Persistent, mobile and largely unknown.

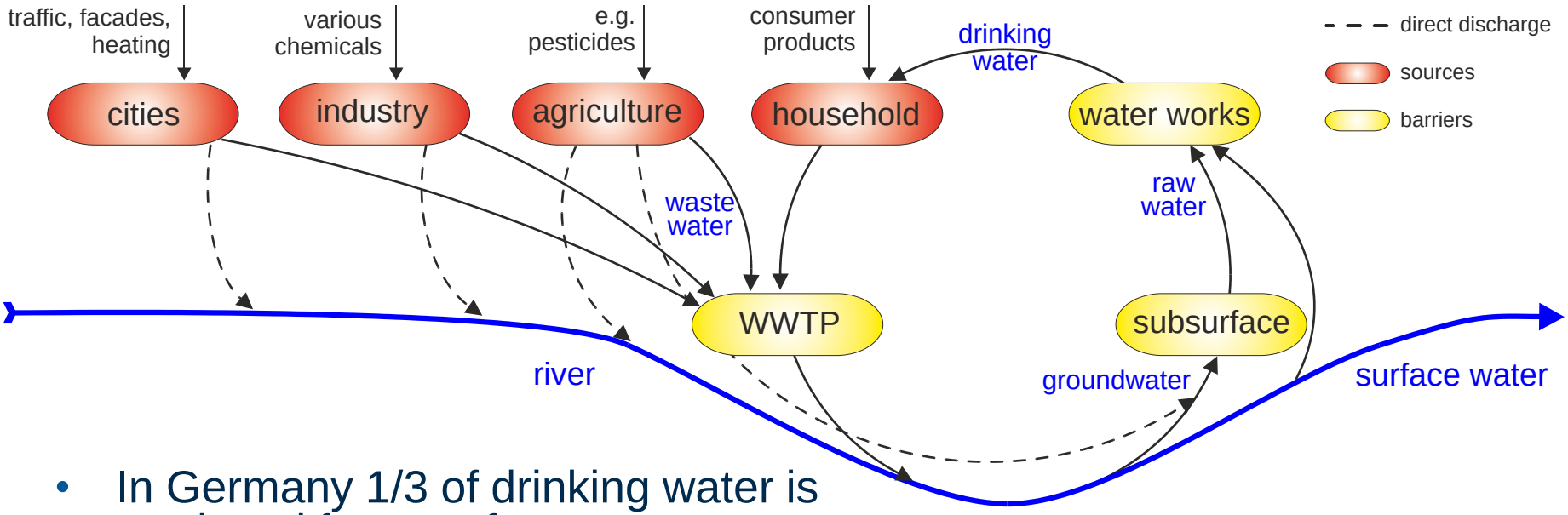
The potential threat to our drinking water resources by persistent, mobile organic contaminants (PMOC)

Stefanie Schulze, Urs Berger, Daniel Zahn, Thomas P. Knepper, Rosa Montes, José Benito Quintana, Thorsten Reemtsma

HELMHOLTZ CENTRE FOR ENVIRONMENTAL RESEARCH – UFZ

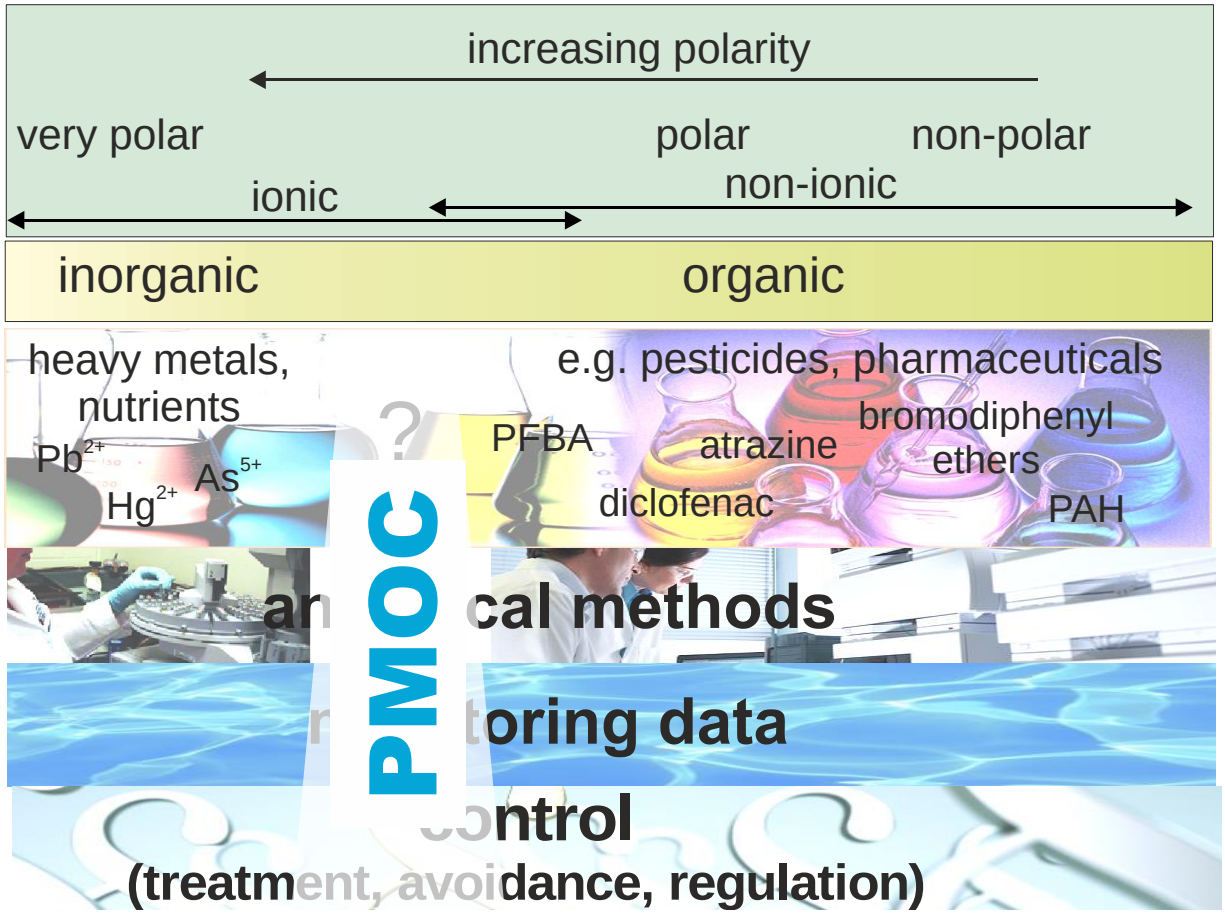
Berlin, 04.05.2017

Partially Closed Water Cycle and PMOC



- In Germany 1/3 of drinking water is produced from surface waters
- Barriers rely on microbial degradation and sorption processes
- For persistent and very polar (mobile) organic compounds (PMOC) these barriers are not effective
  - water cycle may turn into a compound cycle
  - only dilution reduces concentration

