Nachweis von PM (T)-Stoffen im Wasserkreislauf - Herausforderungen bei der Analytik und dem Monitoring

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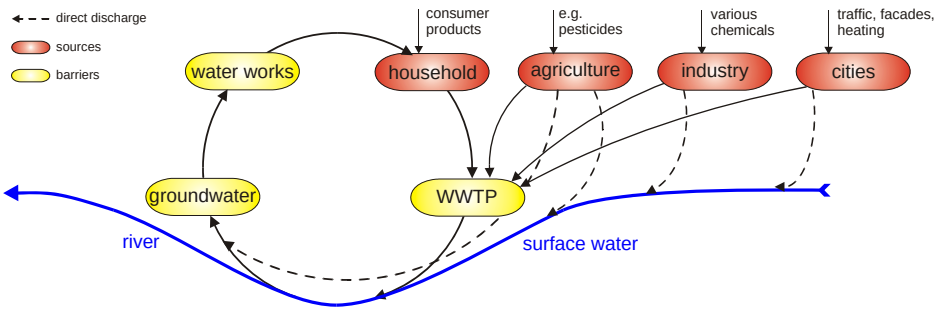
Hans Peter H. Arp, Hervé Gallard, Thomas P. Knepper,
Michael Neumann, José Benito Quintana, Pim de Voogt

Berlin, 04.05.2017

HELMHOLTZ CENTRE FOR ENVIRONMENTAL RESEARCH – UFZ

Partially Closed Water Cycle and PMOC

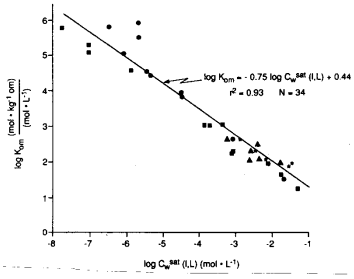


- for persistent and very polar (mobile) organic compounds (PMOC) the water cycle turns into a compound cycle
  - as barriers are not effective

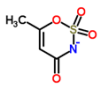
PMOC = PM-Stoffe

What makes a Chemical Mobile?

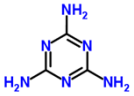
- High polarity
  - high water solubility
  - low octanol-water partition coefficient (log K_{OW})
- Low molecular mass
- High portion of heteroatoms
  - O, S, P, N
- Polarity difficult to assess
- Acidic or basic functional groups: logD_{OW}, $D_{ow} = \frac{K_{ow}}{1+10^{pH-pK_a}}$



