PROMOTE

PROtecting water resources from MObile Trace chEmicals

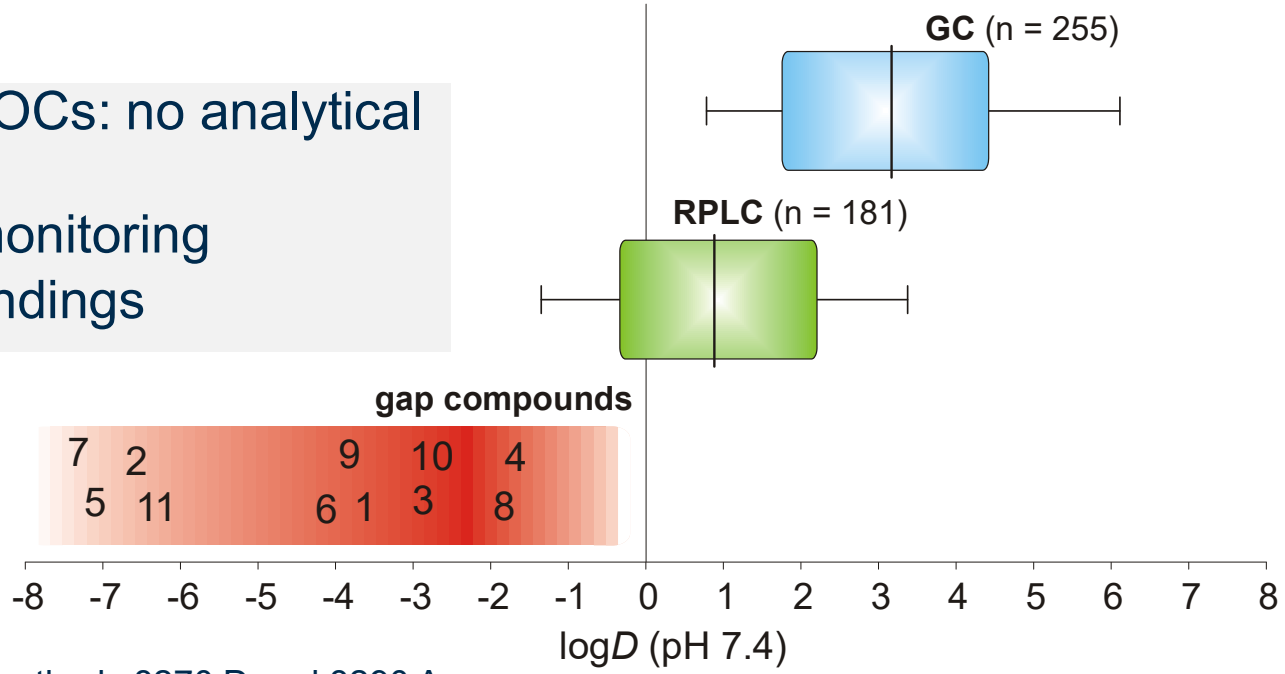
Urs Berger, Hans Peter H. Arp, Hervé Gallard, Thomas P. Knepper, Michael Neumann, José Benito Quintana, Pim de Voogt, Thorsten Reemtsma

Water JPI final evaluation meeting, Helsinki, June 4, 2018

Background: Persistent and mobile organic chemicals (PMOCs)