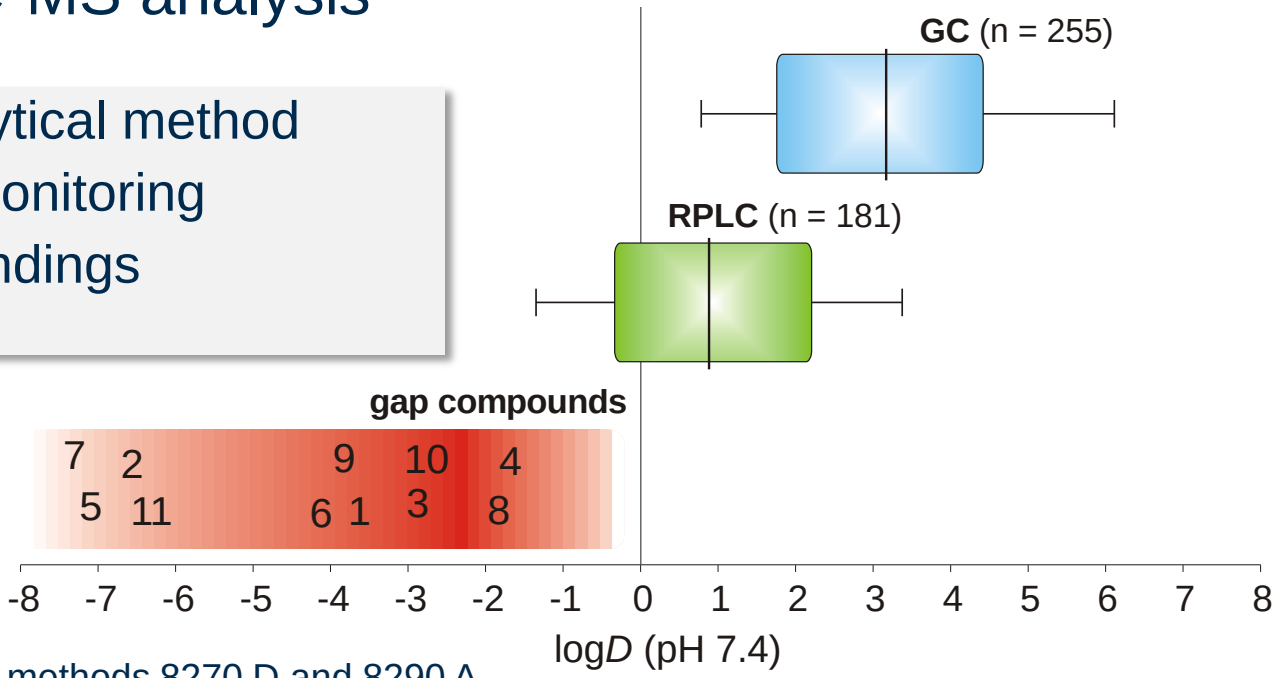
The Analytical Gap



The Analytical Gap

- Polarity (log*Dow*) of analytes covered by GC- or RPLC-MS analysis

no analytical method
→ no monitoring
→ no findings



GC-MS: EPA methods 8270 D and 8290 A

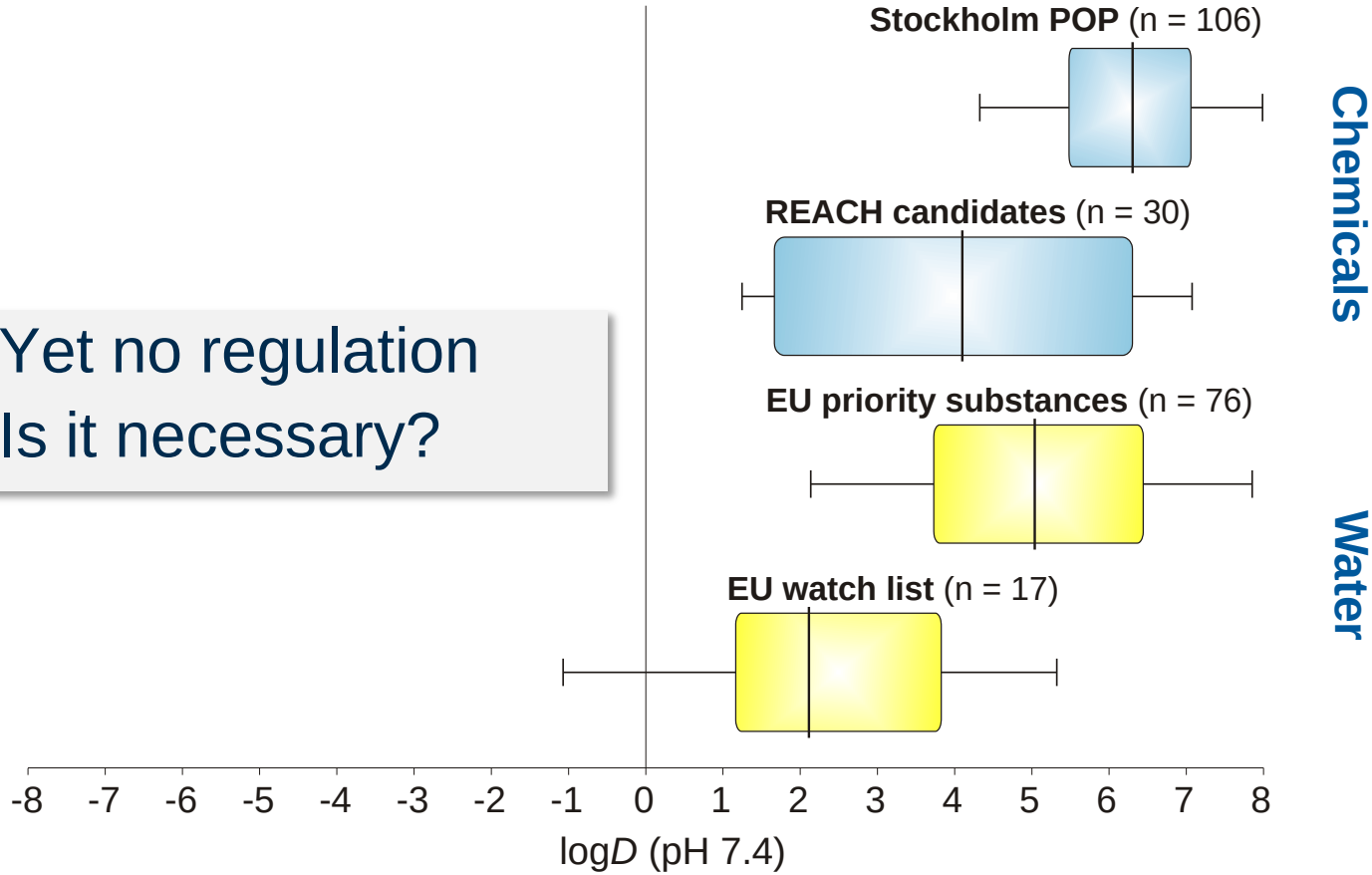
LC-MS: Schymanski et al. (2014) Environ. Sci. Technol. 48, 1811-1818.

1: Aminomethylphosphonic acid (AMPA), 2: Paraquat, 3: Cyanuric acid, 4: DMS, 5: Diquat, 6: 5-Fluorouracil, 7: Glyphosate, 8: Melamine, 9: Metformin, 10: Perfluoroacetic acid, 11: EDTA

Reemtsma et al. (2016) Environ. Sci Technol. 50, 10308

A Regulatory Gap?

- Yet no regulation
- Is it necessary?

