Persistent and Mobile Compounds in the Water Cycle: Challenges and Findings

~

PROMOTE Project

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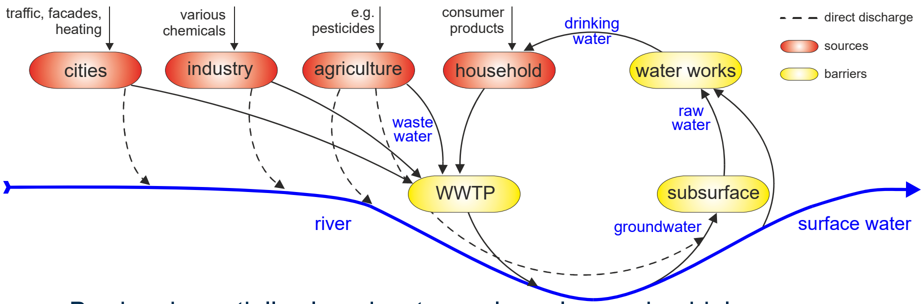
HELMHOLTZ CENTRE FOR ENVIRONMENTAL RESEARCH – UFZ

Paris, 06.03.2019

Prioritizing of Emerging Contaminants

- For which purpose?
  - Define analytes for monitoring?
  - Select contaminants for regulating water quality?
  - For chemical's regulation?
- What to protect?
  - Surface water quality
    - Ecological quality of rivers, habitat and biodiversity
  - Groundwater quality
  - Water resources for future use
    - Depends on use
  - Drinking water quality / human health

The Protection Gap



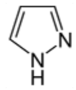
- Barriers in partially closed water cycles rely on microbial degradation and sorption processes
- For persistent (P) and very polar (mobile, M) organic compounds (PM substances) these barriers are not effective
  - water cycle may turn into a compound cycle
  - only dilution reduces concentration

Motivation

- Single very polar compounds incidentally discovered in drinking water, among them
- N,N-Dimethylsulfamide
  - Metabolite of pesticide Tolylfluanide
  - log*D* $_{(pH\ 7.4)}$ = -1.4
    - Schmidt and Brauch (2008) Environ. Sci. Technol. 2008, 42, 6340
  - Precursor of NMDA during ozonation

- Trifluoroacetic acid
  - Released from fluorochemical industry
    - Scheurer et al. (2017) Water Res. 126, 460
  - log*D* $_{(pH\ 7.4)}$ = - 3.1
  - Ion exchange-MS

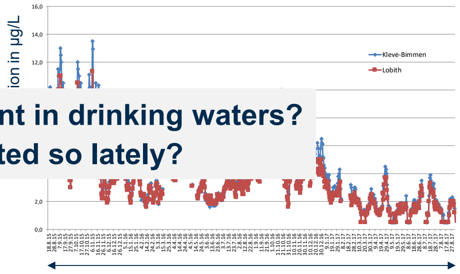
Incidental Findings in Drinking Waters



Pyrazol

- Pyrazole
  - Intermediate in acrylnitrile production
  - Waterworks in the Netherlands using bank filtrate closed down for > 4 months
  - discharge of >1 ton/d
  - log*D* $_{(pH\ 7.4)}$ = 0.4

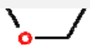
Concentration in River Rhine



Courtesy of C. Schmidt, Rheinenergie

- **Why present in drinking waters?**
- **Why detected so lately?**

- 1,4-Dioxane
  - log*D* $_{(pH\ 7.4)}$ = -0.3
  - Groundwater Bavaria

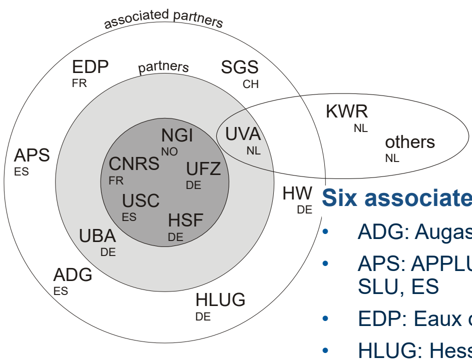


European Project PROMOTE –
Protecting Water Resources from Mobile Trace Chemicals