Polarity (logD_{ow}) of analytes covered by GC- or RPLC-MS analysis

For PMOCs: no analytical method
→ no monitoring
→ no findings



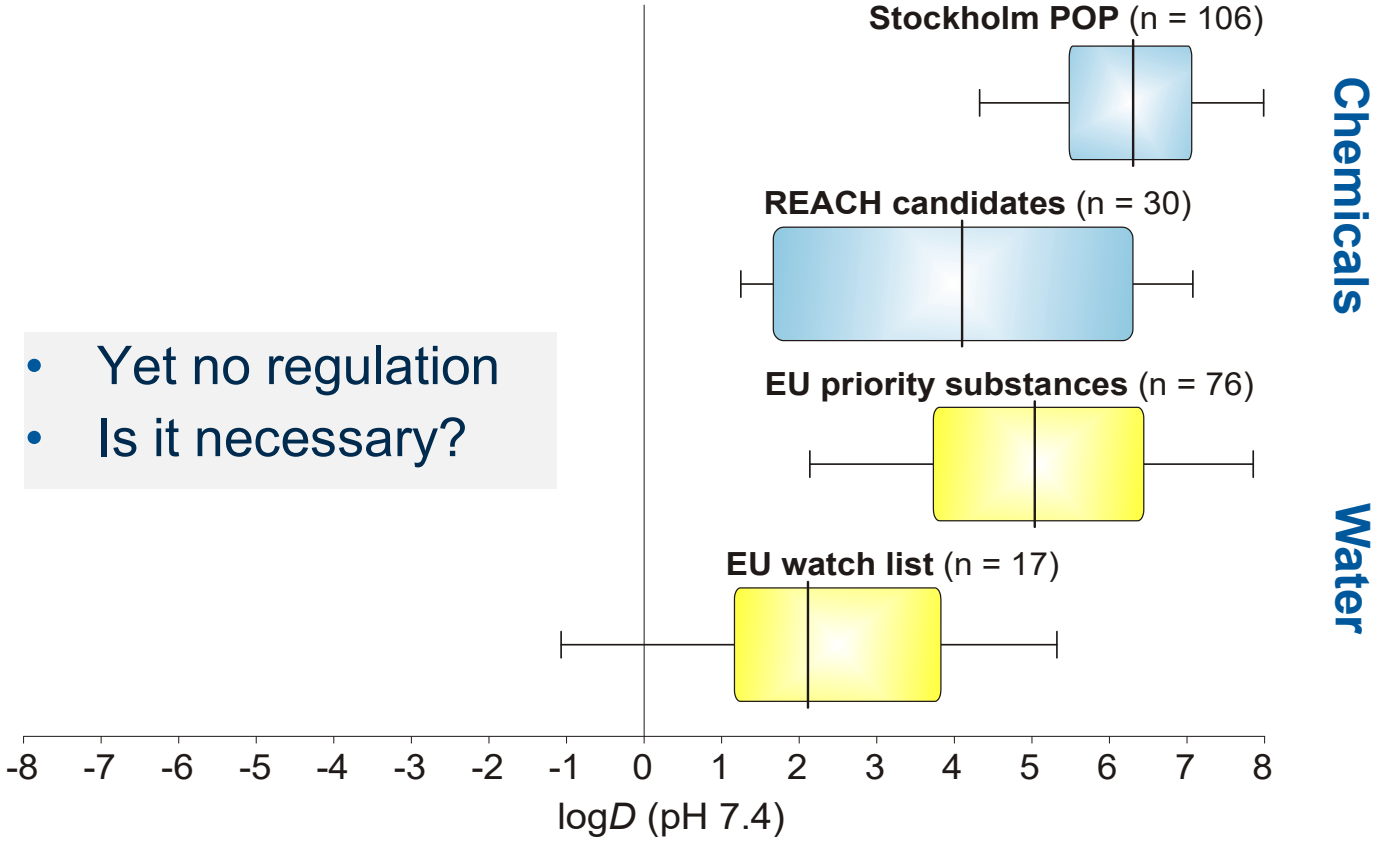
GC-MS: EPA methods 8270 D and 8290 A

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

Background: Persistent and mobile organic chemicals (PMOCs)



- Yet no regulation
- Is it necessary?

REACH candidates of SVHC, REACH, Article 57, d-f

Priority substances according to Water Framework Directive (WFD)