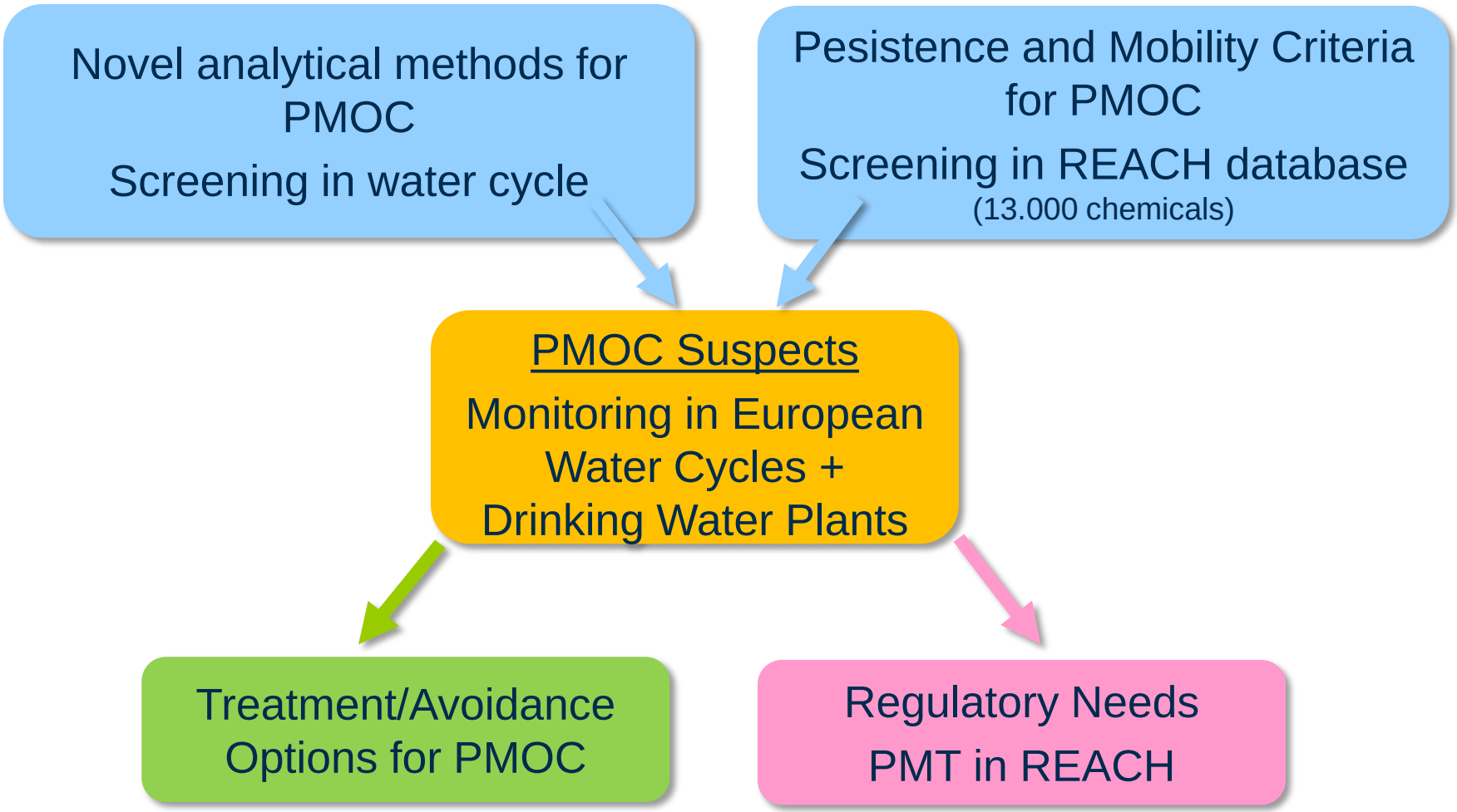


REACH candidates of SVHC, REACH, Article 57, d – f;
Priority substances according to Water Framework Directive (WFD);
Watch list of the WFD

Reemtsma et al. (2016) Environ. Sci. Technol. 50, 10308

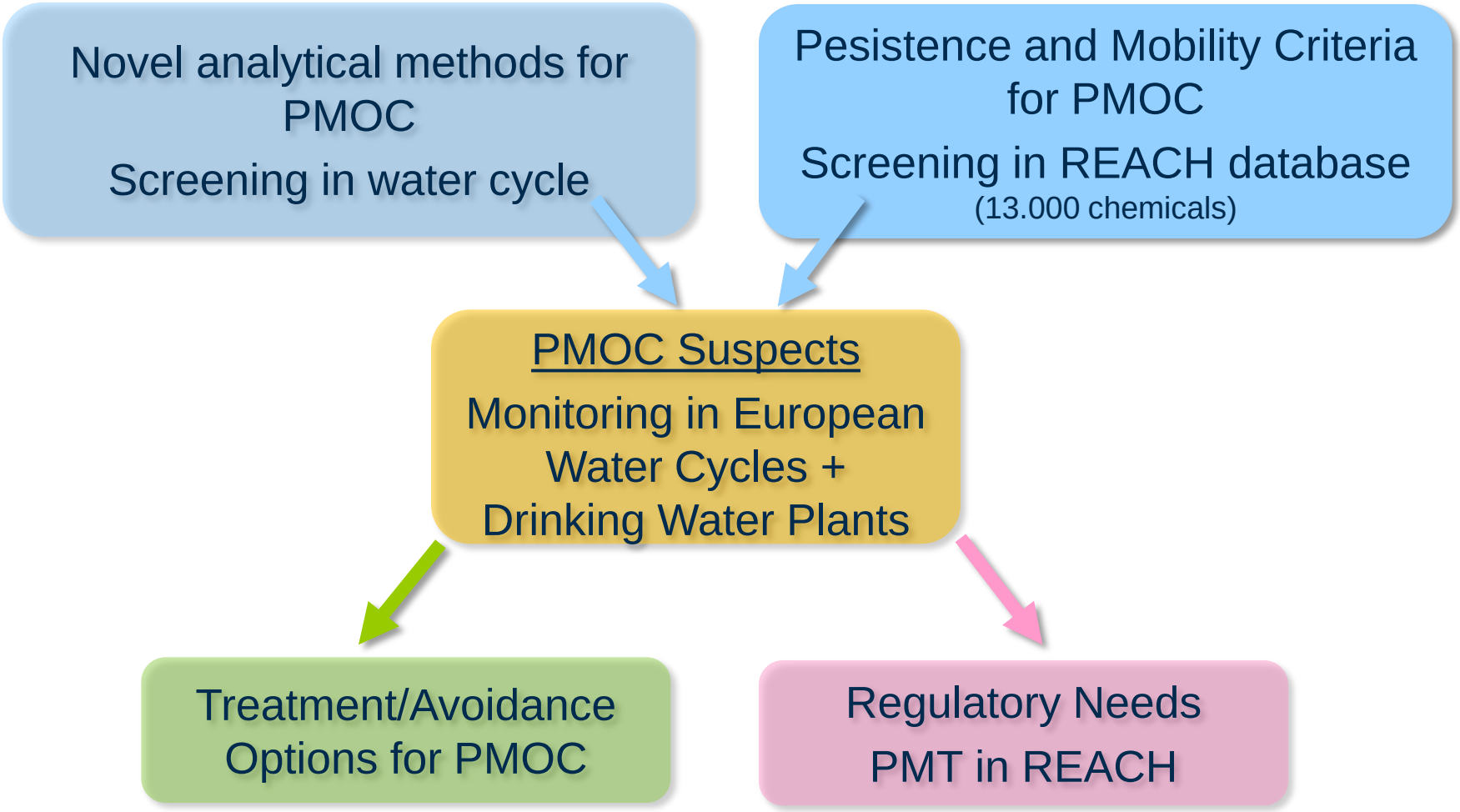
PROMOTE

Protecting water resources from mobile trace chemicals



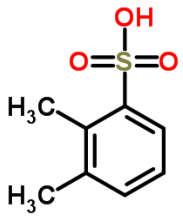
PROMOTE

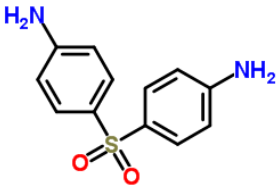
Protecting water resources from mobile trace chemicals



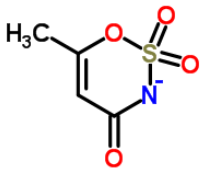
PMOC from REACH Chemicals

- Hazard: PMOC from REACH chemicals
  - Water solubility, Koc
  - Environmental half life
    - Arp et al. 2017
- Risk: Emission into the environment
  - Tonnage
  - use characteristics
    - Schulze et al., 2017