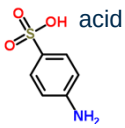
Acesulfame



Melamine

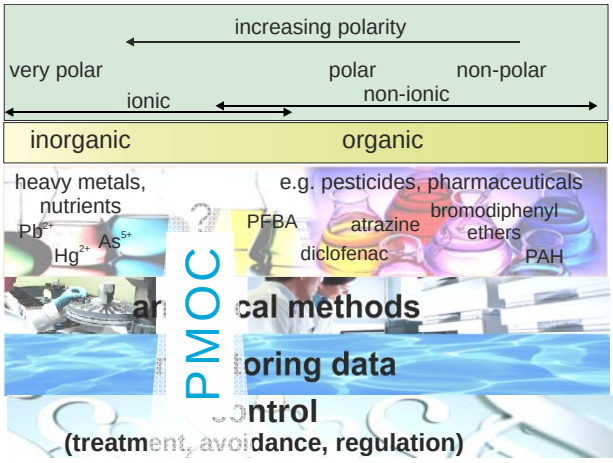


Sulfanilic acid



Saccharin

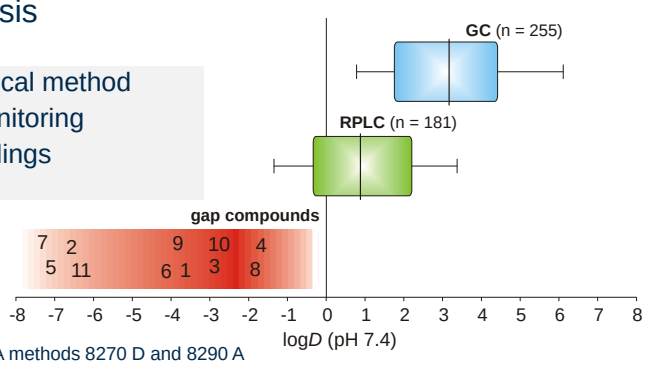
The Analytical Gap



The Analytical Gap

- Polarity (log*D*) of analytes suitable for GC or RPLC-MS analysis

no analytical method
→ no monitoring
→ no findings



GC-MS: EPA methods 8270 D and 8290 A

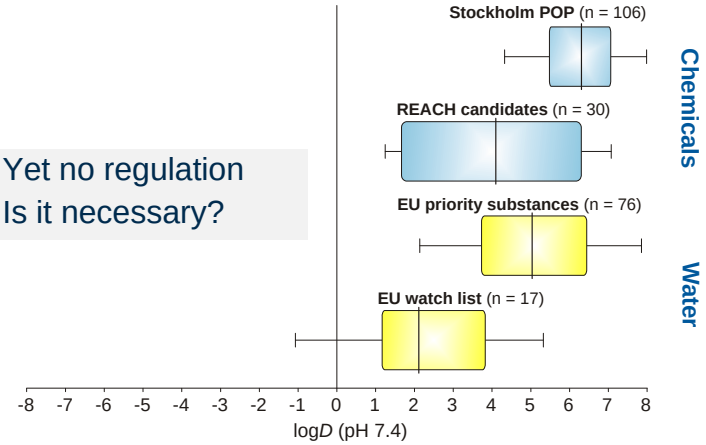
LC-MS: Schymanski et al. (2014) Environ. Sci. Technol. 48, 1811-1818.

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

Novel analytical methods for PMOC
Screening in water cycle

Pesistence and Mobility Criteria for PMOC
Screening in REACH database
(13.000 chemicals)

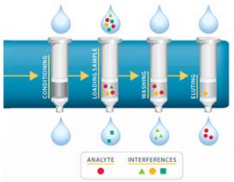
PMOC Suspects
Monitoring in European Water Cycles + Drinking Water Plants

Treatment/Avoidance Options for PMOC

Regulatory Needs
PMT in REACH

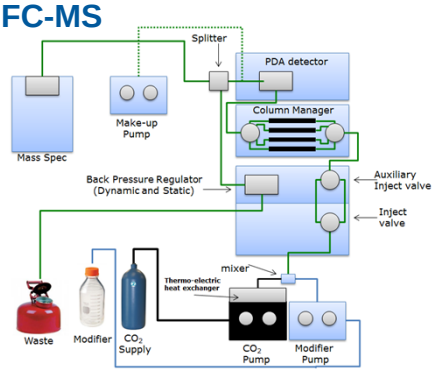
Supercritical Fluzid Chromatography-MS

Extraction



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

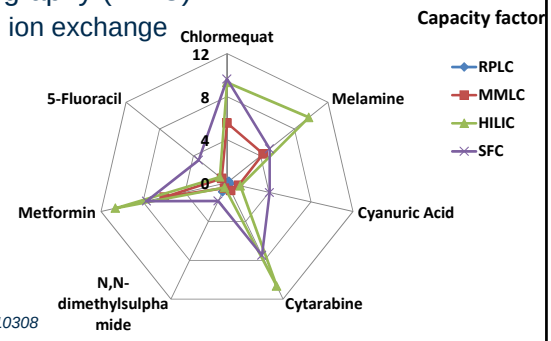
SFC-MS



- Supercritical (fluid) CO_2 as mobile phase
- H_2O and MeOH as additives
- BEH and Torus Diol columns