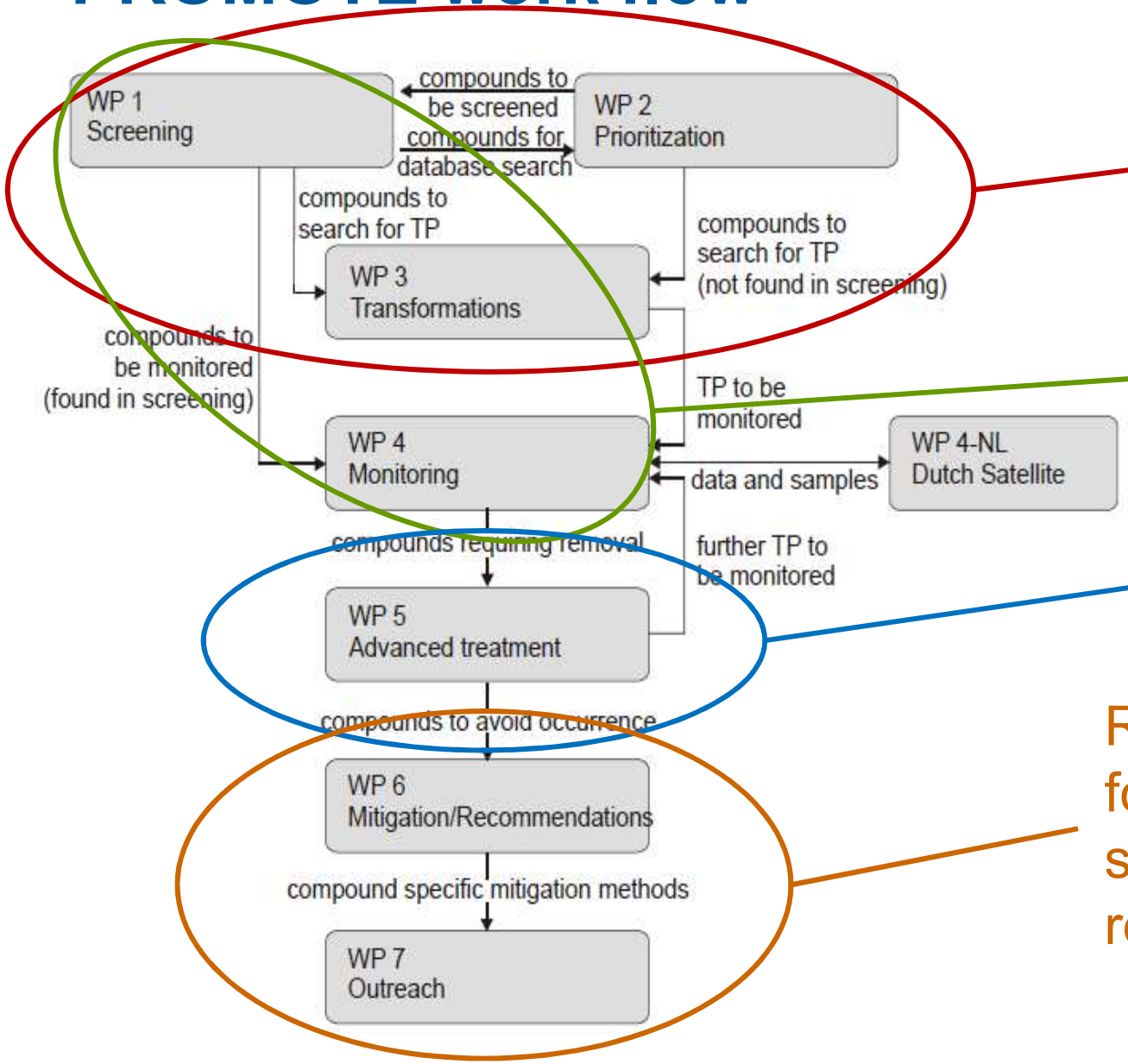
Watch list of the WFD

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

Overarching aim

- PROMOTE aimed at answering the question whether there is a need as well as the potential for regulatory protection of drinking water resources with respect to PMOCs
- PROMOTE linked European chemicals policy (REACH) with water policy (e.g. WFD)

PROMOTE work flow



Identification and prioritization of PMOCs

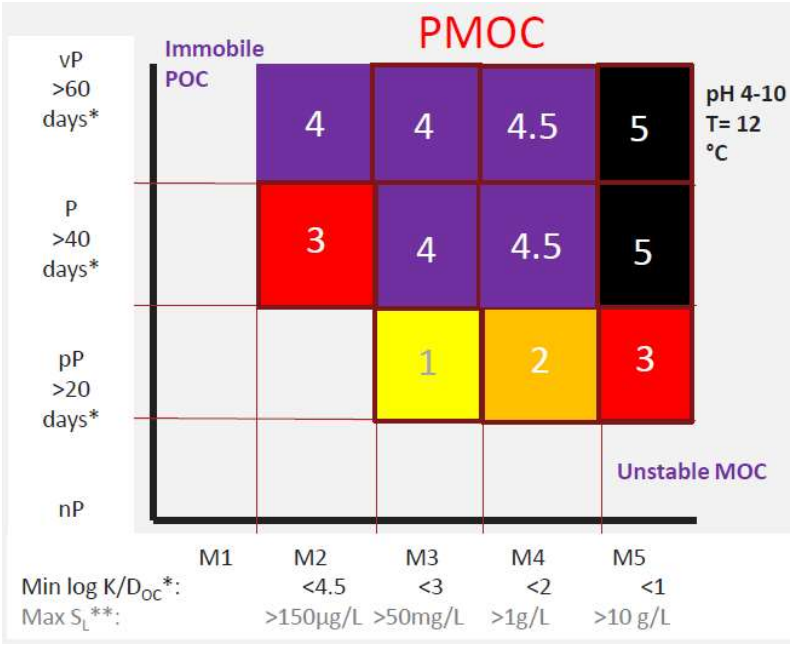
Analytical methods and monitoring

Advanced clean-up strategies

Recommendations for mitigation strategies and regulation

Results: Identification and prioritization of PMOCs by modeling

(H.P.H. Arp, M. Neumann, U. Berger, T. Reemtsma)



