Persistente, mobile und toxische (PMT) Stoffe
~
Eine Herausforderung für die Wasseranalytik und Wasserversorgung

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HELMHOLTZ CENTRE FOR ENVIRONMENTAL RESEARCH – UFZ

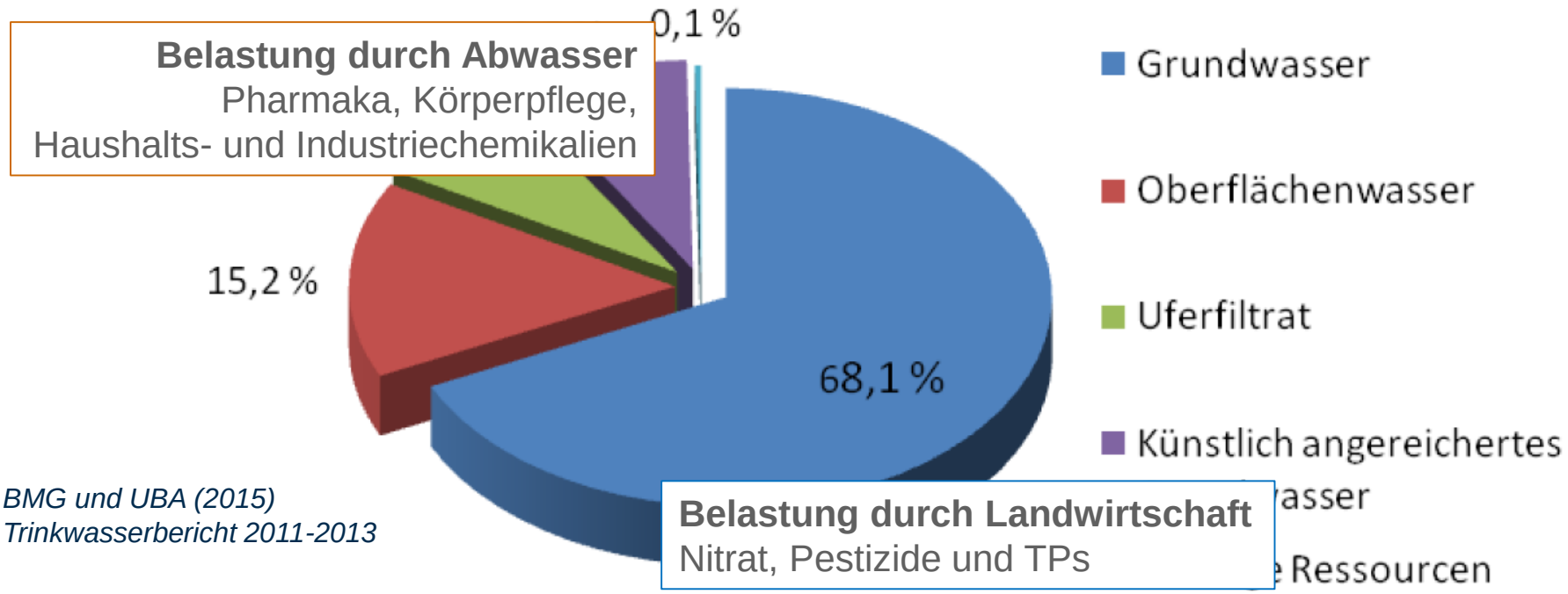
Bad Elster, 06.02.2020

PMT-Stoffe

- Warum ein Thema?
- Wie finden?
- Was ist da?
- Wie entfernen?
- Wie zu bewerten?
- Was tun?

Herkunft des Trinkwassers

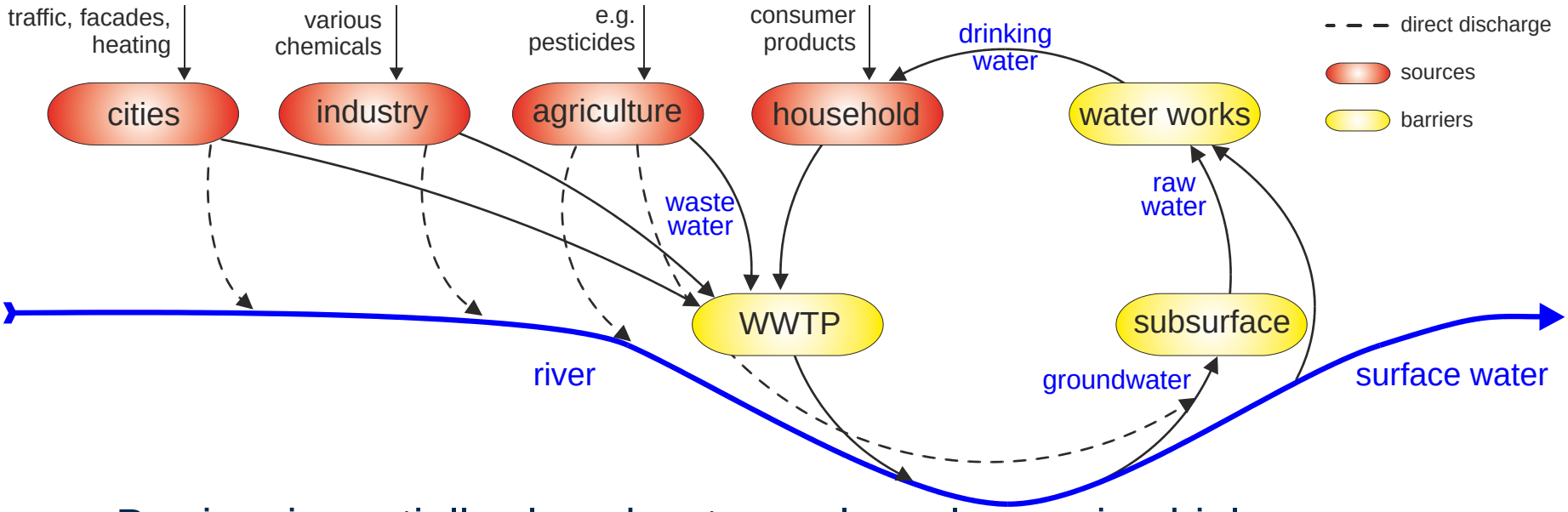
- Anteil der Rohwasser-Ressourcen in Deutschland



BMG und UBA (2015)
Trinkwasserbericht 2011-2013

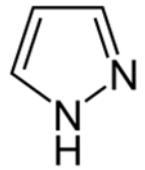
- In densely populated areas WWTP discharges to surface water often exceed 20 %

Der Waserkreislauf – ein Stoffkreislauf?