Chromatographic Approaches to Close the Analytical Gap

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



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

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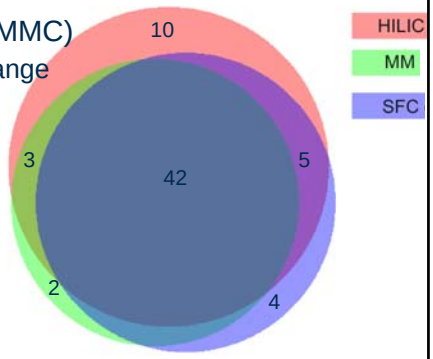
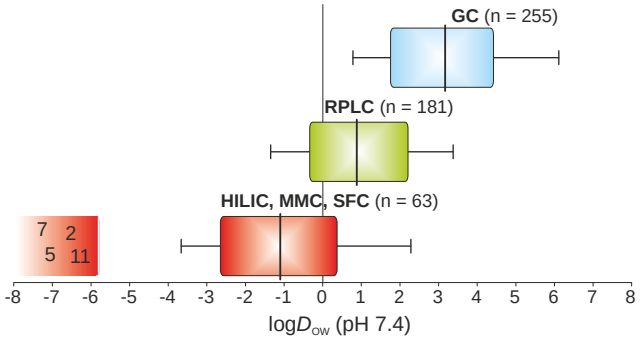


Narrowing The Analytical Gap

- Improvement by HILIC, MMC and SFC

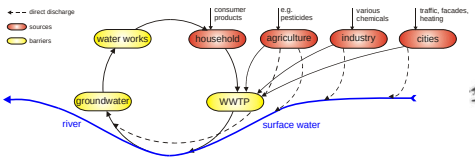


- Enrichment remains challenging

Reemtsma et al., unpubl.

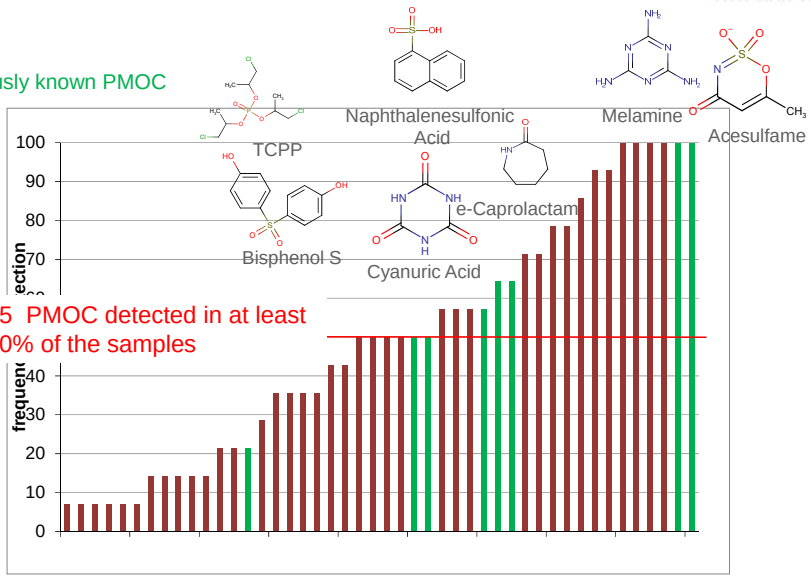
Monitoring Data for PMOC

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



Monitoring Data for PMOC

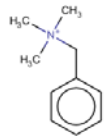
Green:
previously known PMOC



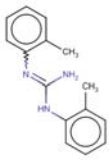
25 PMOC detected in at least 50% of the samples