Use descriptors

Marketing volumes

Estimating P and M

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

Ranking emission potential

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

→ Ranked list of 1100 suspected PMOCs

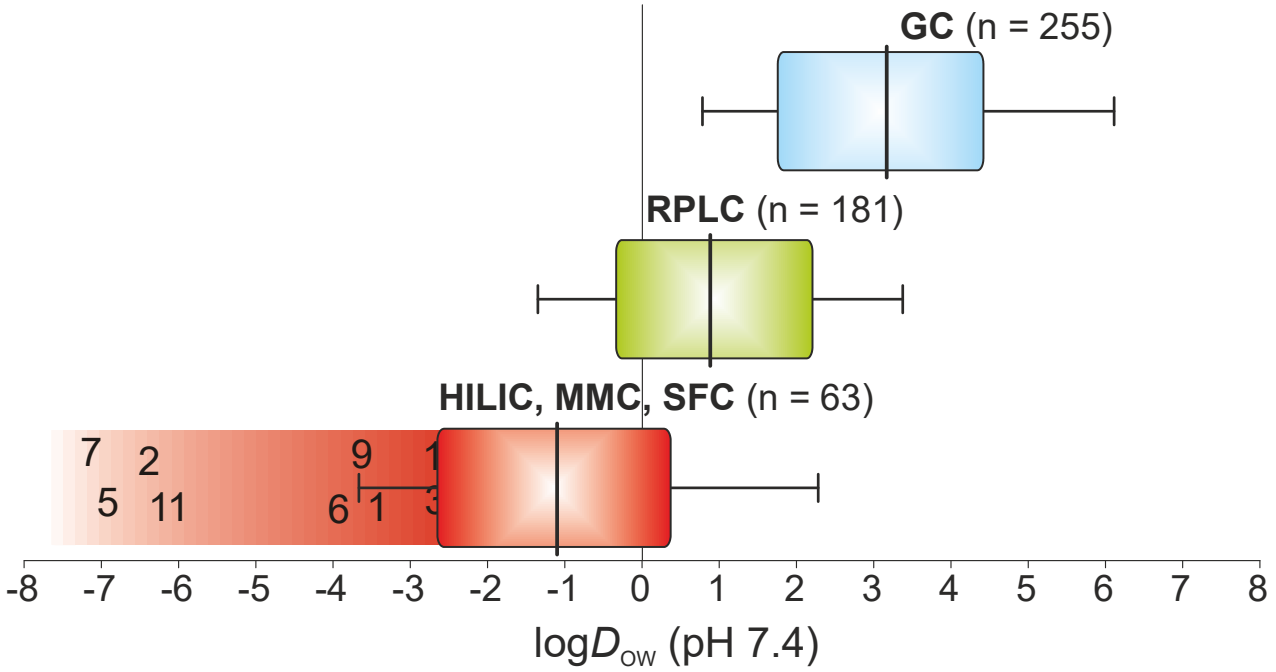
→ 70 compounds chosen for monitoring

Results: Analytical methods

(J.B. Quintana, T. Knepper, U. Berger, T. Reemtsma)

“Novel” separation methods (chromatography) and detection (MS)