- 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

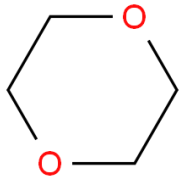
Incidental Findings in Drinking Waters



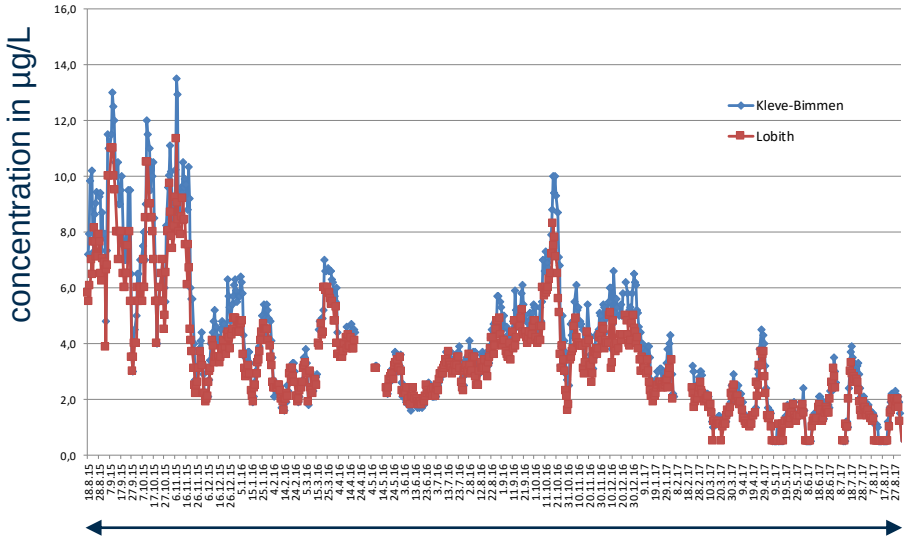
Pyrazol

- 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

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

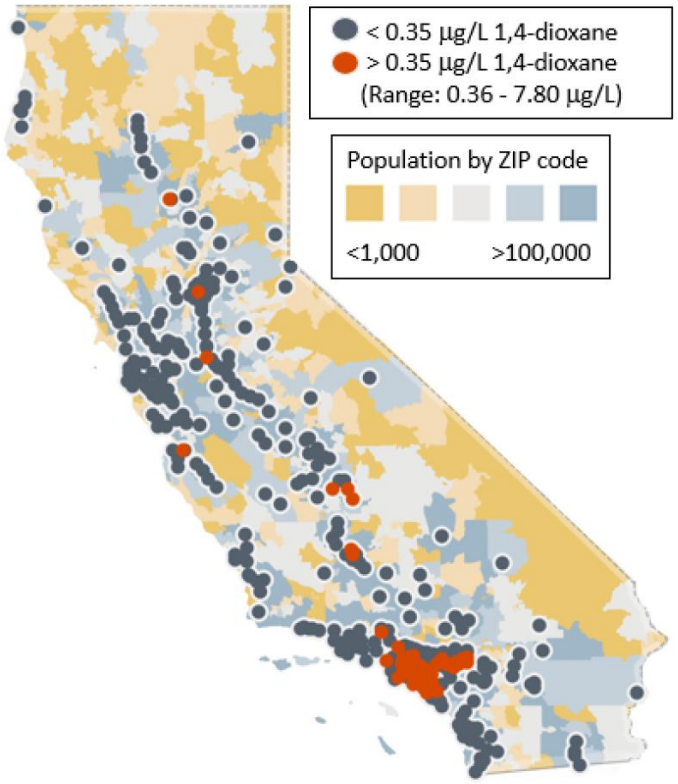


Concentration in River Rhine



Courtesy of C. Schmidt, Rheinenergie

Dioxan in California Drinking Water



Maximum concentrations of 1,4-dioxane in drinking water from the Sate Water Boards (2003 – 2018)

Counties with 1,4-dioxane detections

County	Max. detect (µg/L)	% of CA Population
Los Angeles	53	26%
Orange	26.7	8%
Santa Barbara	16	1%
Monterey	3.9	1%
San Diego	1.2	8%
Sacramento	1.1	4%

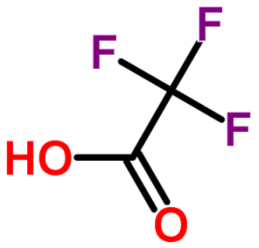
1,4-Dioxane in California drinking water (from UCMR3 (2013-2015).

- EPA's health-based reference concentration: 0.35 µg/L

Motivation

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

- **Present in drinking water since decades?**
- **Why detected so lately?**



Gesundheitliche Orientierungswerte

- Ca. 59 Stoffe/Nennungen
  - 33 Arzneimittel, Arzneimittelmetabolite oder Drogen-Metabolite
  - 8 Synthesezwischenprodukte oder Industriechemikalien
  - 6 perfluorierte Verbindungen + 7 mit TW_{LW}
  - 4 Lösungsmittel

Umwelt Bundesamt

Liste der nach GOW bewerteten Stoffe

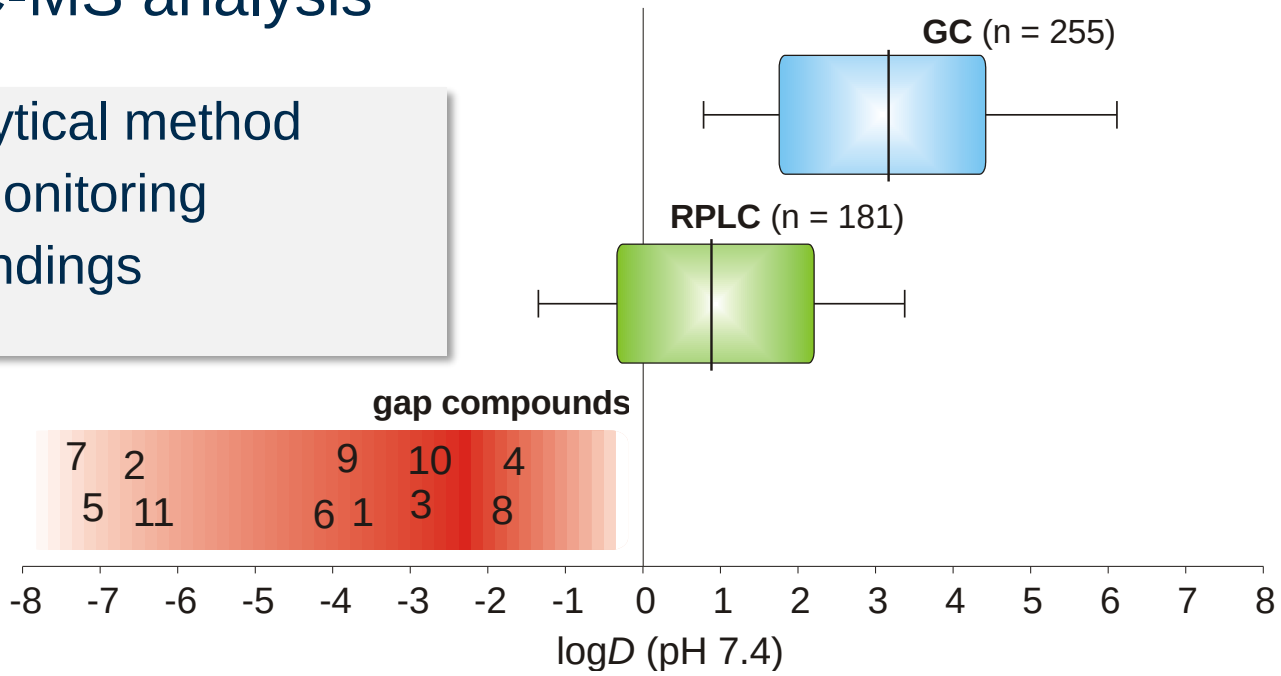
Substanz	CAS Nummer	GOW	Stand	Stoffklasse /Verwendung
Aciclovir	59277-89-3	0,3 µg/l	2016	Arzneimittel
Acridin-9-carbonsäure	332927-03-4	0,1 µg/l	2018	
AMDOPH (1-Acetyl-1-methyl-2				

