 3, 7)

Columns:
- Acclaim Trinity P1, 2.1x50 mm, 3 µm

Gradient:
- ACN / H_2O with NH_4CH_3COO at pH 4.5

ESI - QqQ:
- MRM mode

Screening Results

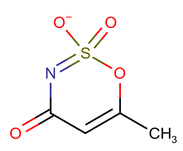
Tab. 1

PMOC No.*	CAS	PMOC No.*	CAS
1 [c]	497-18-7	24 [b, c]	461-58-5
2 [a]	7365-45-9	25 [a, c]	108-80-5
3 [a]	3965-55-7	26 [a, b, c]	52722-86-8
4 [a, b, c]	6331-96-0	27 [a, c]	140-31-8
5 [a, c, d]	51410-72-1	28 [a, b, c]	1561-92-8
6 [c, d]	52556-42-0	29 [a, b, c]	121-57-3 / 121-47-1
7 [a]	104-23-4	30 [c]	622-40-2
8 [b]	101-77-9	31 [c, d]	280-57-9
9 [b]	342573-75-5	32 [a, b, c, d]	13674-84-5
10 [c]	1704-62-7	33 [a, c, d]	105-60-2
11 [a]	81-04-9	34 [a, b]	70-55-3 / 88-19-7
12 [a, b, c, d]	5205-93-6	35 [a, b, c]	834-12-8
13 [c]	2855-13-2	36 [a, b, c, d]	768-94-5
14 [c]	288-88-0	37 [a, b, c, d]	1493-13-6
15 [a, b, c, d]	81-07-2	38 [a, b, c, d]	25321-41-9 / 1300-72-7
16 [a, b, d]	80-09-1	39 [c]	19715-19-6
17 [a]	23386-52-9	40 [a, b, c, d]	55589-62-3
18 [c, d]	103-83-3	41 [a, b, d]	97-39-2
19 [a, b, c]	542-02-9	42 [a, b, c, d]	5165-97-9
20 [a, b, d]	56-93-9	43 [a, b, c]	104-15-4
21 [a, b, d]	85-47-2	44 [a, b, c, d]	102-06-7
22 [c]	3039-83-6	45 [a, b, c, d]	108-78-1
23 [a, c, d]	512-42-5		

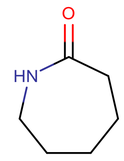
* Letters a-d indicate the methods for detection of the PMOC

- A total of **45** PMOCs were detected in the analyzed water samples with the chosen methods (Tab. 1)

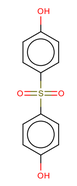
Acesulfame **(40)**



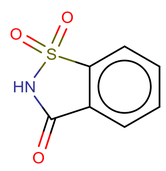
ε - Caprolactam **(33)**



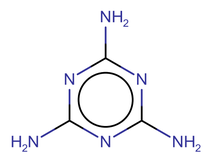
Bisphenol S **(16)**



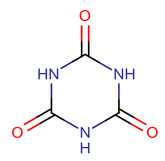
Saccharine **(15)**



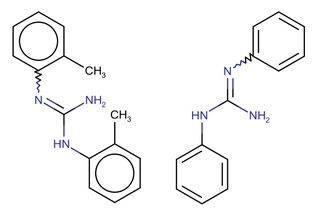
Melamine **(45)**



Cyanuric Acid **(25)**

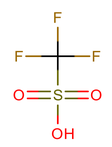


Guanidines **(41, 44)**

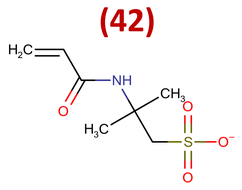


Sulfonic Acids

(37)



(42)



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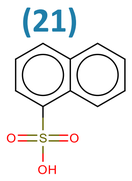

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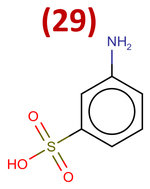

Fig. 4: Examples of detected PMOCs

- Some PMOCs were frequently detected in water samples and others rarely (Fig. 5)
- Detection of **known** water contaminants as well as **novel** PMOCs (Fig. 4 + 5)

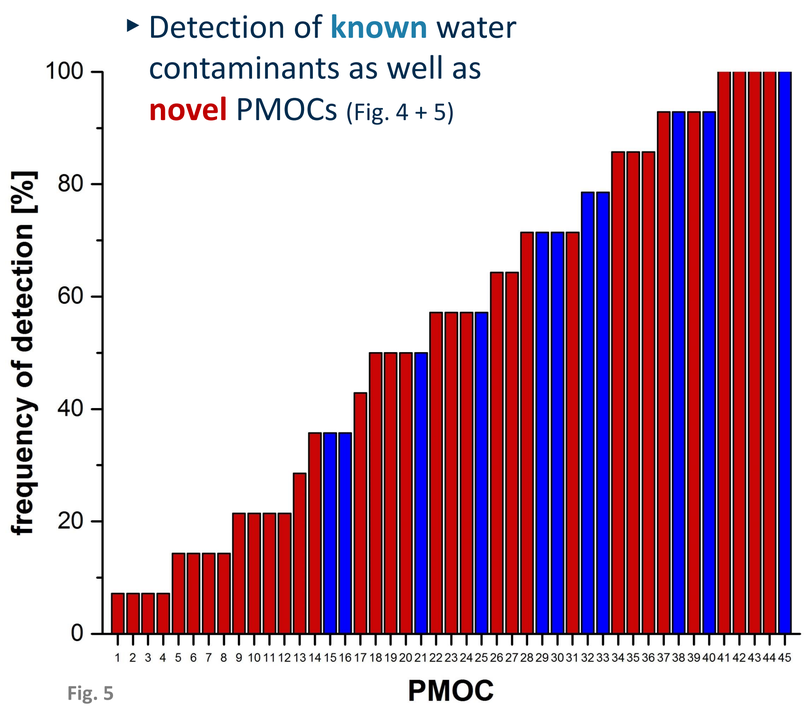

Fig. 5

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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