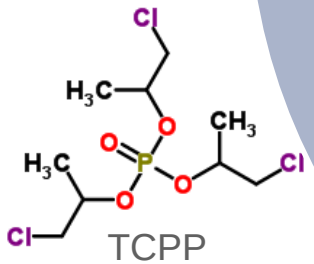




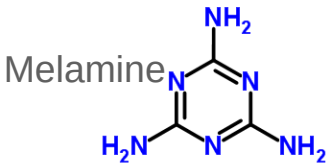
Dapson



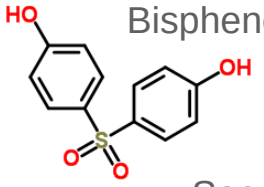
Acesulfame



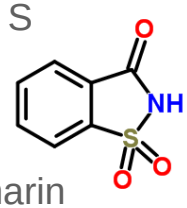
TCPP



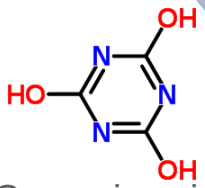
Melamine



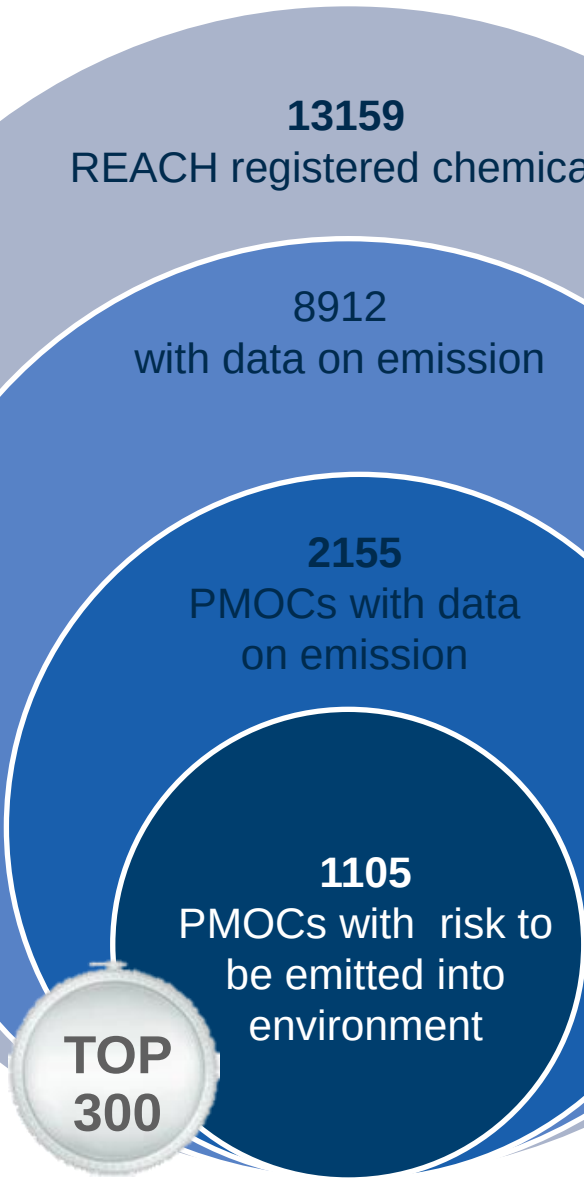
Bisphenol S



Saccharin



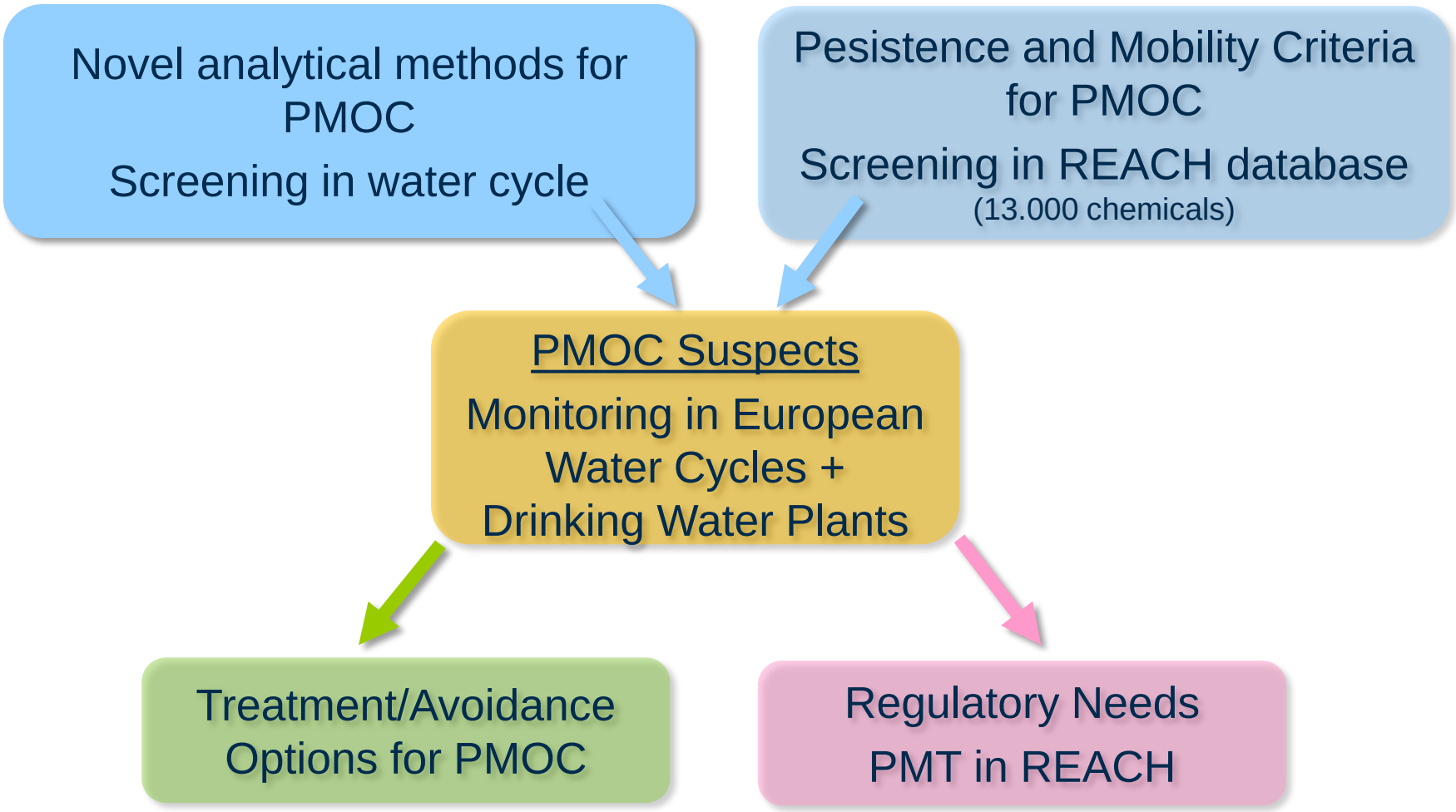
Cyanuric acid



Arp et al. (2017) Environ Sci Proc Impact, in press.; Schulze et al (2017) subm.

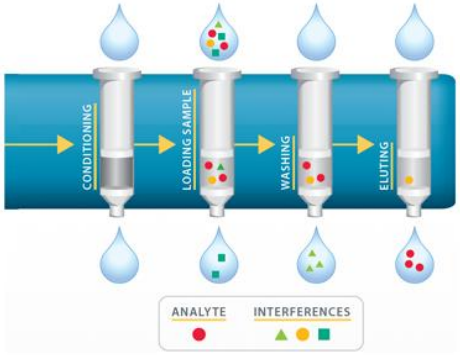
PROMOTE

Protecting water resources from mobile trace chemicals



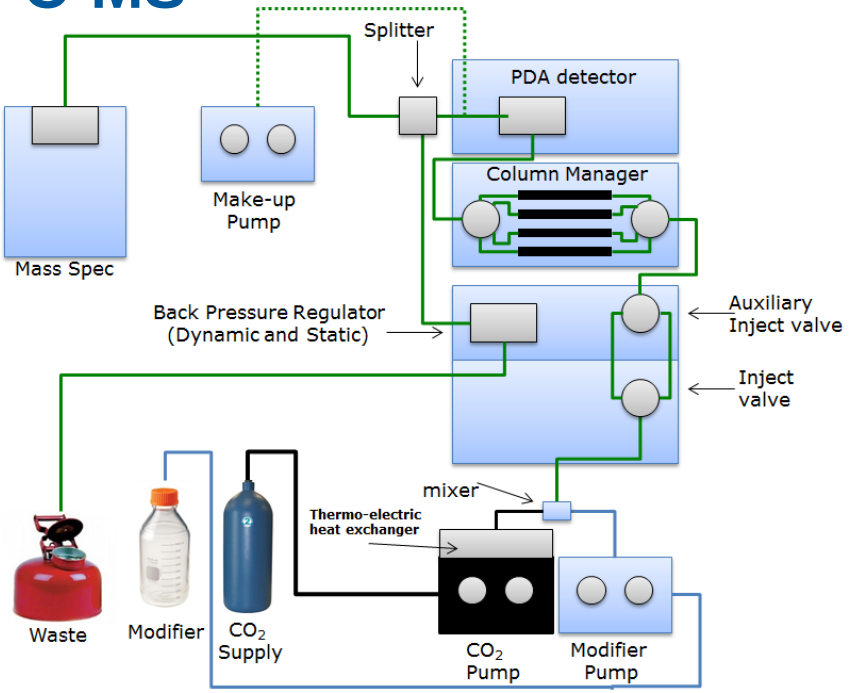
Supercritical Fluid Chromatography-MS

Extraction



- Graphitized carbon black (ENVICarb)
- weak anion exchanger (WAX)
- moderate cation exchanger (MCX)
- weak cation exchanger (WCX)
- hydroxylated polystyrene-divinylbenzene (ENV+)
- and combinations thereof