Water JPI PROMOTE

Seven Partners

- CNRS
  Hervé Gallard
- HSF
  Thomas Knepper
- NGI
  Hans Peter Arp
- UFZ
  Urs Berger
  Thorsten Reemtsma
- UBA
  Michael Neumann
- UVA
  Pim de Voogt
- USC
  Jose Benito Quintana



Six associated partners

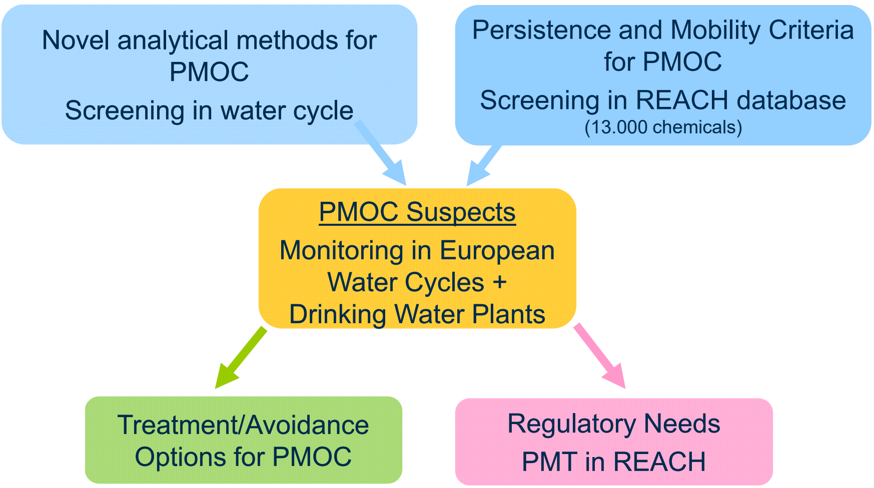
- ADG: Augas de Galicia, ES
- APS: APPLUS Norcontrol SLU, ES
- EDP: Eaux de Paris, FR
- HLUG: Hessisches Landesamt für Umwelt und Geologie, DE
- HW: Hessenwasser, DE
- KWR: Watercycle Research Institute, NL
- SGS: SGS Institute Fresenius, CH

01.01.15 - 30.06.18

NGI

PROMOTE

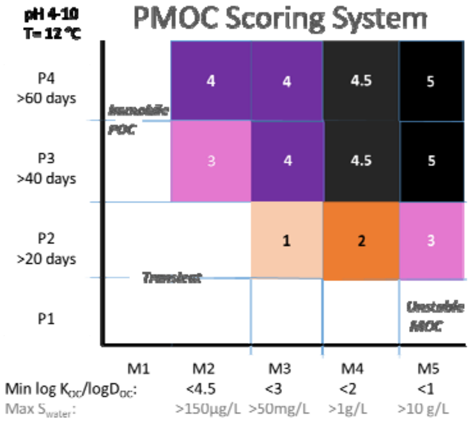
Protecting water resources from mobile trace chemicals



Water JPI Project PROMOTE

- Search for PM-substances in REACH Database
  - 14.000 registered substances (2015)
  - Data provided by the registrants
  - P (ersistence)
    - Half-life in marine water >60 days OR
    - half-life in fresh or estuarine water >40 days
  - M (obility)
    - Water solubility ≥150 µg/L AND
    - log K_{oc} ≤ 4.5
  - Limited data quality for P and M
    - experimental data
    - modeling data

PM Scoring System



PM scores

- Combination of P and M
- Score 5 being the compounds most likely to be PM chemical
- Non PM chemicals sorted as
  - unstable but mobile
  - persistent but immobile
  - transient

Arp et al. (2017) Environ. Sci. Process Impacts, 19, 939-955

Prioritizing PM Chemicals by Risk of Occurrence in the Water Cycle

hazard

exposure

PM score

Emission Score

- Emission score
  - Based on
    - Tonnage
    - Use characteristics
    - →Emission release category