Newly Detected PMOCs

BENZYLTRIMETHYL-AMMONIUM

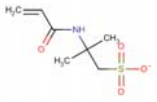


1,3-DI-O-TOLYLGUANIDINE

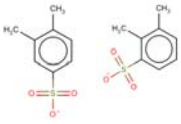


TRIFLUOROMETHANE-SULFONIC ACID *

2-ACRYLAMINO-2-METHYLPROPANE SULFONATE *

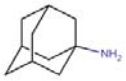


DIMETHYLBENZENE-SULFONIC ACID

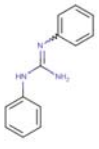


4-METHYLBENZENE-SULFONIC ACID

ADAMANTAN-1AMINE



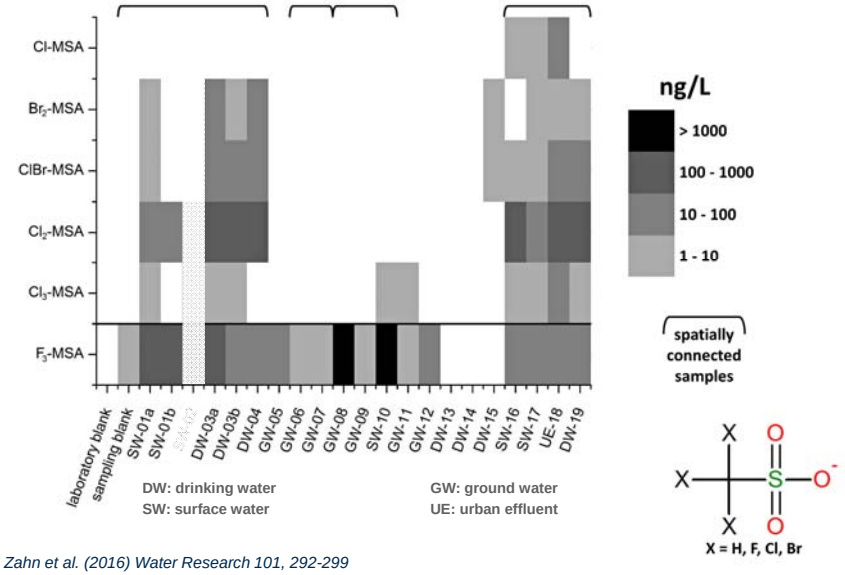
1,3-DIPHENYLGUANIDINE



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

* Estimated in the µg/L range

Halogened Methanesulfonic Acids



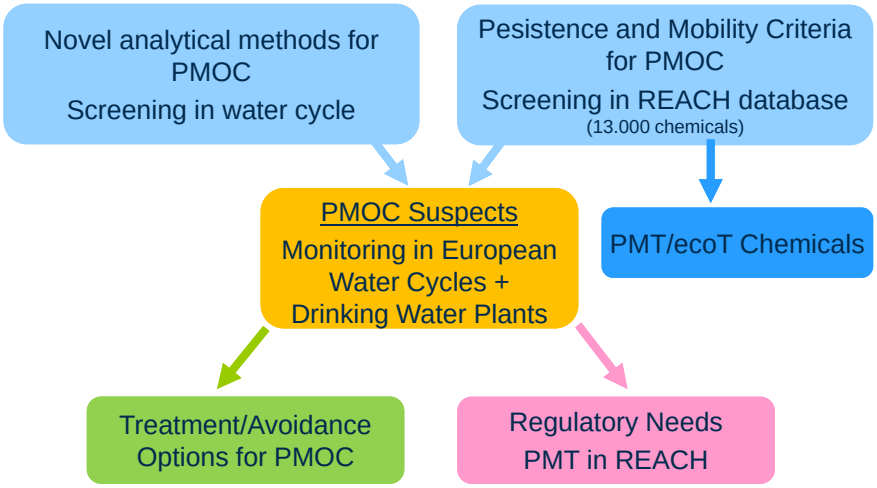
Zahn et al. (2016) Water Research 101, 292-299

PMOC in Drinking Water Preparation

- 2nd Monitoring
  - 3 partners, 4 associated partners
  - 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

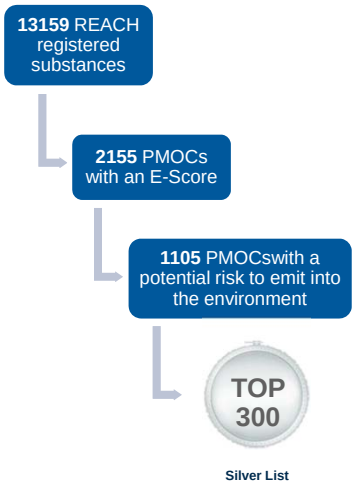
PROMOTE

Protecting water resources from mobile trace chemicals



PMOC from REACH Chemicals

- Of approx. 13000 REACH chemicals 1000 are potential PMOCs or PMOC precursors with risk of emission into environment
- Ranking according to expected emission
  - tonnage, use characteristics
- Top 150 (re-)evaluated for P, M and T