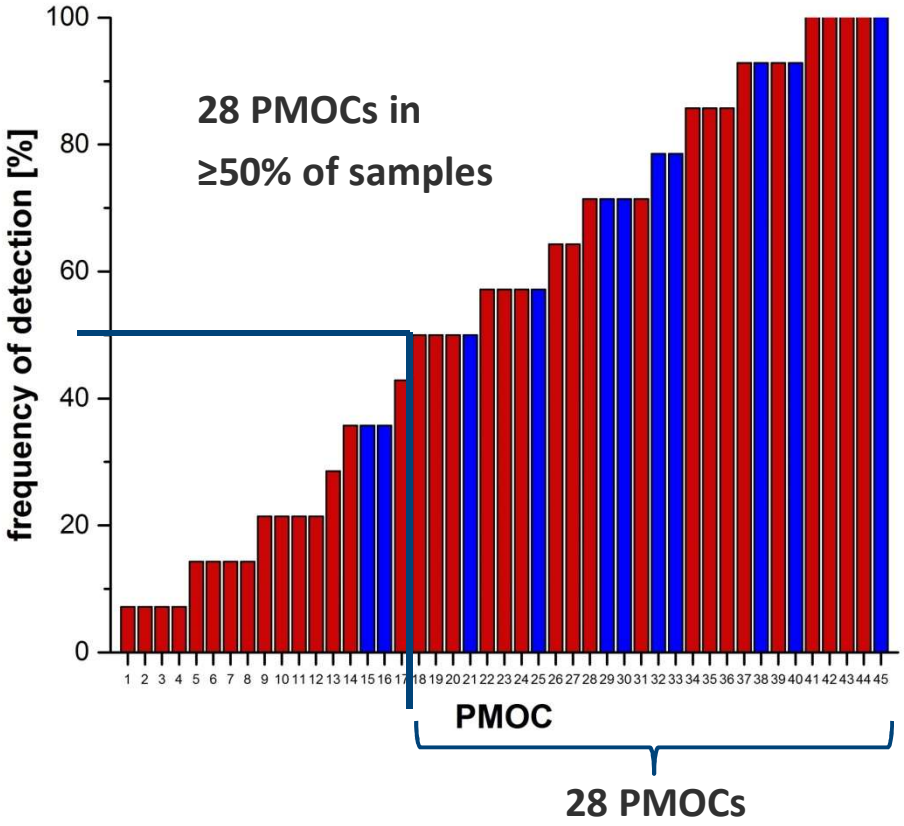
- Supercritical Fluid Chromatography (**SFC**)-qTOF-HRMS
- Hydrophilic Interaction Liquid Chromatography (**HILIC**)-MS/MS
- Mixed Mode Liquid Chromatography (**MMLC**)-qTOF-HRMS



Results: Environmental monitoring

(U. Berger, J.B. Quintana, T. Knepper, P. de Voogt, T. Reemtsma)

14 water samples (surface water, groundwater, bank filtrate, from drinking water treatment steps) from 5 European countries analyzed



A total of 45 (of 70 analyzed) PMOCs detected

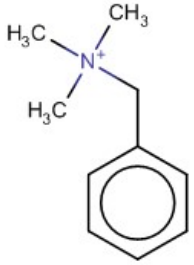
- Some PMOCs frequently detected, others in single samples
- Detection of „**known**“ as well as „**novel**“ PMOCs

Results: Environmental monitoring

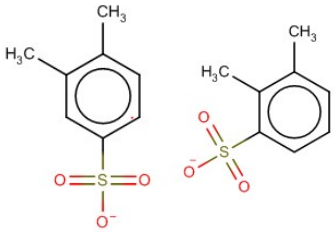
(U. Berger, J.B. Quintana, T. Knepper, P. de Voogt, T. Reemtsma)

Examples of „**novel**“ PMOCs

Benzyltrimethyl ammonium

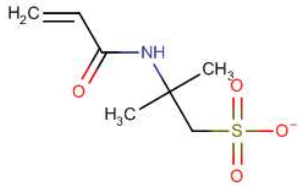


Dimethylbenzene sulfonic acid

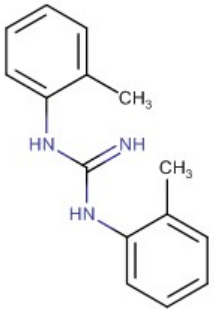


Trifluoro and Cl/Br methanesulfonic acids

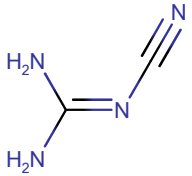
2-Acrylamido-2-methylpropane sulfonic acid