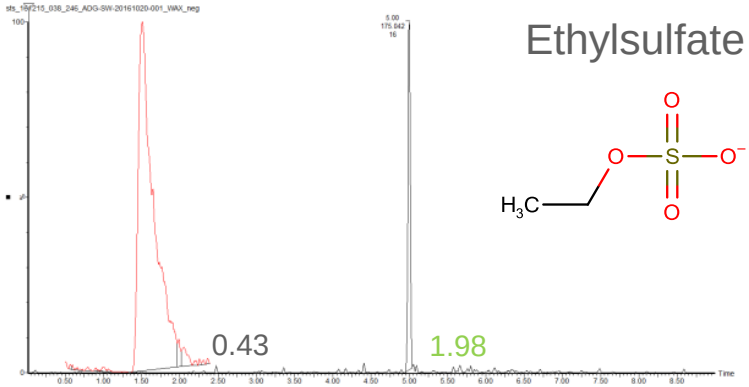
SFC-MS



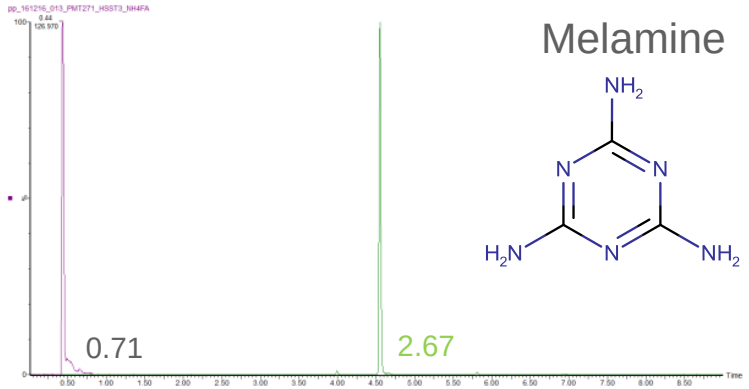
- Supercritical (fluid) CO_2 as mobile phase
- H_2O and MeOH as additives
- Normal phase column (BEH)

SFC-MS vs. RPLC-MS

- Three PMOC in real samples

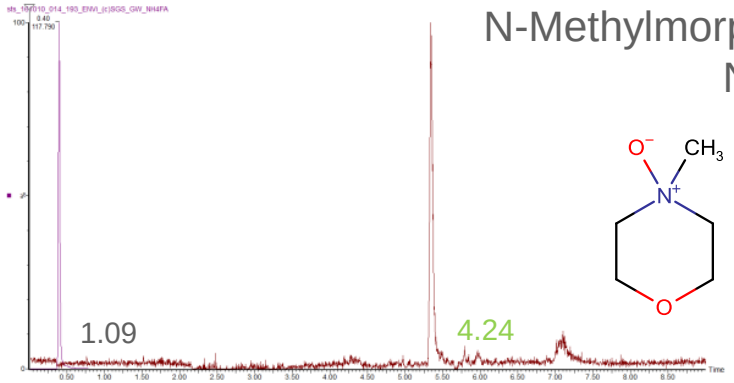


Ethylsulfate



Melamine

- Stronger retention of PMOC analytes
- Better peak shape
- Sensitivity increase by a factor of 4 - 5



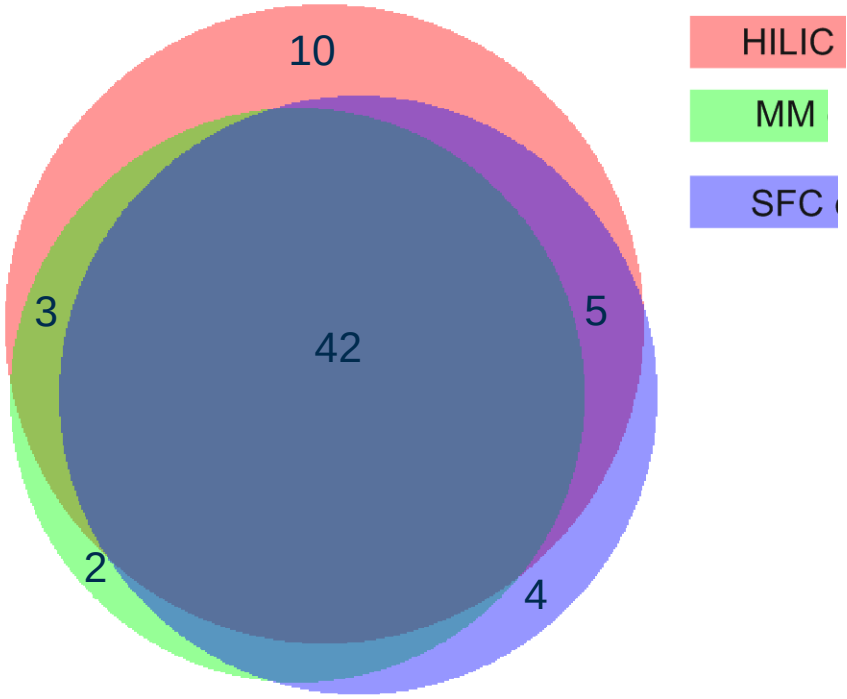
N-Methylmorpholin-N-Oxid

Verhältnis Probe/Standard

(bei gleicher Standardkonzentration und gleicher SPE-Probe)

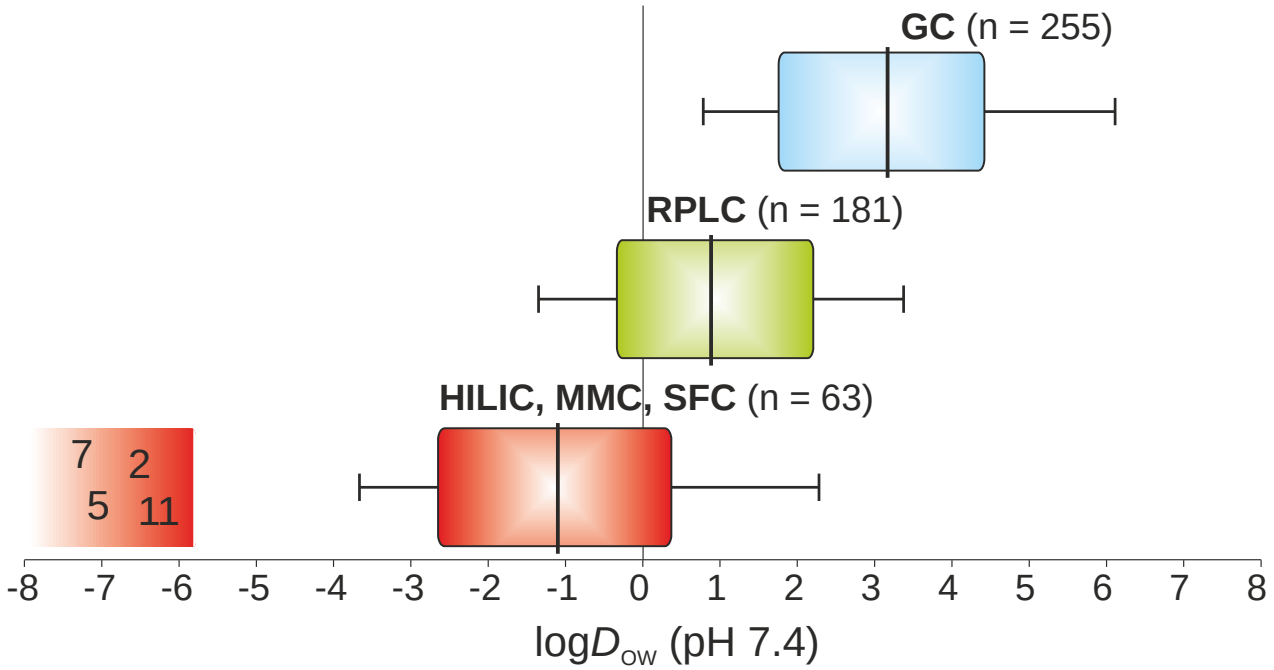
Chromatographic Approaches to Close the Analytical Gap