Emission Release Category in REACH	Score for TRUE	Score for FALSE
High release to environment	7	3
Wide dispersive use	4	1
Intermediate use	0	3
Closed system use	1	3
Professional use	1.5	0.5
Consumer use	2	0.5
Substance in article	0.5	0

Schulze et al. (2018) Sci. Total Environ. 625, 1122–1128

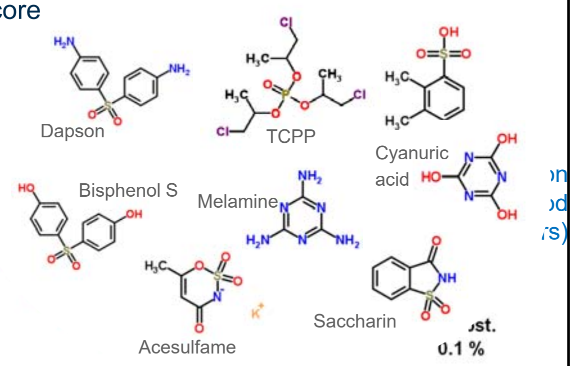
Prioritizing PM Chemicals (score 4 – 5) by Risk of Occurrence

- High emission likelyhood
- Ranking according to E-score

1105 PM chemicals with a potential risk to emit into the environment

TOP 300

„Silver List“



high emission likelyhood substances/precursors

Schulze et al. (2018) Sci. Total Environ. 625, 1122–1128

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Protecting water resources from mobile trace chemicals

Novel analytical methods for PMOC
Screening in water cycle

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

PMOC Suspects
Monitoring in European Water Cycles + Drinking Water Plants

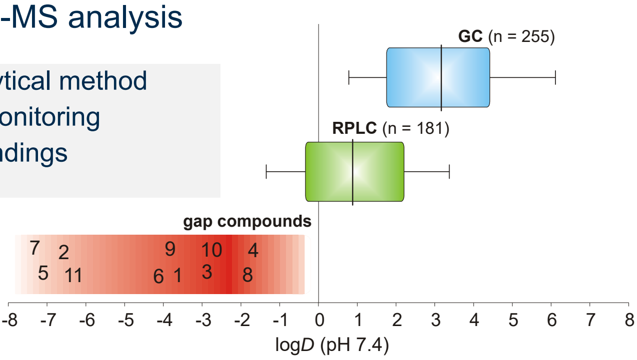
Treatment/Avoidance Options for PMOC

Regulatory Needs
PMT in REACH

The Analytical Gap

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

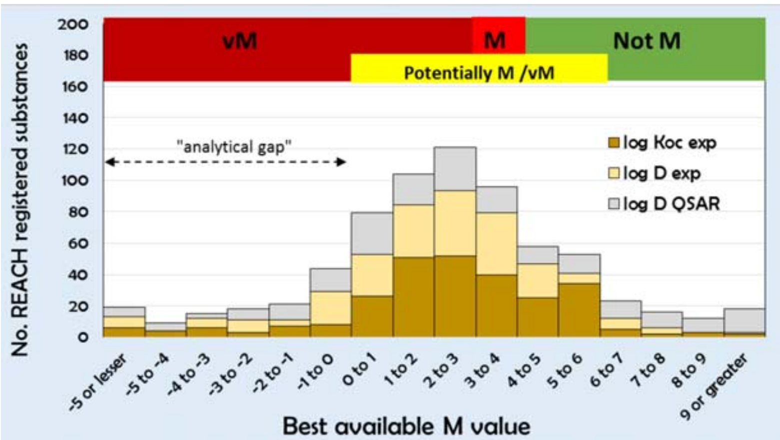
no analytical method
→ no monitoring
→ no findings