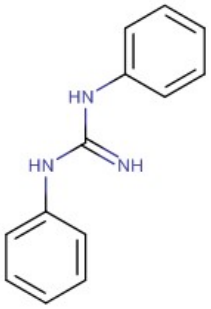
1,3-Di-*o*-tolylguanidine



Cyanoguanidine



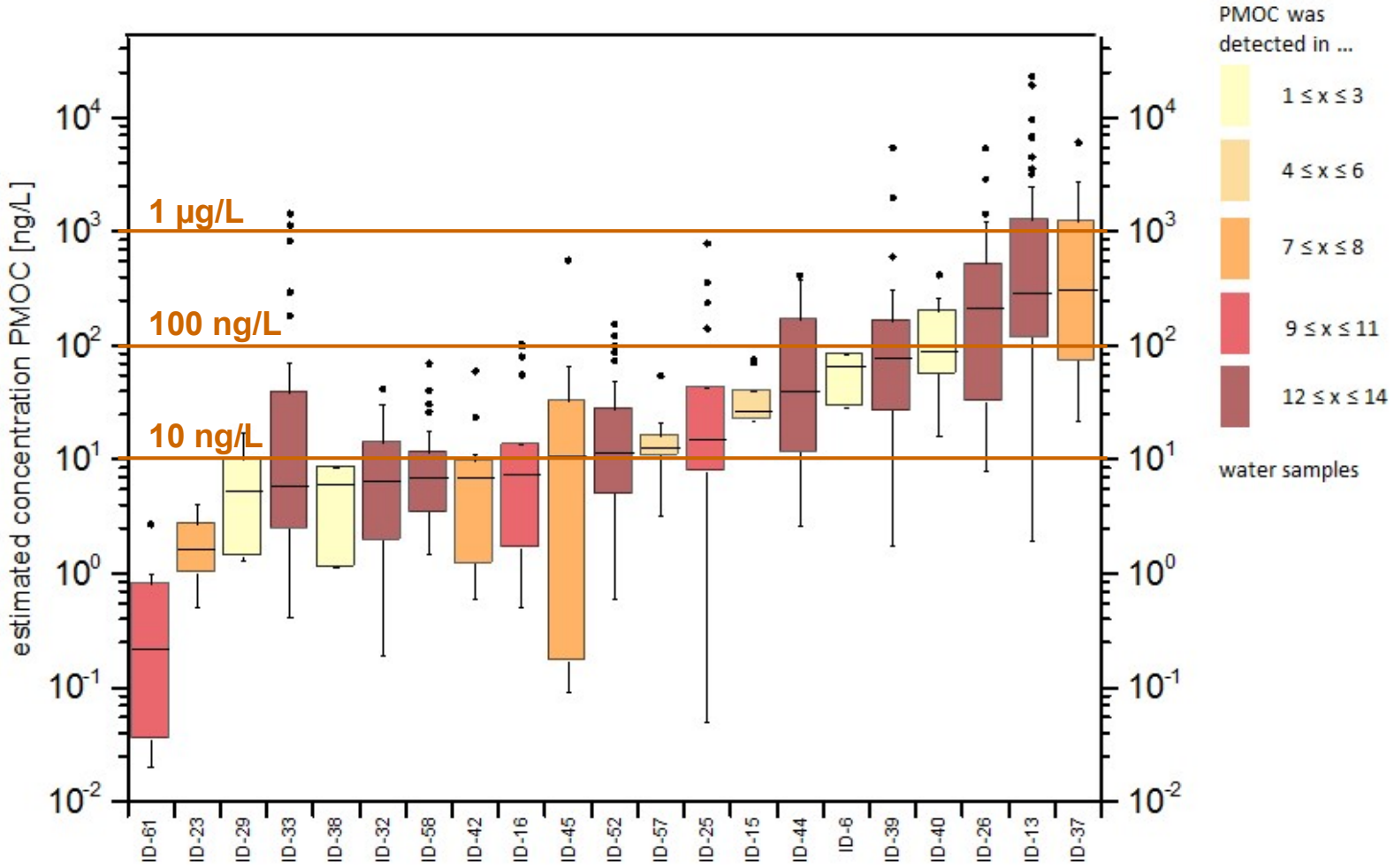
1,3-Diphenylguanidine



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

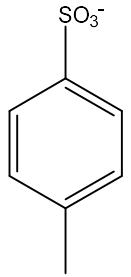
Results: Environmental monitoring

(U. Berger, J.B. Quintana, T. Knepper, P. de Voogt, T. Reemtsma)

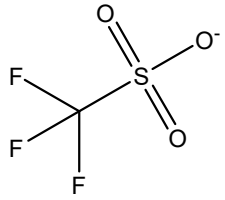


Results: Advanced drinking water treatment (H. Gallard, J.B. Quintana)

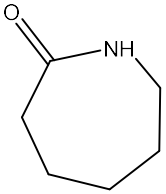
Examples of PMOCs that are only poorly or not at all removed by ozonation and activated carbon treatments