- + 43 GOW-Werte für nr-Metabolite von PSM-Wirkstoffen

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

PMT-Stoffe

- Warum ein Thema?
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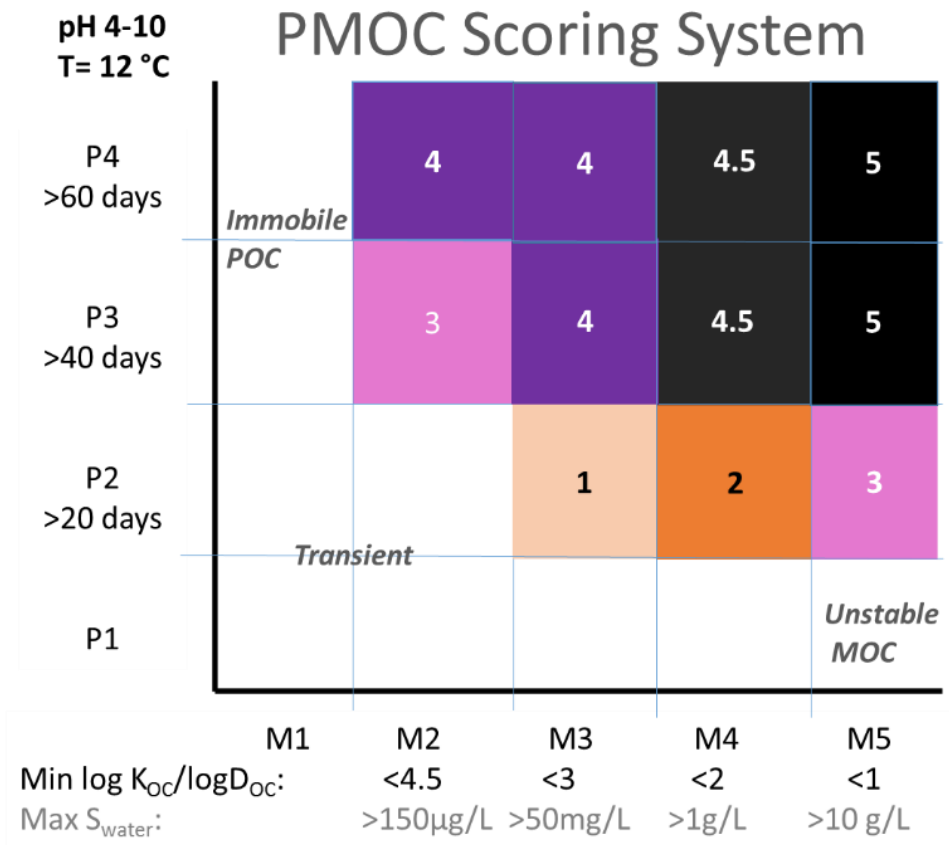
A Knowledge Gap

- 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)
    - log K_{oc} preferred

- Limited data quality for P and M
  - experimental data
  - modeling data

PM Scoring System



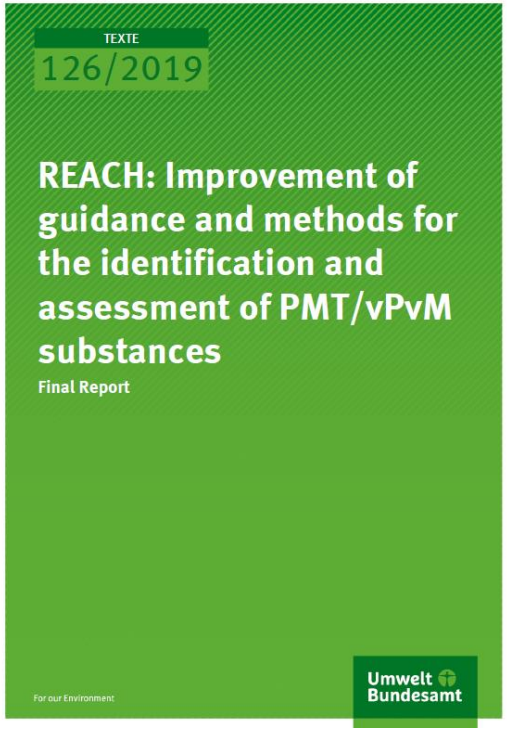
PM scores

- 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

Follow Up



- Hans Peter Arp, Sarah Hale
  - Norwegian Geotechnical Institute (NGI), Olso, Norway

Prioritizing PM Chemicals by Risk of Occurrence in the Water Cycle

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

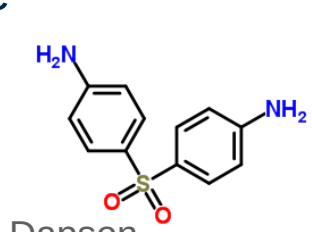
Prioritizing PM Chemicals (score 4 – 5) by Risk of Occurrence

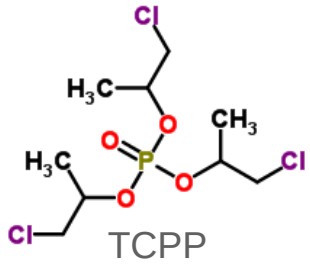
- High emission likelyhood
- Ranking according to E-score

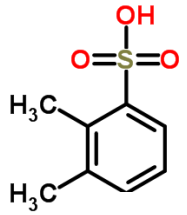
1105 PM chemicals with a potential risk to emit into the environment