Arp et al. (2017) subm.
Schulze et al. (2017) in prep

From PMOC to PMT

- 167 chemicals
- Case by case compilation and validation of data for P and M
  - Documents and modeling
- Collection and validation of data for T and ecoT
- Evaluation of chemicals according to criteria of Kalberlah et al. (2014) for P, M and T using the validated data
- Development of criteria for ecoT
- Traffic light scheme applied

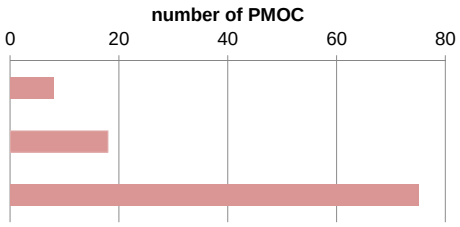
  - Criterion fulfilled according to available data
  - Criterion likely fulfilled, but available data not fully clear
  - Criterion not fulfilled according to available data
  - White: Information is missing and an indication or assessment if the criterion is fulfilled is not possible

Berger et al. (2017) UBA Report, subm.

Results of the PMT Evaluation

- 101 of 167 evaluated chemicals with P, M, T red or yellow

P	M	T
r	r	r
r	r	y
r/y	r/y	r/y



Berger et al. (2017) UBA Report, subm.

PMT Compounds

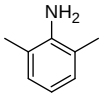
- PMT all Red Chemicals

Substance name	P	M	T	Eco-T	Em
2,6-Dimethylaniline	R	R	R	R	R
1,2,4-Triazole	R	R	R	G	R
1,4-Dioxane	R	R	R	G	R
4-Mesyl-2-nitrotoluene	R	R	R	G	R
4-Aminophenol	R	R	R	R	R
1,2-Dichloroethane	R	R	R	G	R
Trichloroethene	R	R	R	W	R
Tetrachloroethene	R	R	R	R	R

Berger et al. (2017) UBA Report, subm.

P, M, T All Red Chemicals

- 2,6-Dimethylaniline (2,4-xylidine)
  - T: classified as carcinogenicity category 1B
  - Intermediate use and other uses
  - Reports in water: ?



- 1,2,4-Triazole
  - T: reproduction toxicity category 2
  - Intermediate use, other uses: additive in fertilizer as nitrification inhibitor
  - Reports in water
    - Scheurer et al. (2016) Environ Sci. Proc. Impact 18, 999-1010
      - no biodegradation, no hydrolysis, no sorption
      - ozonation and AC not effective

- 1,4-Dioxane
  - T: carcinogenicity category 2
  - solvent and stabilizer
  - Reports in water
    - Stepien et al. (2014) Water Res. 48, 406-419
      - No removal in WWTP, no removal in bank filtration

1,4-Dioxane

Nr. 44 / Mittwoch, 30. November 2016

Kategorie Analytik/Stoffe

Umweltmonitoring wird ausgeweitet

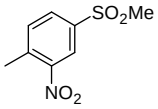
LfU setzt neue Messmethodik ein

+++ Das laufende Umweltmonitoring durch das Bayerischen Landesamt für Umwelt (LfU) wird ausgebaut. Als weiteren Baustein hat das LfU ein neues Analyseverfahren für die Industriechemikalie 1,4-Dioxan entwickelt. 1,4-Dioxan wird als Lösungsmittel bei der Produktion von Klebstoffen, Abbeizmitteln, Farbstoffen, Entfettern, Gewebereinigern, Papier und Elektronik verwendet. Weiter entsteht 1,4-Dioxan als Nebenprodukt bei einigen chemischen Produktionsprozessen weshalb es in Spuren auch in Alltagsprodukten wie Flüssigwaschmitteln und Flüssigseifen enthalten sein kann. Zur Bestimmung von 1,4-Dioxan war bisher ein aufwändiges Spezialverfahren erforderlich, das in Deutschland nur in wenigen Forschungslaboren verfügbar ist. Künftig werden regelmäßig Gewässerproben in Bayern auf Dioxan untersucht.

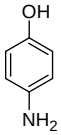
Mit dem neuen Analyseverfahren konnte 1,4-Dioxan in bayerischen Gewässern nachgewiesen werden. Schwerpunkte der Nachweise liegen an der Donau und deren Nebenflüssen Lech, Wertach und Inn. Eine Gefährdung der öffentlichen Trinkwasserversorgung besteht nicht, eine

P, M, T All Red Chemicals

- 4-Mesyl-2-nitrotoluene
  - T. reproduction toxicity category 2
  - Intermediate use, other uses incl. consumer use
  - Reports in water: ?