- Liquid Chromatography-Mass Spectrometry with other stationary phases
  - Supercritical fluid chromatography (SFC)
    - with normal phase columns
  - Hydrophilic interaction liquid chromatography (HILIC)
    - comparable to NPLC
  - Mixed-mode chromatography (MMC)
    - polar interaction and ion exchange
  - Approx. 67 analytes



Narrowing The Analytical Gap

- Improvement by HILIC, MMC and SFC

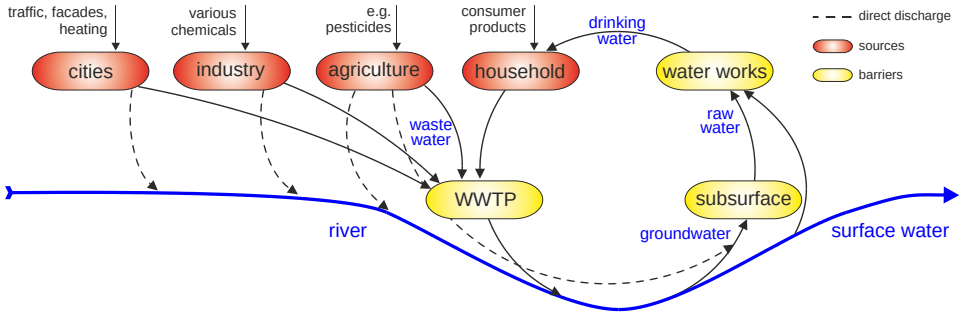


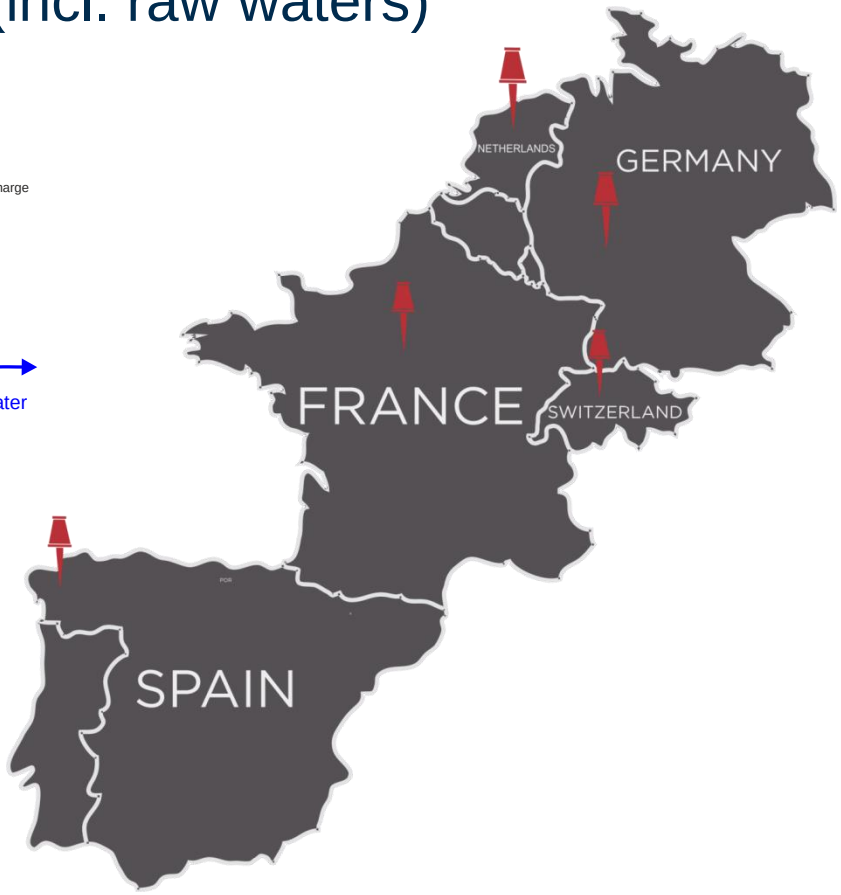
- Enrichment remains challenging

Reemtsma et al., unpubl.

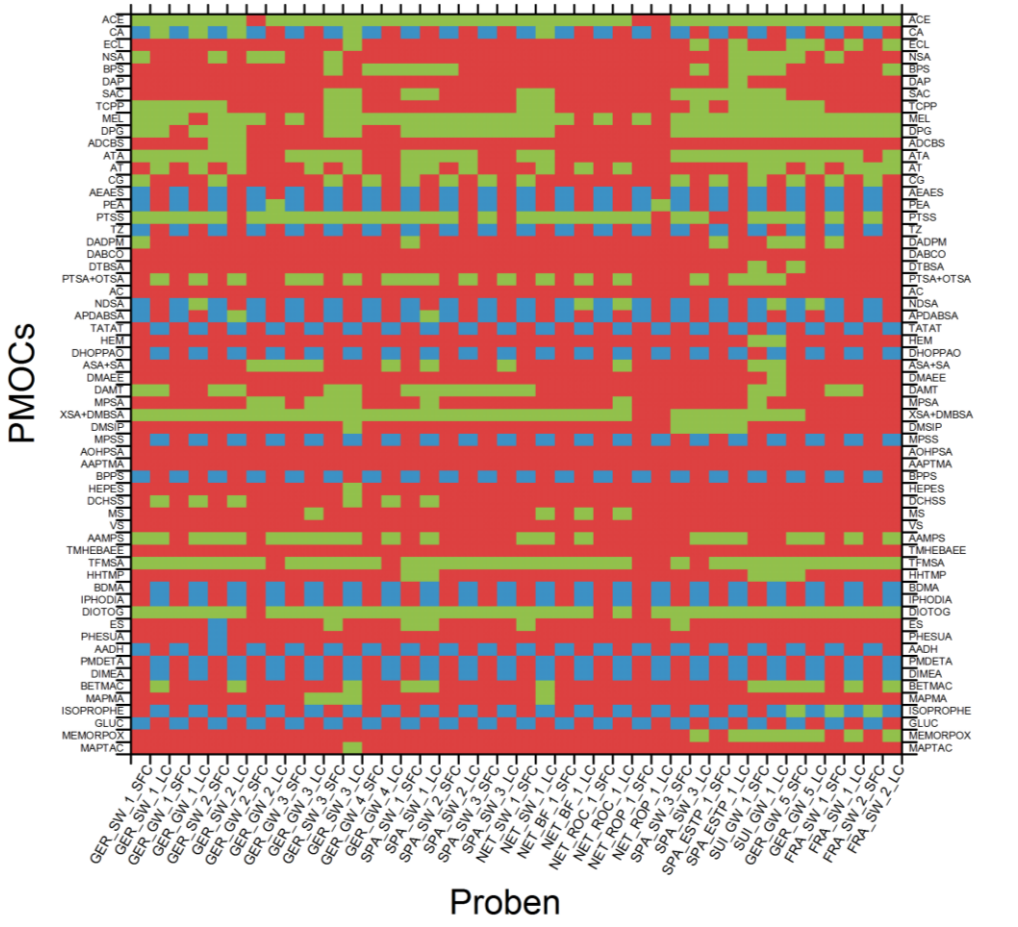
Screening for PMOC

- First Screening
  - Surface water, groundwater (incl. raw waters)
  - 20 samples