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

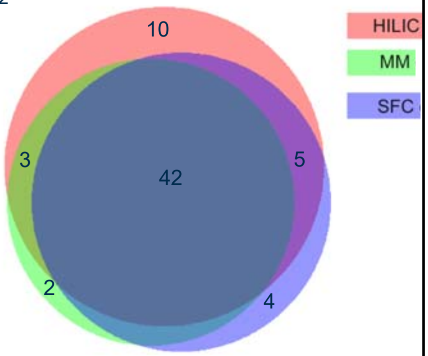
Mobility of REACH Substances



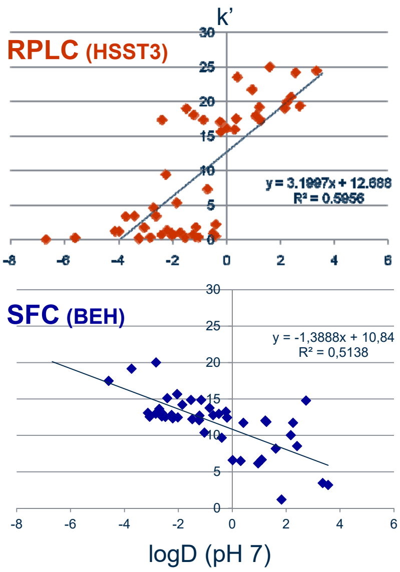
Arp and Hale (2018) NGI, DOC.NO. 20160426-TN-01 2018-03-06

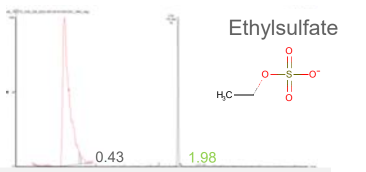
Chromatographic Approaches to Close the Analytical Gap

- Liquid Chromatography-Mass Spectrometry with other stationary phases
  - Hydrophilic interaction liquid chromatography (HILIC)
    - comparable to NPLC
      - Zahn et al. (2016) Wat. Res. 101, 292
  - Mixed-mode chromatography (MMC)
    - polar interaction and ion exchange
      - Montes et al. (2017) Environ. Sci. Technol. 51, 6250
  - Supercritical fluid chromatography (SFC)
    - with normal phase columns
      - Schulze et al., in prep.
  - Approx. 67 analytes of the “silver list”

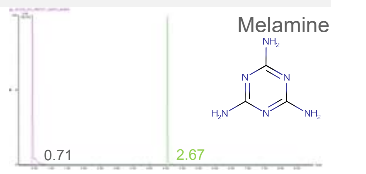


Determination of M Compounds by SFC-MS



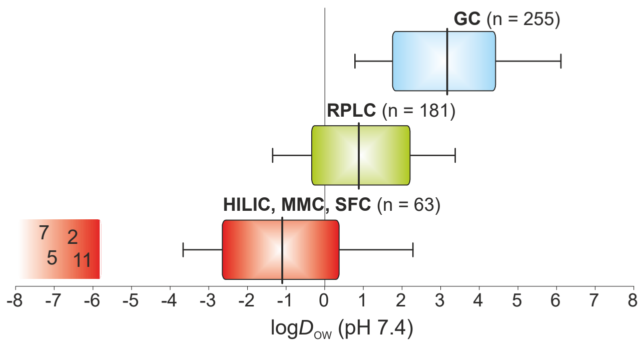


- Stronger retention of very polar analytes
- Better peak shape
- Sensitivity increase by a factor of 4 - 5



Narrowing The Analytical Gap

- Improvement by HILIC, MMC and SFC



- Enrichment remains challenging

Reemtsma et al., unpubl.