- 4-Aminophenol
  - T: mutagenicity category 2, reproduction toxicity category 2
  - ecoT: acute and chronic hazard class 1.
  - Intermediate use and other uses
  - Reports in water
    - Badea et al. (2013) Environ. Monit. Assess. 185, 2367-2375
    - Facile oxidation to quinone imine; reactive (Michael substrate)



Summary

- With respect to drinking water quality PMT rather than PBT compounds are of concern
- Very polar (M) chemicals fall in an analytical gap
- The extent of the analytical gap has been reduced
  - 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 for
  - List of suspects available
- Treatment options for those PMOC detected will be studied
- 8 PMT compounds identified from a list of 167 PMOC
  - 18 PM with T at screening level

Conclusions

- PMT Prediction
  - Quality of REACH data not always convincing
  - Data gaps exist
  - No tools for reliable prediction of phys chem properties for ionizable and ionic compounds (QSAR)
- PMOC findings
  - The analytical gap is only partially closed
  - Extent of the gap in water protection is not fully clear
- Consequences
  - Mitigation options need to be elaborated
    - Improved treatment
      - Source, wastewater, drinking water
    - Avoiding release
      - Changing use (open/closed systems)
      - Substitution
    - Regulation

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  - Steffi Schulze, Urs Berger
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  - Hans Peter H. Arp, Hervé Gallard, Thomas P. Knepper, Michael Neumann, José Benito Quintana, Pim de Voogt
- UFZ colleagues
  - Norbert Ost, Ralph Kühne, Gerrit Schüürmann
- UBA Fachgebiet IV 2.3 collaborators
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GEFÖRDERT VOM
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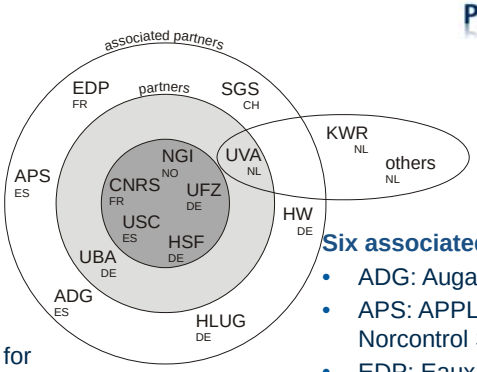
For more information: www.promote-water.eu

PROMOTE Consortium

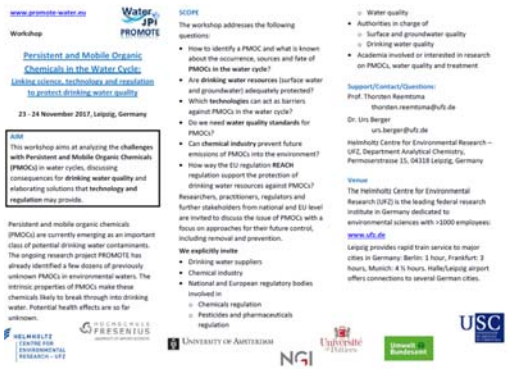


Seven Partners
- CNRS: University of Poitiers
- HSF: University of Applied Sciences Fresenius
- NGI: Norwegian Geotechnical Institute
- UFZ: Helmholtz Centre for Environmental Research
- UBA: German Federal Environment Agency (DE), FG IV II.3
- UVA: University of Amsterdam
- USC: University of Santiago de Compostela

Six associated partners
- ADG: Augas de Galicia
- APS: APPLUS Norcontrol SLU
- EDP: Eaux de Paris
- HLUG: Hessisches Landesamt für Umwelt und Geologie
- HW: Hessenwasser
- SGS: SGS Institute Fresenius

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



www.promote-water.eu

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.

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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Helmholtz Centre for Environmental Research – UFZ, Department Analytical Chemistry, Permoserstrasse 15, 04318 Leipzig, Germany

Venue

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