Screening for PMOC by SFC-MS

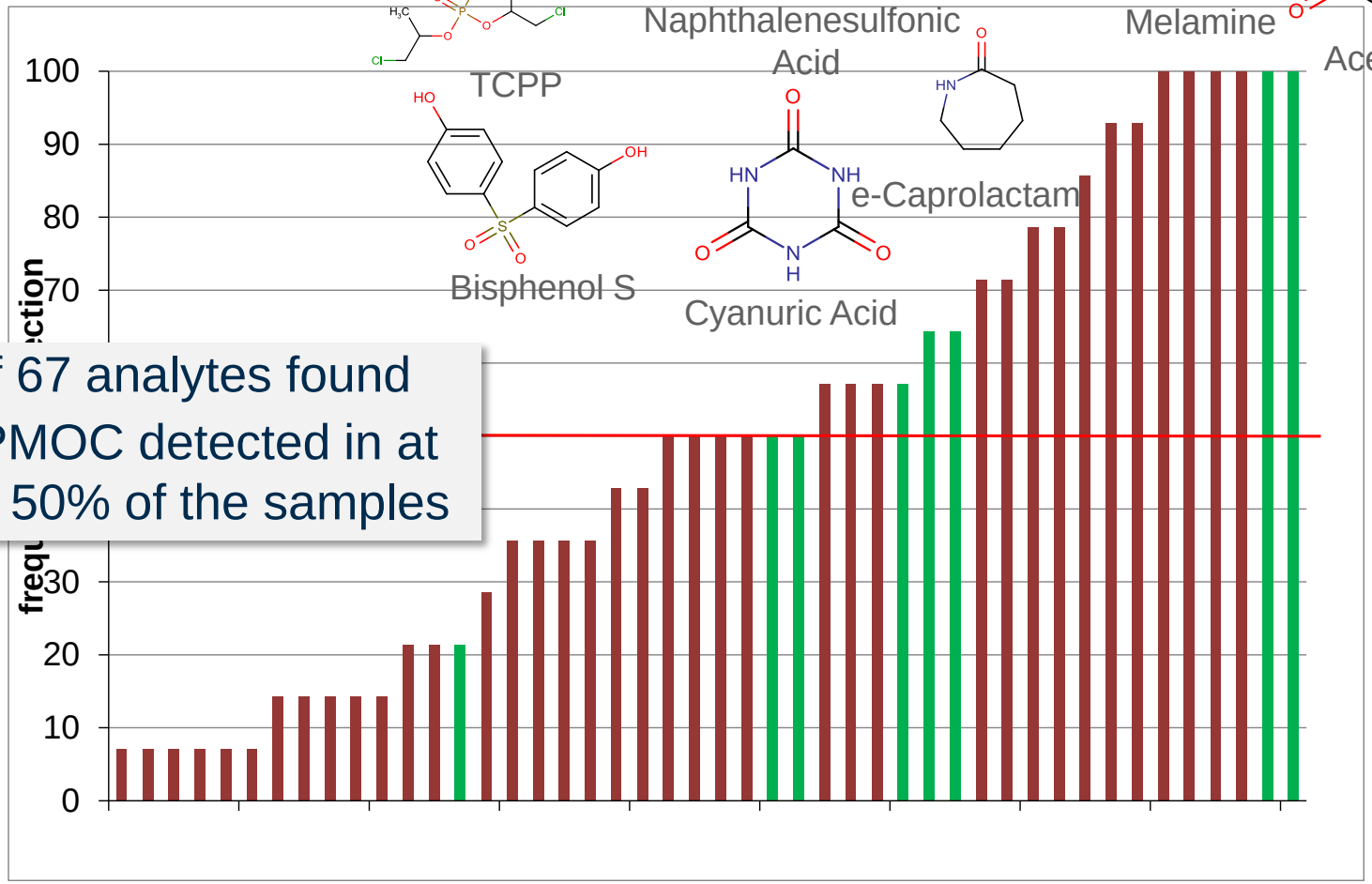


SFC-MS

- 41 of the 60 PMOCs screened for were found in the 20 samples

Screening Data for PMOC – 3 Methods

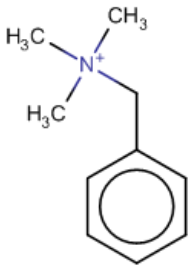
Green:
Previously known PMOC



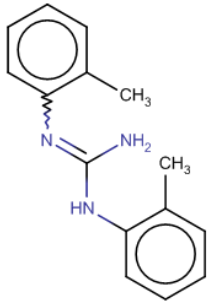
- 46 of 67 analytes found
- 25 PMOC detected in at least 50% of the samples

Newly Detected PMOCs

BENZYLTRIMETHYL-AMMONIUM

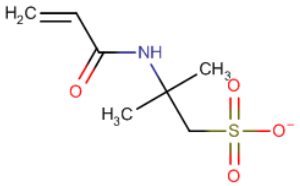


1,3-DI-O-TOLYLGUANIDINE

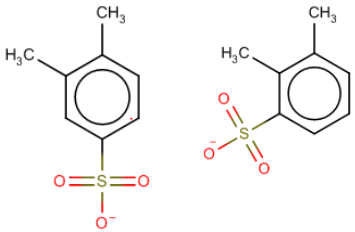


TRIFLUOROMETHANE-SULFONIC ACID *

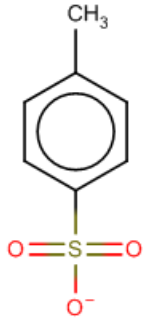
2-ACRYLAMINO-2-METHYLPROPANE SULFONATE *