PROMOTE

Protecting water resources from mobile trace chemicals

Novel analytical methods for PM Compounds
Screening in water cycle

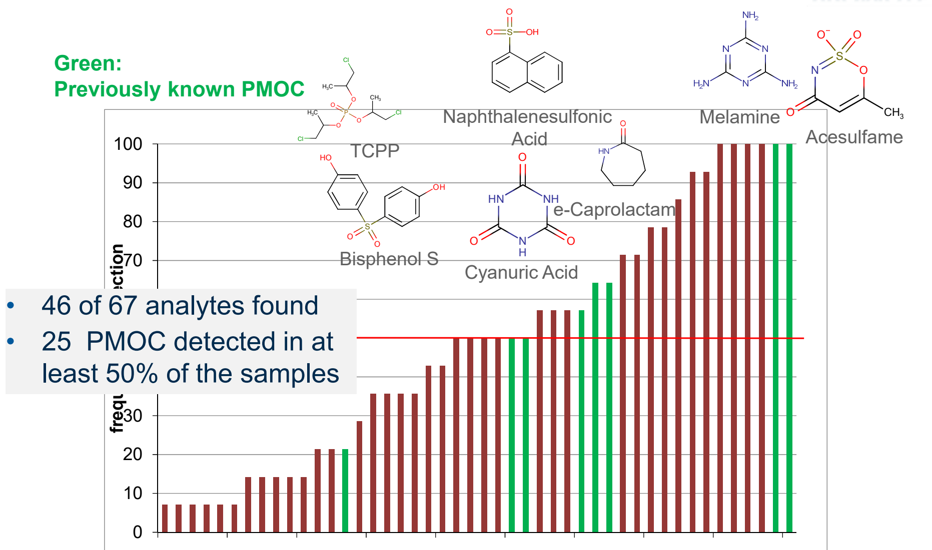
Persistence and Mobility Criteria for PM Compounds
Screening in REACH database
(13.000 chemicals)

PM Suspects
Monitoring in European Water Cycles + Drinking Water Plants

Treatment/Avoidance Options for PM Compounds

Regulatory Needs
PMT in REACH

Screening Data for PMOC – 3 Methods



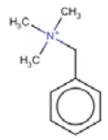
- 46 of 67 analytes found
- 25 PMOC detected in at least 50% of the samples

14 water samples (surface water, groundwater, bank filtrate) from 5 European countries

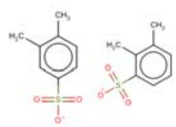
Results: Environmental monitoring

- Previously unknown PM compounds

Benzyltrimethyl ammonium

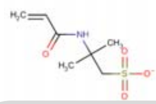


Dimethylbenzene sulfonic acid

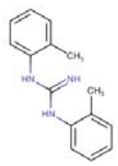


Trifluoro and Cl/Br methanesulfonic acids

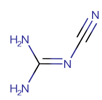
2-Acrylamido-2-methylpropane sulfonic acid



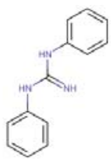
1,3-Di-*o*-tolylguanidine



Cyanoguanidine



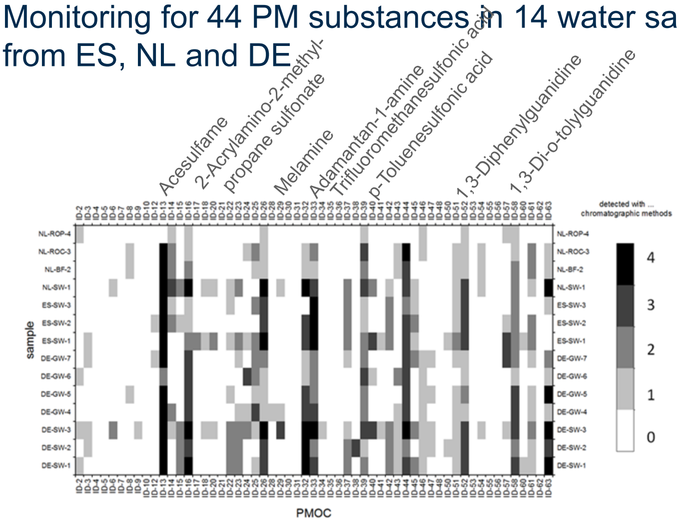
1,3-Diphenylguanidine



- Processing agents in
  - polymerization
  - vulcanization
  - production of resins
- Tires and rubber
- Disinfectants
- Washing and cleaning agents
- Textile industrie
- Water treatment
- Fertilizer