TOP 300

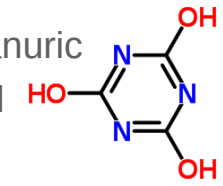
„Silver List“

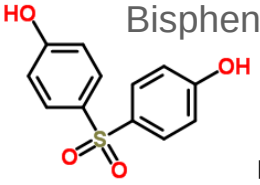


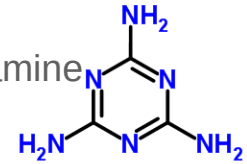


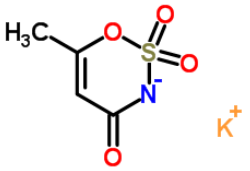


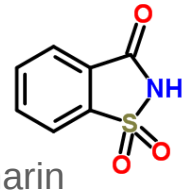
Cyanuric acid









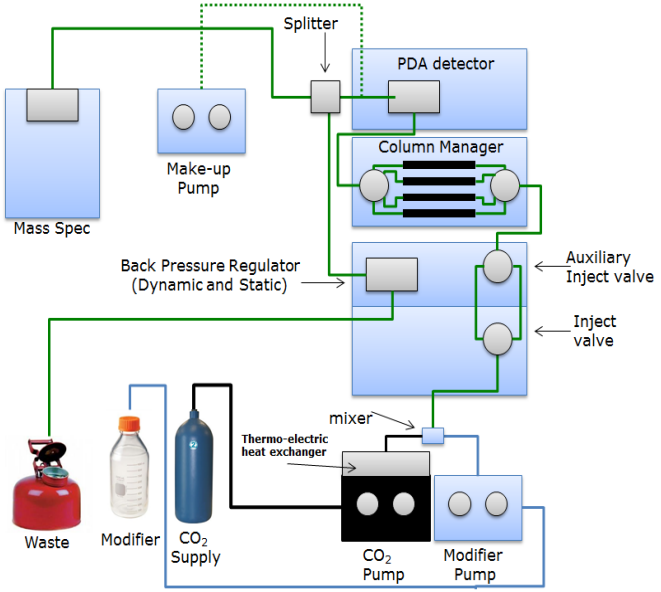


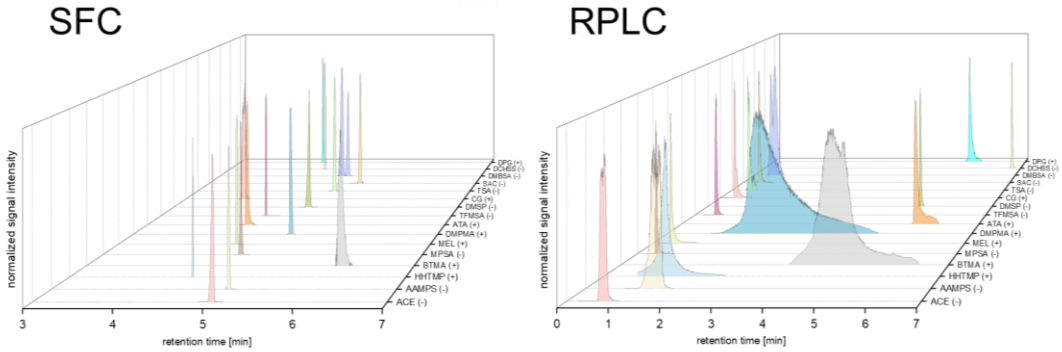
high emission likelyhood substances/precursors

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

Analytical gap for PM substances
The challenge with mobility

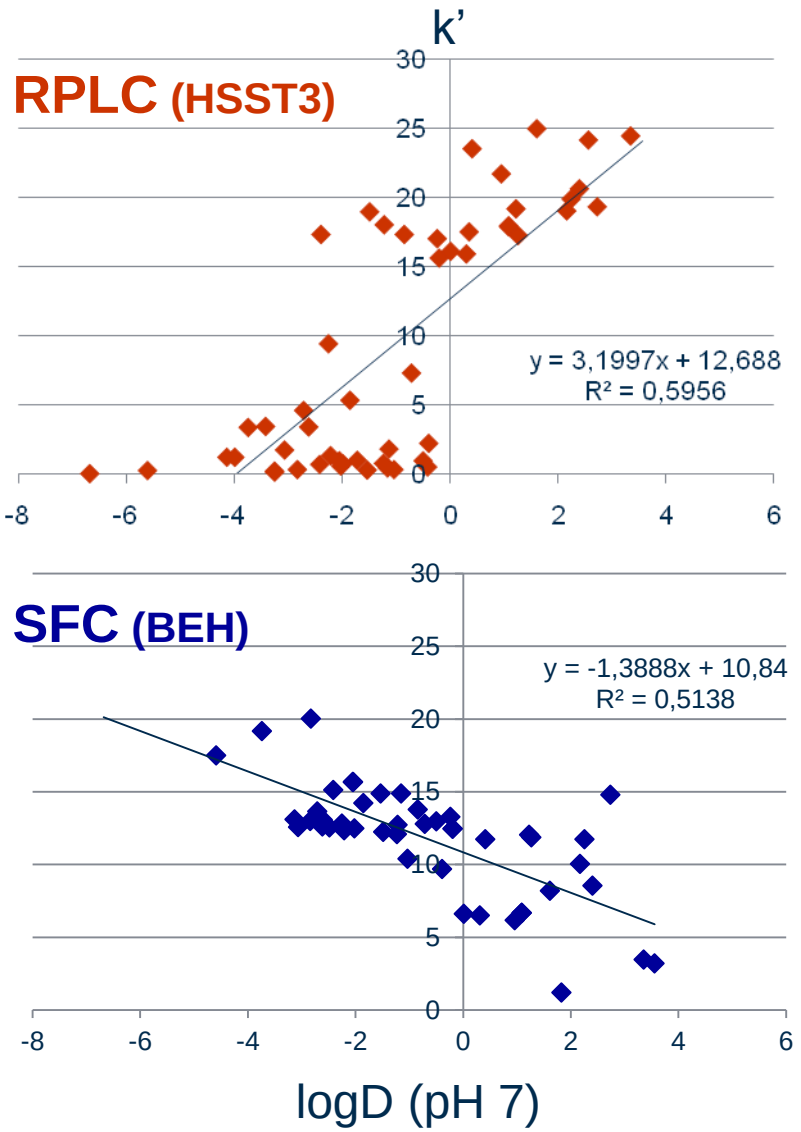
- Ion (exchange) chromatography
  - selective method for either anionic or cationic analytes
  - e. g. for TFA, Scheurer et al., 2017
- Mixed-mode LC
  - Montes et al., 2019
- HILIC (hydrophilic interaction liquid chromatography)
  - Zahn et al., 2016
- SFC (supercritical fluid chromatography)
  - Schulze et al., 2019

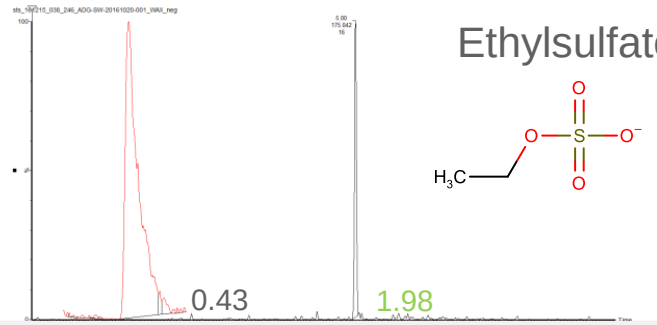




Zahn et al. (2016) Water Res., 101, 292
Scheurer et al. (2017) Water Res., 126, 460
Montes et al. (2019) Anal. Chem., 91, 5176
Schulze et al. (2019) Water Res., 153, 80