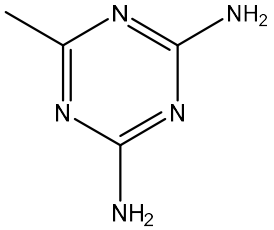
p-Toluenesulfonate



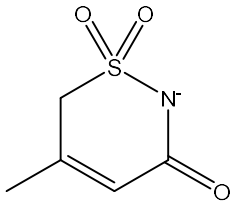
Trifluoromethanesulfonate



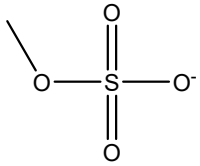
ε-Caprolactam



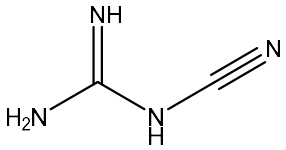
Acetoguanamine



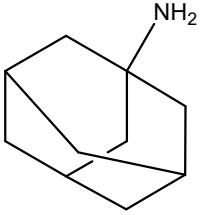
Acesulfame



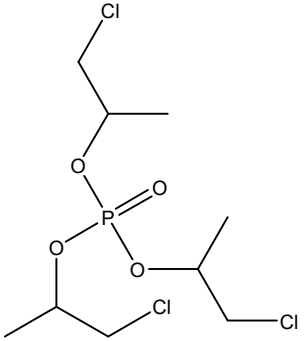
Methylsulfate



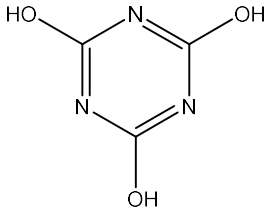
Cyanoguanidine



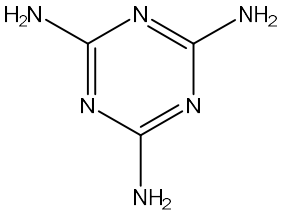
Adamantan-1-amine



TCPP



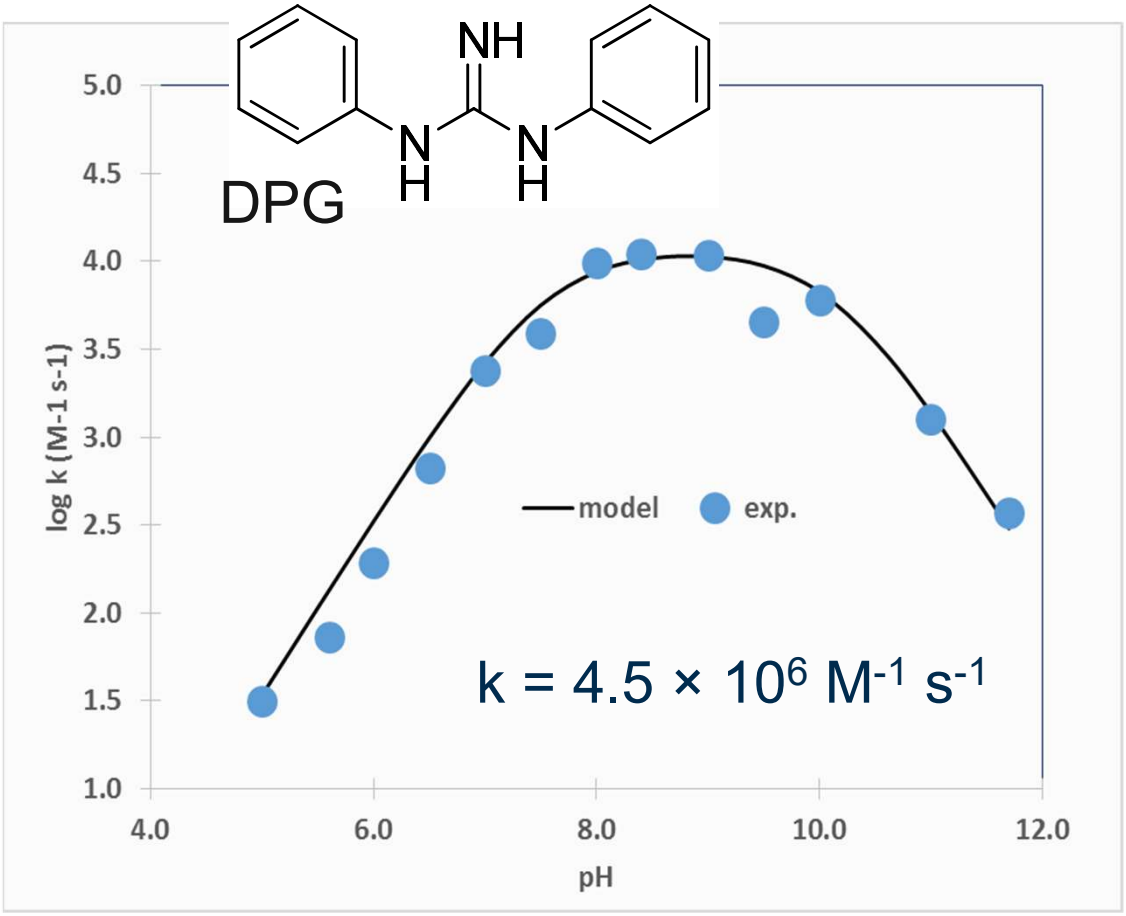
Cyanuric acid



Melamine

Results: Advanced drinking water treatment (H. Gallard, J.B. Quintana)

Other options? → Transformation with chlorine



Very fast reaction with chlorine

$t_{1/2}$ <10 s (1 mg Cl_2/L, pH >7)

BUT

A suite of chlorinated TPs formed that are more persistent and more toxic than DPG!

Kinetic model

HOCl + DPG → Products k

$HOCl = ClO^- + H^+$ Ka_{HOCl}

$DPG^+ = DPG + H^+$ Ka_G

Results: Advanced drinking water treatment (H. Gallard, J.B. Quintana)

Other options? → High pressure membrane processes

- **Nanofiltration (NF) as a polishing treatment after conventional treatments**
  - Efficiency depends mainly on the molecular weight (MW) and MW cut-off of the membranes (e.g. NF90 or NF270)
  - Removal rates between 10-20% (small molecules <200-220 g mol^{-1}) and 90% (largest molecules) for NF270 membrane

- **Reverse Osmosis (RO) instead of conventional treatments**
  - Removal rates usually >80% (e.g. 86% for Caprolactam at 8 bars with BW30LE membrane)
  - High removal rates for ionic (even small) compounds (repulsion)
  - Lower removal rates for neutral small compounds (diffusion)
  - Practicability?

Collaboration

- Highly collaborative environment, strong interactions between WPs and between partners (each WP involved several partners)

  Examples

  - Analytical method transfer
  - PMOC identification and prioritization
  - Sampling campaigns (associated partners)
  - “Transformation” and “Advanced Treatment” WPs
  - Currently ongoing: Recommendations for mitigation

Coordination, mobility