Monitoring in European Waters

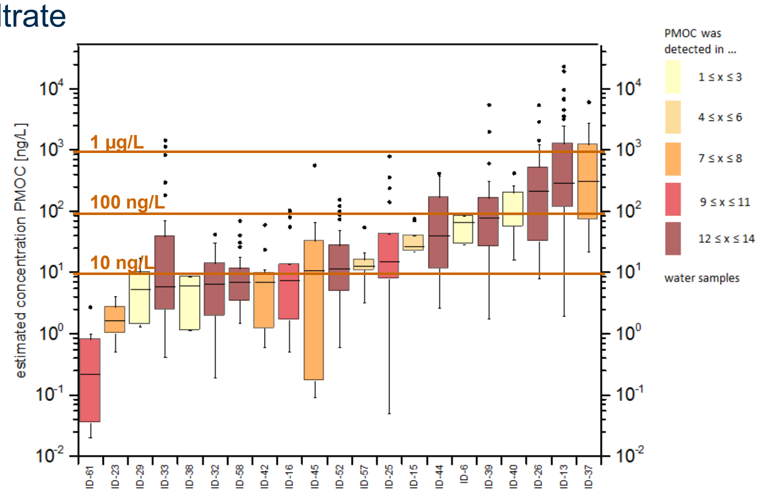
- Monitoring for 44 PM substances in 14 water samples from ES, NL and DE



Schulze et al. (2918) Water Res., Water Res. 153, 80.

Monitoring of PM Compounds

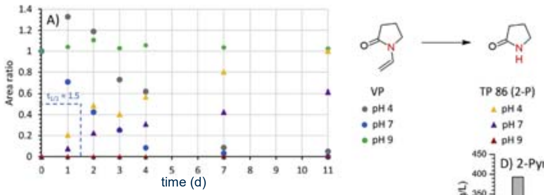
- Concentrations in surface water, groundwater, bank filtrate



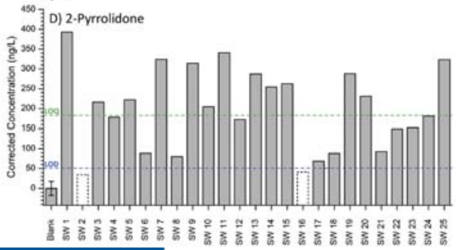
Schulze et al. (2918) Water Res., Water Res. 153, 80.

Formation of PM Substances from REACH Precursors

- Hydrolysis, photolysis, microbial transformation and abiotic oxidation (MnO_2)
- 12 PM precursors studied



Lab experiment on pH-dependent hydrolysis of 2 Vinylpyrrolidone



Search for 2-P in Hessian surface waters by HILIC-HRMS

Zahn et al. (2019) Water Res. 150, 86

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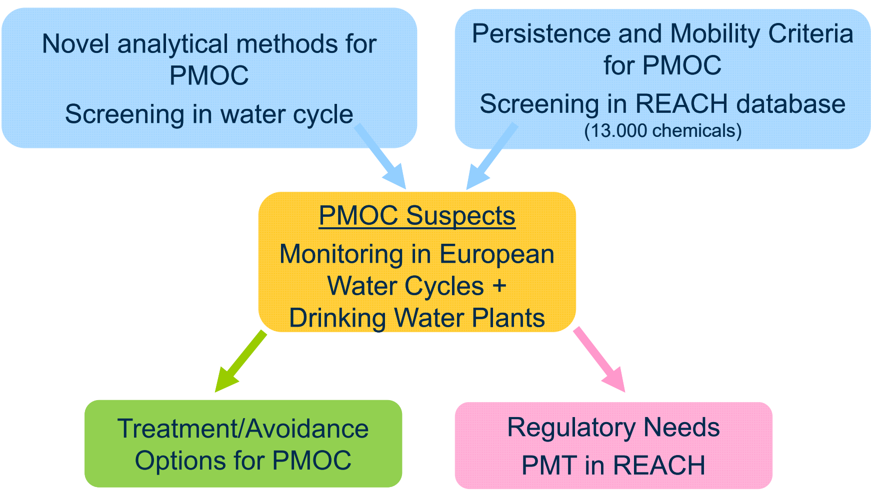
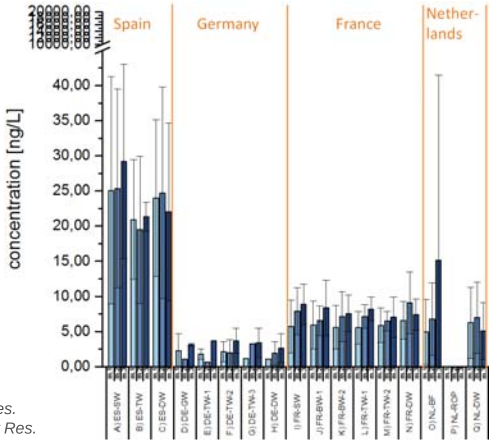
Protecting water resources from mobile trace chemicals