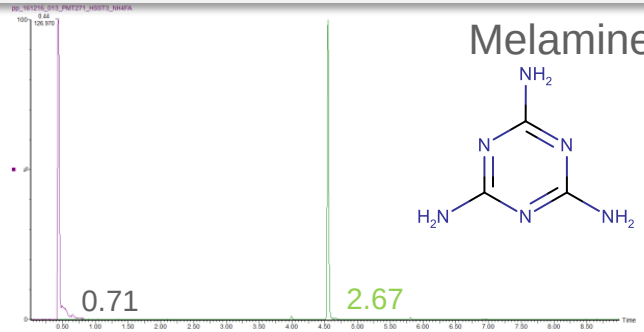
Determination of M Compounds by SFC-MS





Ethylsulfate

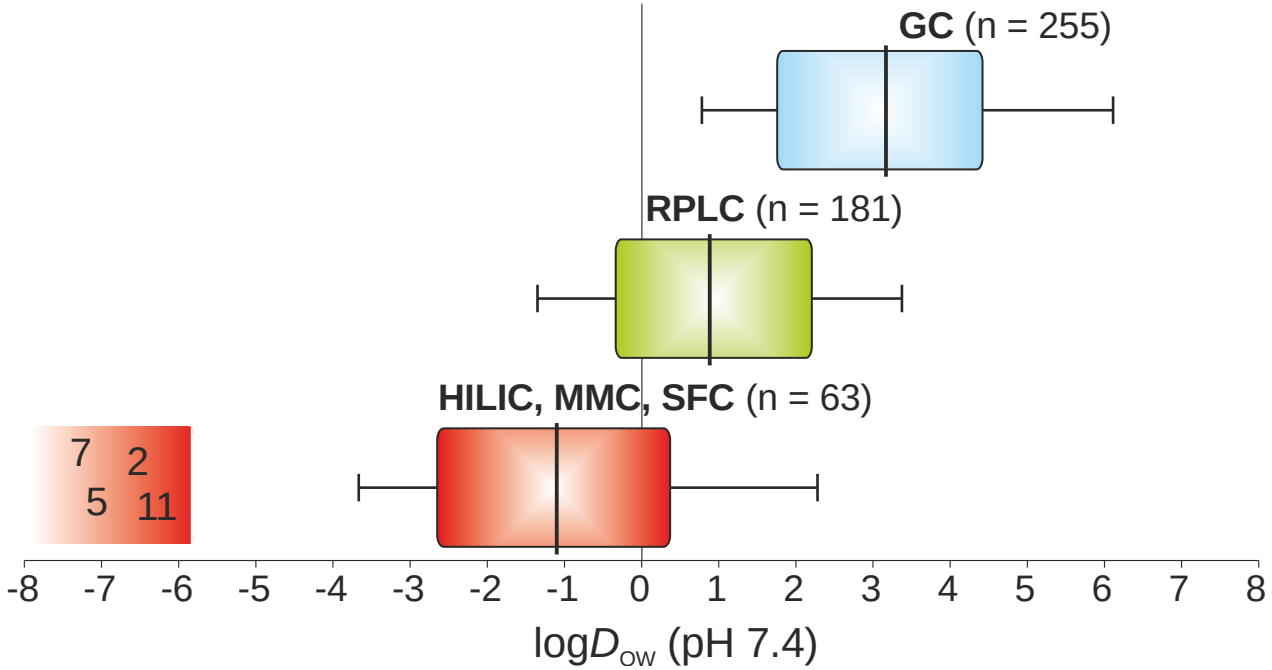
- Stronger retention of very polar analytes
- Better peak shape
- Sensitivity increase by a factor of 4 - 5



Melamine

Narrowing The Analytical Gap

- Improvement by HILIC, MMC and SFC

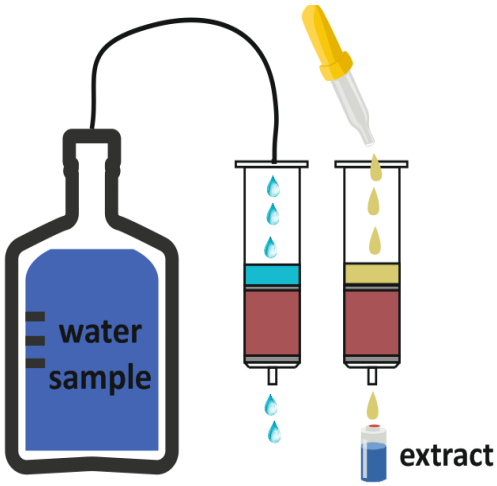


- Enrichment remains challenging

Reemtsma et al., unpubl.

Challenges in Enrichment from Water

- Solid-phase extraction
  - Retention too low or too specific
  - Mixed-mode SPE (graphitized carbon black, anion exchage, cation exchange)
    - (Köke et al., 2018)
- Freeze-drying
  - (Montes et al., 2017)
- (Azeotropic) evaporation
  - (Köke et al., 2018; Schulze et unpubl.)
- Inherent problem of all methods (of M substances!)
  - efficient separation from water matrix (e.g. DOM/salts) not possible



Montes et al. (2017) Environ. Sci. Technol., 51, 6250
Köke et al. (2018) Anal. Bioanal. Chem., 410, 2403

PMT-Stoffe

- Warum ein Thema?
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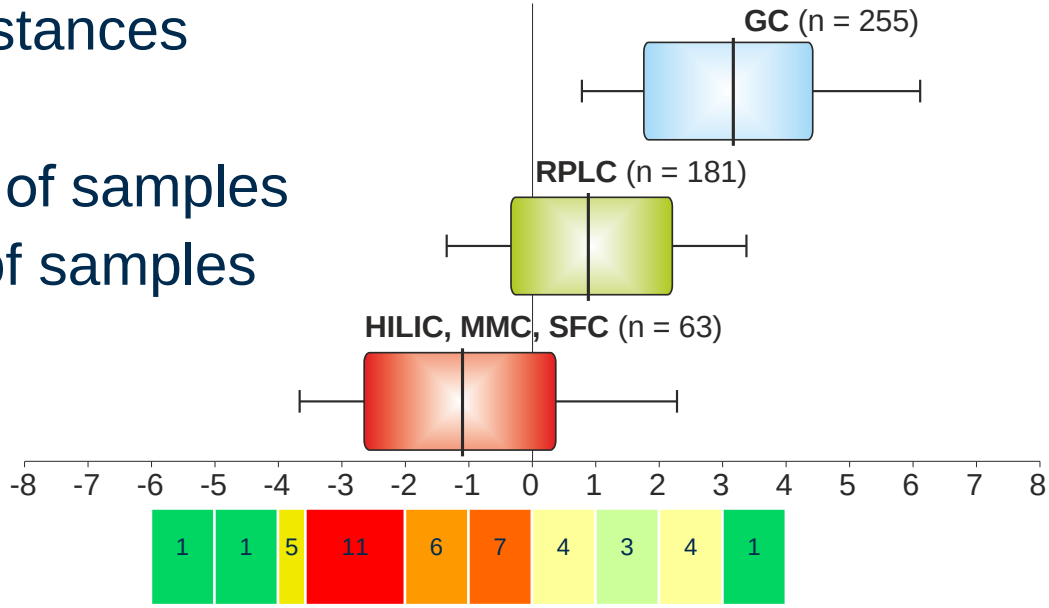
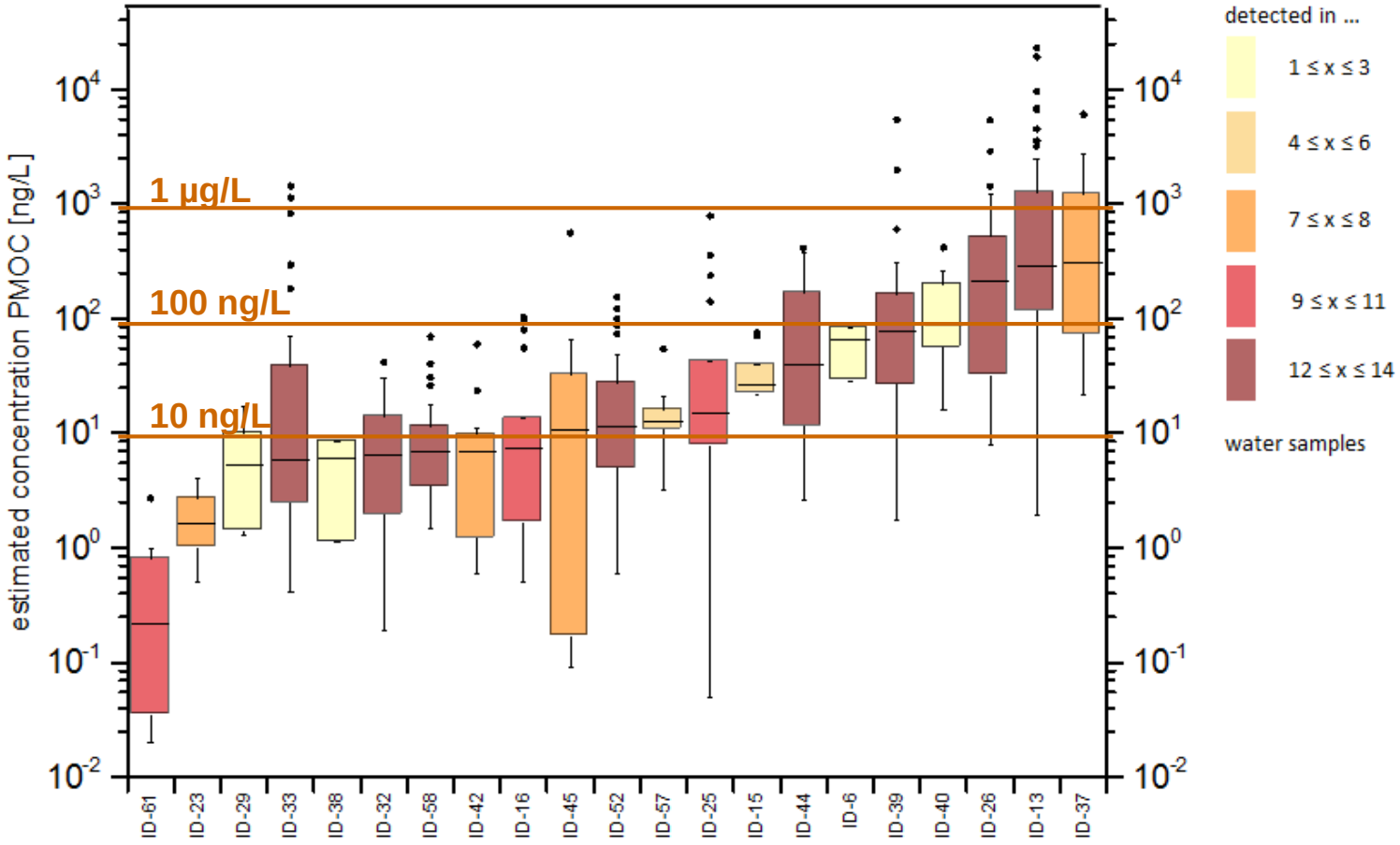
Recent Advances in Monitoring of PM Substances