- **Coordination** and organization was efficient, based on the active participation of all partners and associated partners supporting the consortium
- **Mobility**: 5 mobility actions performed
  - Method transfer
  - Emission model
  - Regulation (PMOCs as SVHC)
  - Identification of TPs
  - Advanced water treatment methods

Stakeholder engagement

- Important stakeholders were directly involved as partners (German Environment Agency) or associated partners (drinking water suppliers) → prerequisite for accomplishment of objectives
- Europe-wide dissemination workshop for stakeholders

Persistent and Mobile Organic Chemicals in the Water Cycle:

Linking science, technology and regulation to protect drinking water quality

23 – 24 November 2017, in Leipzig, Germany

Contributions from (amongst others)

- European Commission DG Environment
- ECHA
- European Chemical Industry
- National environmental protection agencies
- EU CIS Working Group on Groundwater

Impact and knowledge output

- Scientific papers: 10 published/10 manuscripts
- Feature article in ES&T chosen as third runner up of ES&T's best Feature Article of the year 2016
- Project results feed into PMT/vPvM regulatory efforts
- Prioritized PMOC list and analytical methods published → way forward is mapped

Continuation of the work in the future

- Two partners and stakeholder have applied for a follow-up project in Germany (BMBF)
- Two partners collaborate on PMT/vPvM regulatory issues
- Two partners and stakeholders prepare a follow-up proposal for INTERREG
- Several single-partner follow-up activities ongoing

Conclusions from PROMOTE

- Number of PMOCs in European water cycles much larger than anticipated
- Analytical gap narrowed, but still many PMOCs not covered by current screening methods
- Water quality monitoring should direct more effort towards PMOCs to ensure drinking water quality
- European chemicals' legislation should consider mobility
- TPs tend to be more mobile than parent chemicals and need to be considered

Acknowledgements

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Thank you for your attention!

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