PM Chemicals in Drinking Water Preparation

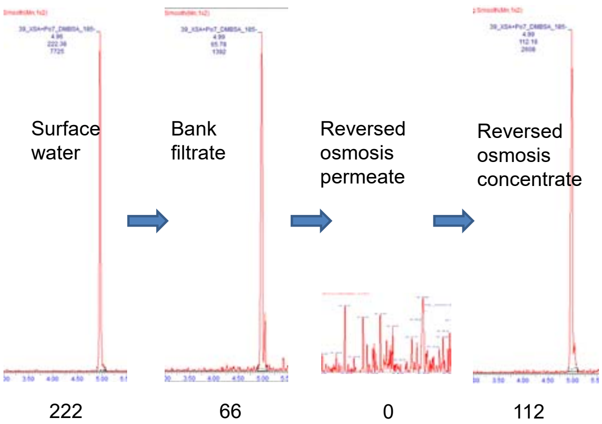
- Trifluoromethanesulfonic acid



Zahn et al., (2016) Water Res.
Schulze et al., (2019) Water Res. 153, 80.

PM Chemicals in Drinking Water Preparation

- 2,3-dimethylbenzenesulfonic acid by SFC-MS
  - Bank filtration with full scale reversed osmosis (NL)

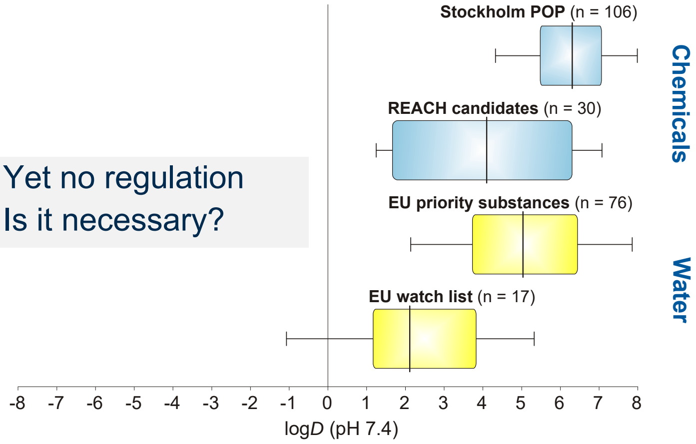


Mitigation Measures

- Need depends on health risk associated with the PMOC
  - PMT substances most urgent
- Measures depend on PMOC characteristics
  - Source (municipal/industrial/else)
  - PMOC as parent compound or transformation product
  - Discharge characteristics (permanent/event driven)
- Possible
  - Remove - Improve treatment
    - source, wastewater, drinking water
  - Reduce - Avoid discharge/release
    - Change use (open/closed systems)
    - Substitution
  - Regulate - Regulation of PMT substances

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

Conclusions

- PM compounds in the water cycle and in drinking water are an issue in partially closed water cycles and in wastewater reuse
- Data quality on P and M properties of chemicals still limited
- Analytical methdos for very polar contaminants need ongoing improvement
- Occurrence of only 70 (of 1000?) PM compounds studied yet
- Removal measures are limited
  - No sorption, no biodegradation
  - Oxidation?
- Avoiding the release of PM compounds important, if also toxic (PMT)

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- Joint Program Initiative (Water JPI) Pilot Call 2013
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  - Spanish Ministry of Economy and Competitiveness (JPIW2013-117)

Thank you very much for your attention!