- Application of MMLC-, HILIC- and SFC-MS
- 14 samples surface water, groundwater and bank filtrate from 5 European Countries
  - 57 analyzed PM substances
  - 43 detected (75%)
  - 21 detected in ≥50% of samples
  - 5 detected in 100% of samples



Monitoring of PM Compounds

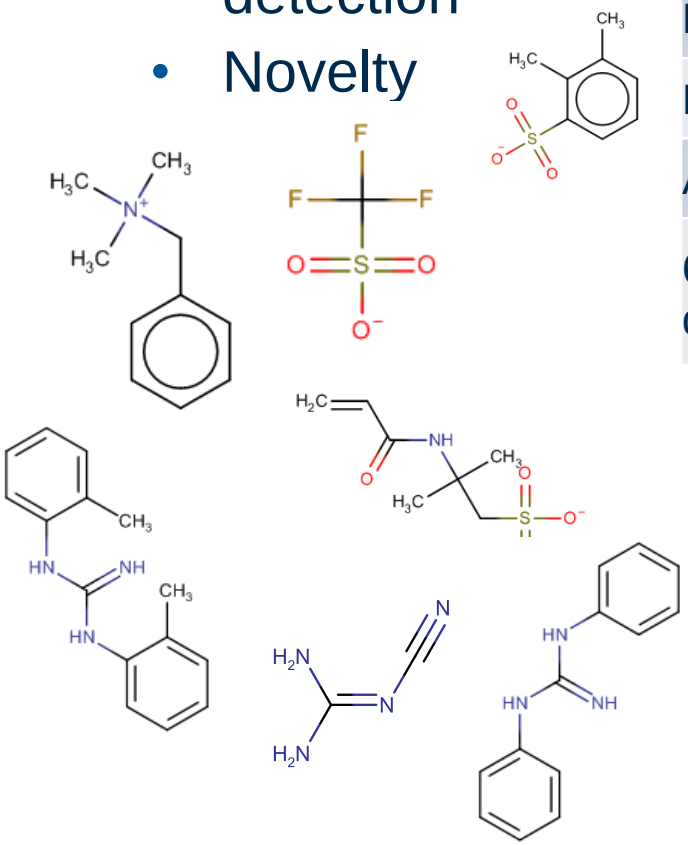
- Estimated concentrations in surface water, groundwater, bank filtrate



Schulze et al. (2919) Water Res.153, 80

PM Compounds Detected

- Prioritization by
  - frequency of detection
  - Novelty



Amines, amides, ammonium ions
Benzyldimethylamine
Benzyltrimethylammonium
Adamantan-1-amine
6-Methyl-1,3,5-triazine-diamine

Guanidines
Cyanoguanidine
1,3-Diphenylguanidine
1,3-Di-o-tolylguanidine

Sulfonic acids
Trifluoromethanesulfonic acid
p-Toluenesulfonic acid
Dimethylbenzenesulfonic acid
2-Acrylamino-2-methylpropane sulfonic acid

Sulfonamide
Toluenesulfonamide

Other
Methyl sulfate

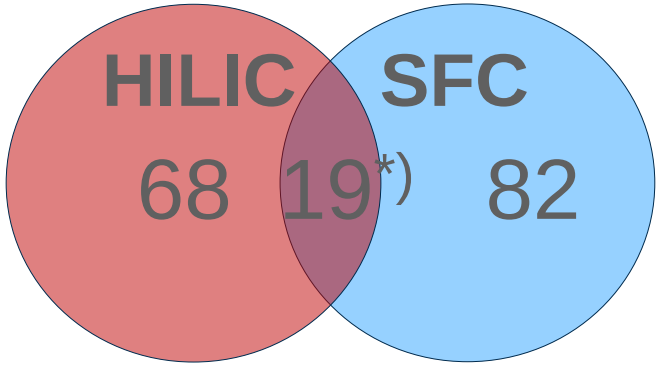
Schulze et al. (2019) Water Res. 153, 80-90.

Suspect Screening for 1400 PM Substances

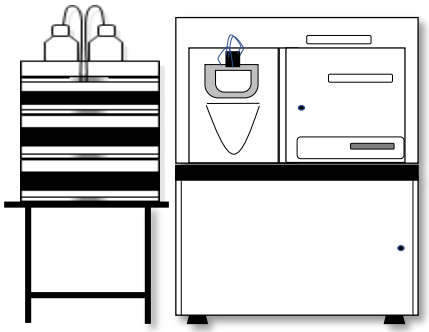
HILIC-HRMS (HSF)

SFC-HRMS (UFZ)

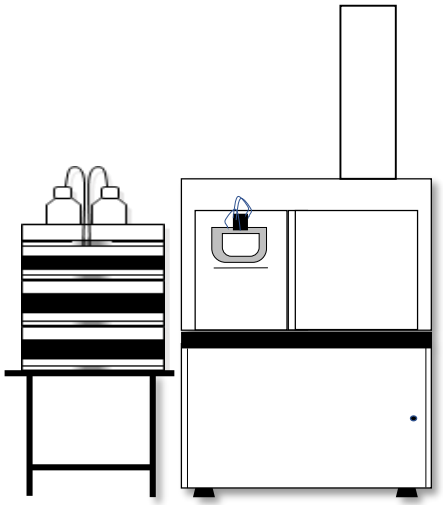
- 169 tentatively identified compounds:



*) based on exact *m/z* values



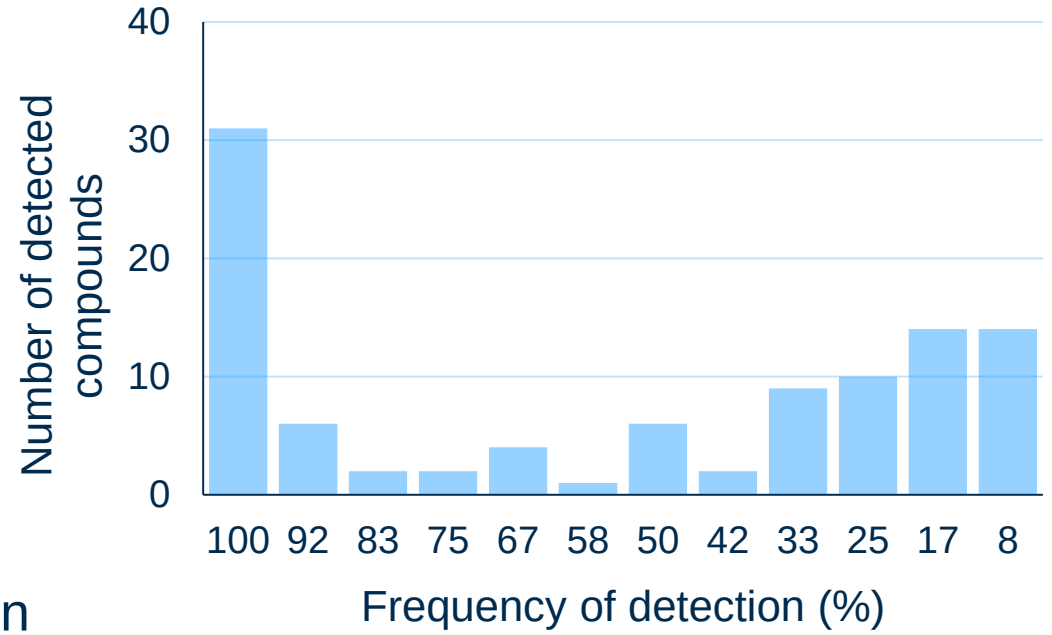
Eluent A: 5mM NH_4HCOO in ACN/H_2O (95/5)
Eluent B: 5mM NH_4HCOO in ACN/H_2O (5/95)
MS: Orbitrap Velos Pro (Thermo)



Eluent A: CO2
Eluent B: 10 mM NH_4HCOO in (H2O/MeOH 95/5)
MS: TOF (Synapt G2-S, Waters)

Befunde SFC-MS Suspect Screening

- Befunde

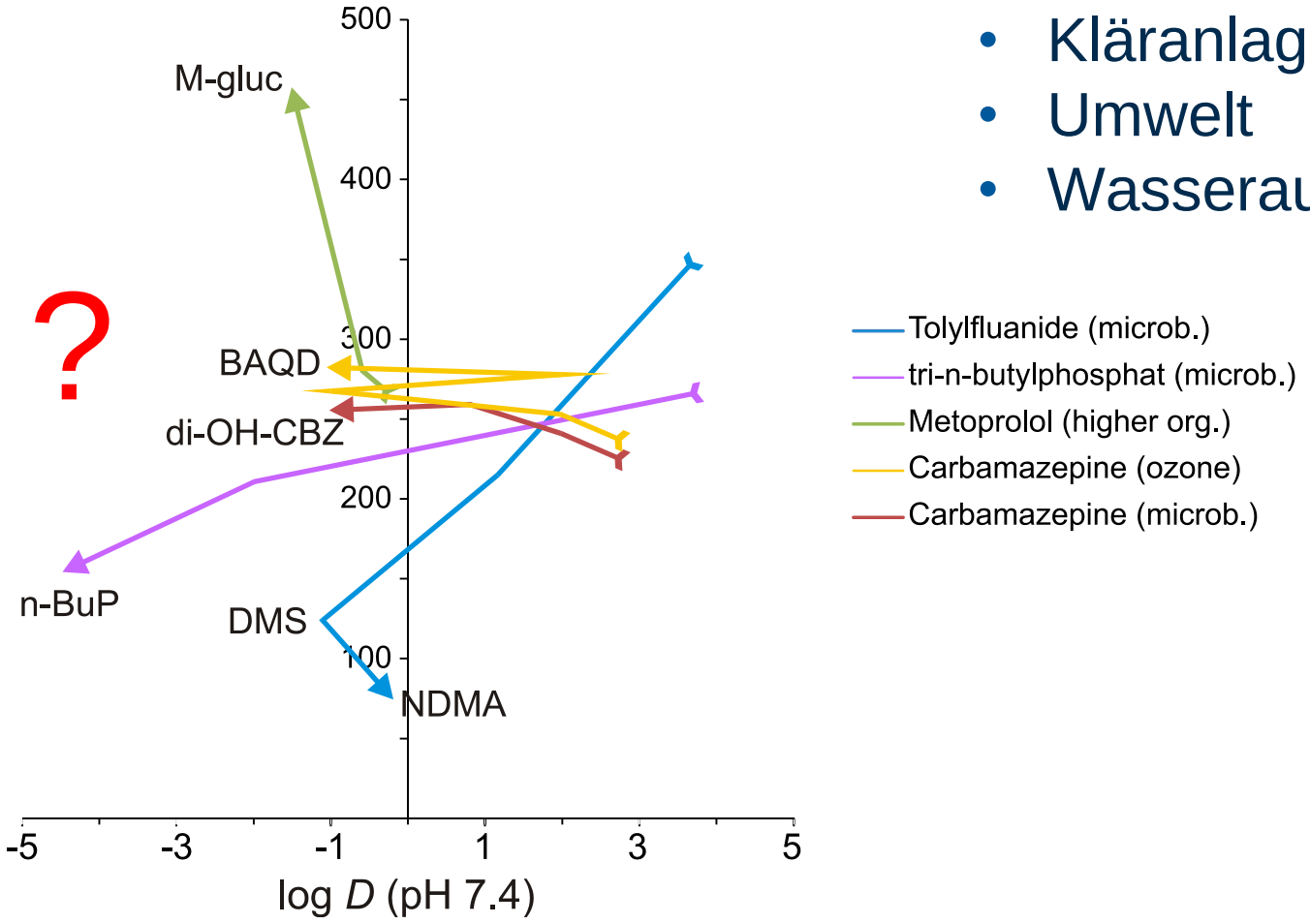


a. Omnipräsente Stoffe
   - Unspezifische Quellen
   - in „moderaten“ Konzentrationen im Oberflächenwasser
b. Lokale Kontaminationen
   - Aus spezifischen Emissionsquellen, z.B. einzelne Indu
   - mit h asser

- Was ist schlimmer?
  - b) schwieriger zu ermitteln als a)