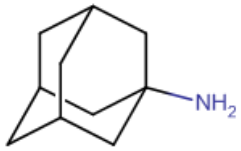
DIMETHYLBENZENE-SULFONIC ACID



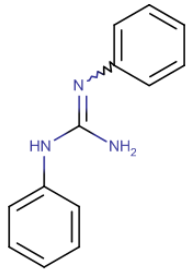
4-METHYLBENZENE-SULFONIC ACID



ADAMANTAN-1AMINE



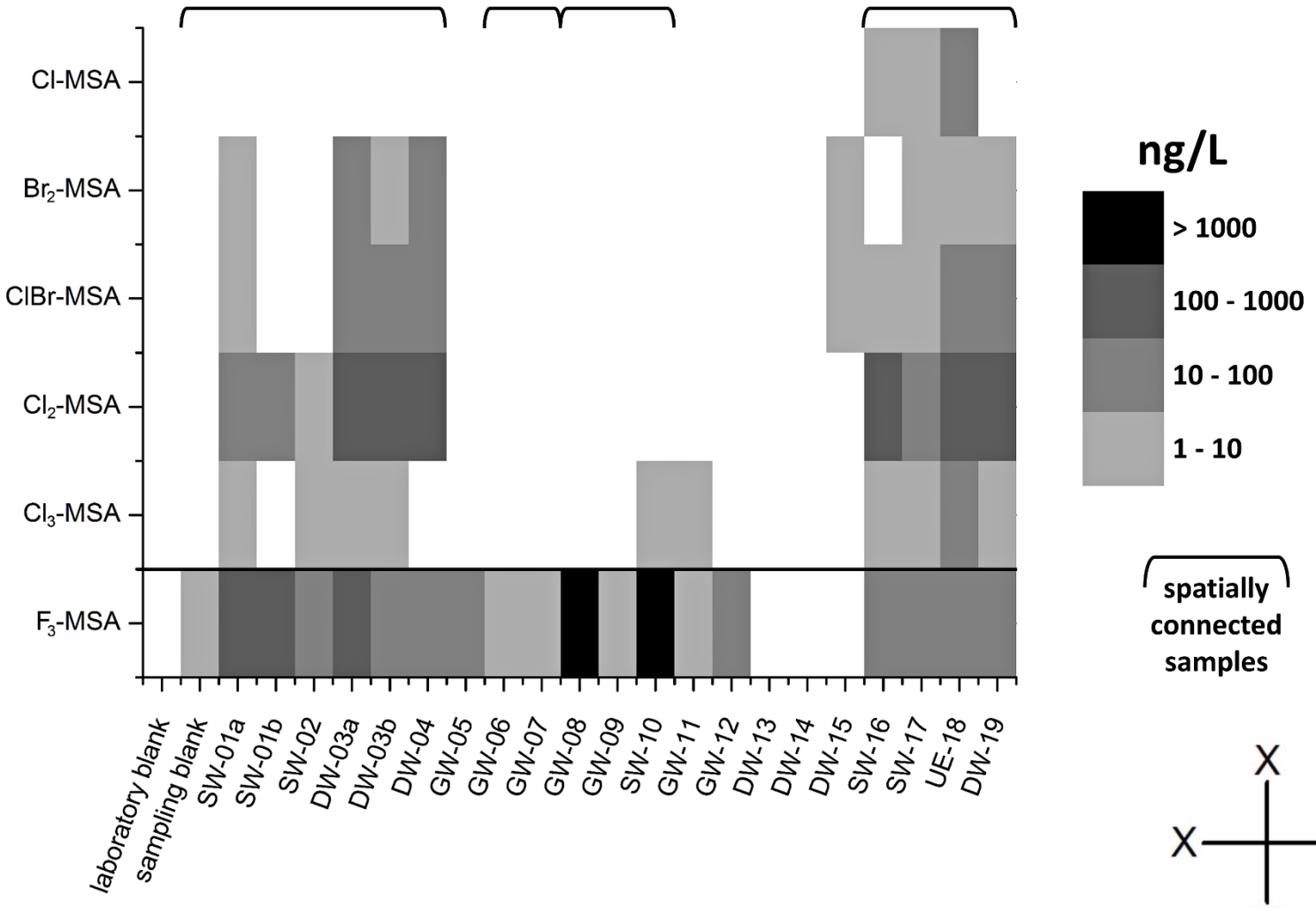
1,3-DIPHENYLGUANIDINE

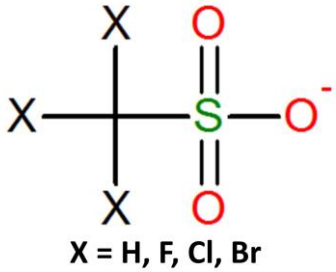


+ „known PMOCs: melamine *, TCPP, saccharin, bisphenol S, caprolactam, cyanuric acid, acesulfame *

* Estimated in the µg/L range

Halogened Methanesulfonic Acids





Zahn et al. (2016) Water Research 101, 292-299

Quantitative Monitoring

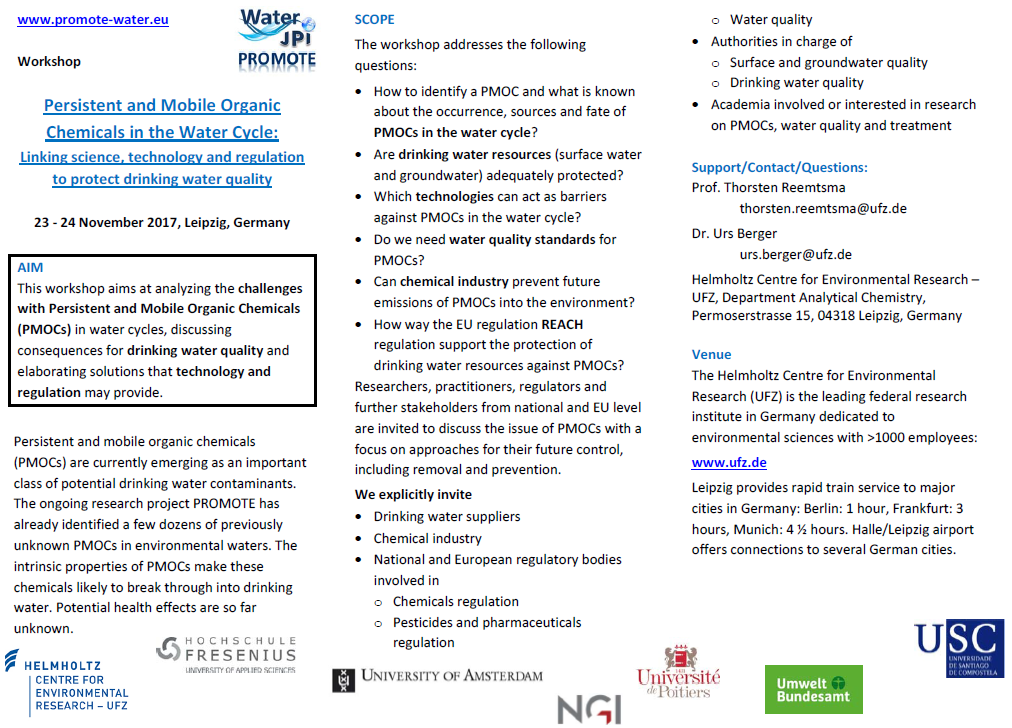
- 2nd Monitoring
  - 5 European countries
  - 60 samples, 80 PMOCs
- DW treatment processes to be covered
  - Iron removal
    - Aeration, flocculation, sand filtration
  - Disinfection
    - Ozonation, UV irradiation
  - Surface water treatment
    - Preozonation, flocculation, filtration, slow sand filtration
  - Reversed osmosis

Conclusions

- With respect to drinking water quality PMOC are of high concern
  - The number of potential PMOC with emission potential in the REACH database exceeds 1000
- The size of the analytical gap for PMOC has been reduced due to HILIC-, MMC and SFC-MS
  - but it is not closed, yet
- Many (> 40) new PMOC were detected (from a list of 67 analytes) in partially closed water cycles
- Most of the predicted PMOC not yet searched for
  - Some hundreds of compounds need to be analyzed
  - List of suspects available
- Mitigation options need to be elaborated
  - Improved treatment (at source, wastewater, drinking water)
  - Avoiding release (changing use (open → closed systems), substitution
  - Regulation

Workshop Announcement

- Persistent and Mobile Organic Chemicals in the Water Cycle: Linking science, technology and regulation to protect drinking water quality
- 23 - 24 November 2017, Leipzig, Germany



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Water JPI PROMOTE

Workshop

Persistent and Mobile Organic Chemicals in the Water Cycle: Linking science, technology and regulation to protect drinking water quality

23 - 24 November 2017, Leipzig, Germany

AIM

This workshop aims at analyzing the **challenges with Persistent and Mobile Organic Chemicals (PMOCs)** in water cycles, discussing consequences for **drinking water quality** and elaborating solutions that **technology and regulation** may provide.

Persistent and mobile organic chemicals (PMOCs) are currently emerging as an important class of potential drinking water contaminants. The ongoing research project PROMOTE has already identified a few dozens of previously unknown PMOCs in environmental waters. The intrinsic properties of PMOCs make these chemicals likely to break through into drinking water. Potential health effects are so far unknown.

HELMHOLTZ CENTRE FOR ENVIRONMENTAL RESEARCH – UFZ

HOCHSCHULE FRESENIUS UNIVERSITY OF APPLIED SCIENCES

SCOPE

The workshop addresses the following questions:

- How to identify a PMOC and what is known about the occurrence, sources and fate of **PMOCs in the water cycle**?
- Are **drinking water resources** (surface water and groundwater) adequately protected?
- Which **technologies** can act as barriers against PMOCs in the water cycle?
- Do we need **water quality standards** for PMOCs?
- Can **chemical industry** prevent future emissions of PMOCs into the environment?
- How way the EU regulation **REACH** regulation support the protection of drinking water resources against PMOCs?

Researchers, practitioners, regulators and further stakeholders from national and EU level are invited to discuss the issue of PMOCs with a focus on approaches for their future control, including removal and prevention.

We explicitly invite

- Drinking water suppliers
- Chemical industry
- National and European regulatory bodies involved in
  - Chemicals regulation
  - Pesticides and pharmaceuticals regulation
  - Water quality
- Authorities in charge of
  - Surface and groundwater quality
  - Drinking water quality
- Academia involved or interested in research on PMOCs, water quality and treatment

Support/Contact/Questions:

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Venue

The Helmholtz Centre for Environmental Research (UFZ) is the leading federal research institute in Germany dedicated to environmental sciences with >1000 employees:

www.ufz.de

Leipzig provides rapid train service to major cities in Germany: Berlin: 1 hour, Frankfurt: 3 hours, Munich: 4 ½ hours. Halle/Leipzig airport offers connections to several German cities.

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Université de Poitiers

Umwelt Bundesamt

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

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  - German Federal Ministry for Education and Research (02WU1347A/B)

Thank you very much for your attention!

Bundesministerium für Bildung und Forschung

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