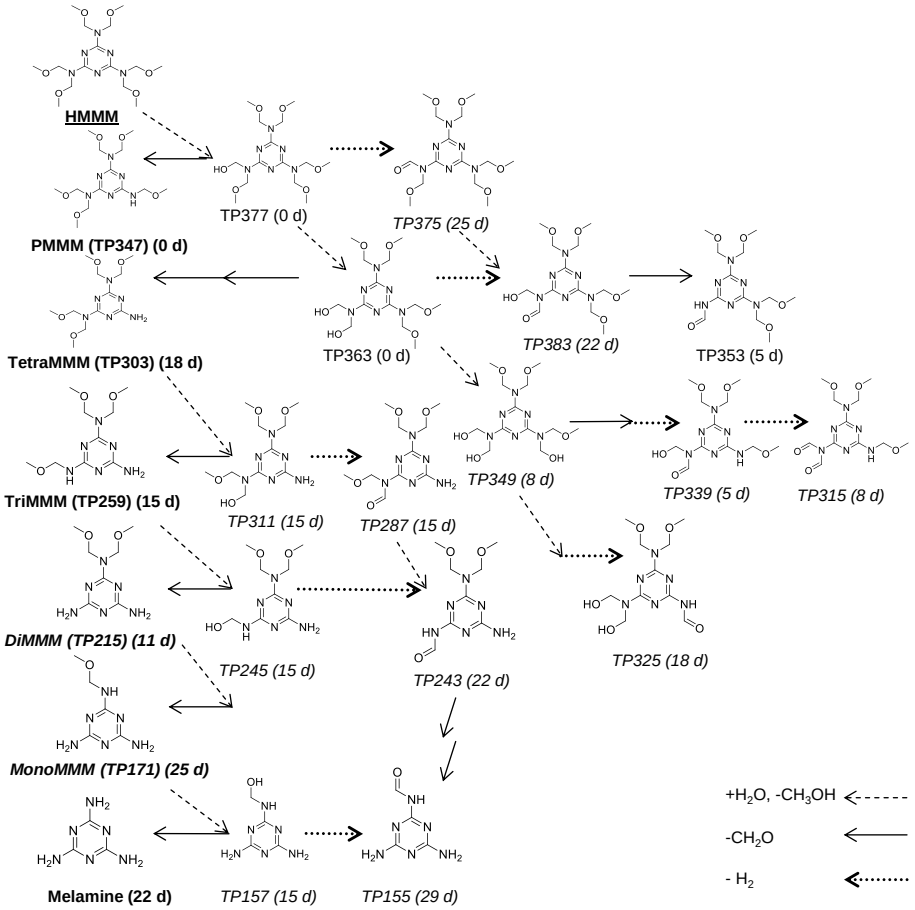
P and M: Effect of (Bio-) Transformation

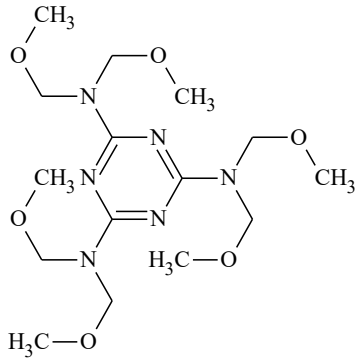
- Molecular mass vs. Polarity (log D)

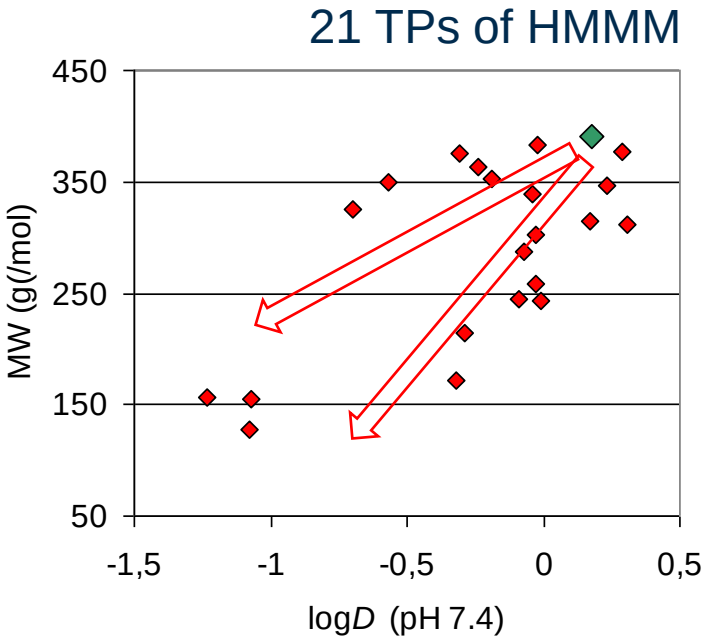


- Verwendung
- Kläranlagen
- Umwelt
- Wasseraufbereitung

Biotransformation of Hexamethoxymethylmelamine (HMMM)







Alhelou et al., Water Res. (2020)

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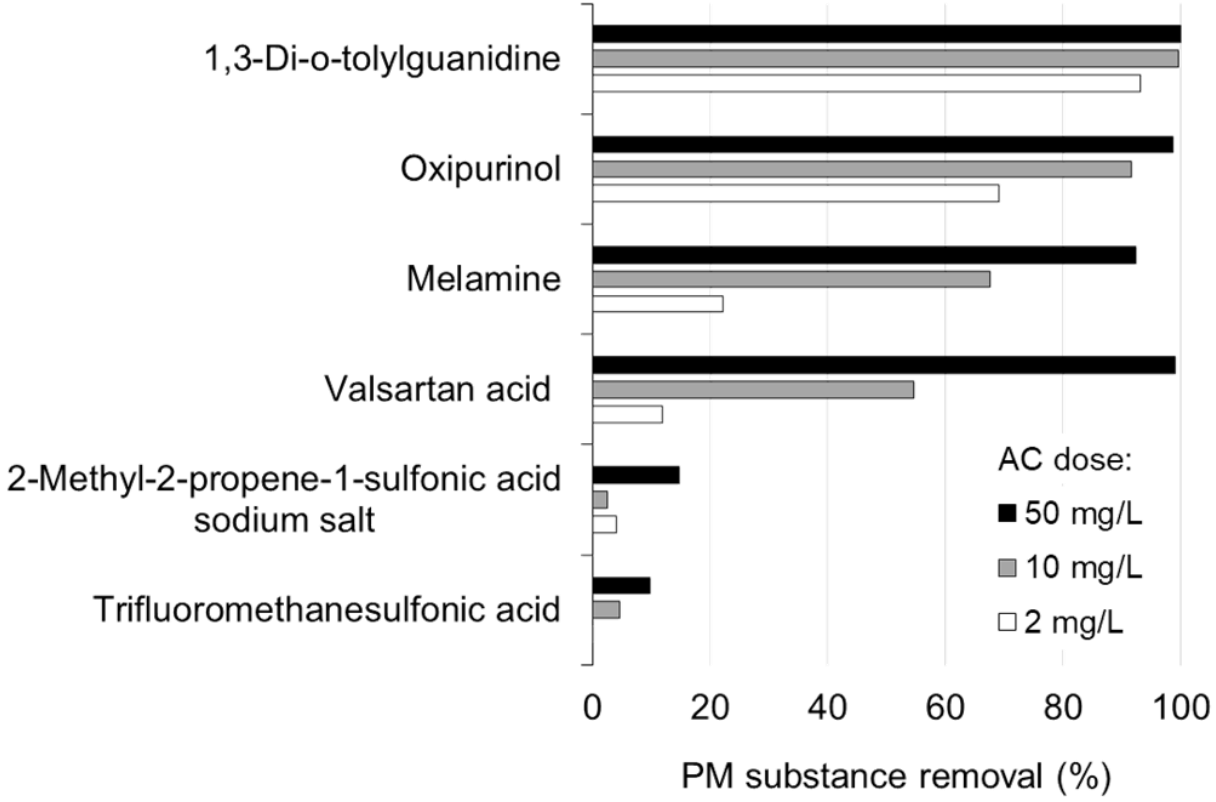
Wirkung von Aktivkohle (GAC)

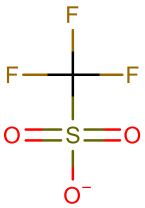
- PM substances exhibit very different tendency to adsorb onto activated carbon

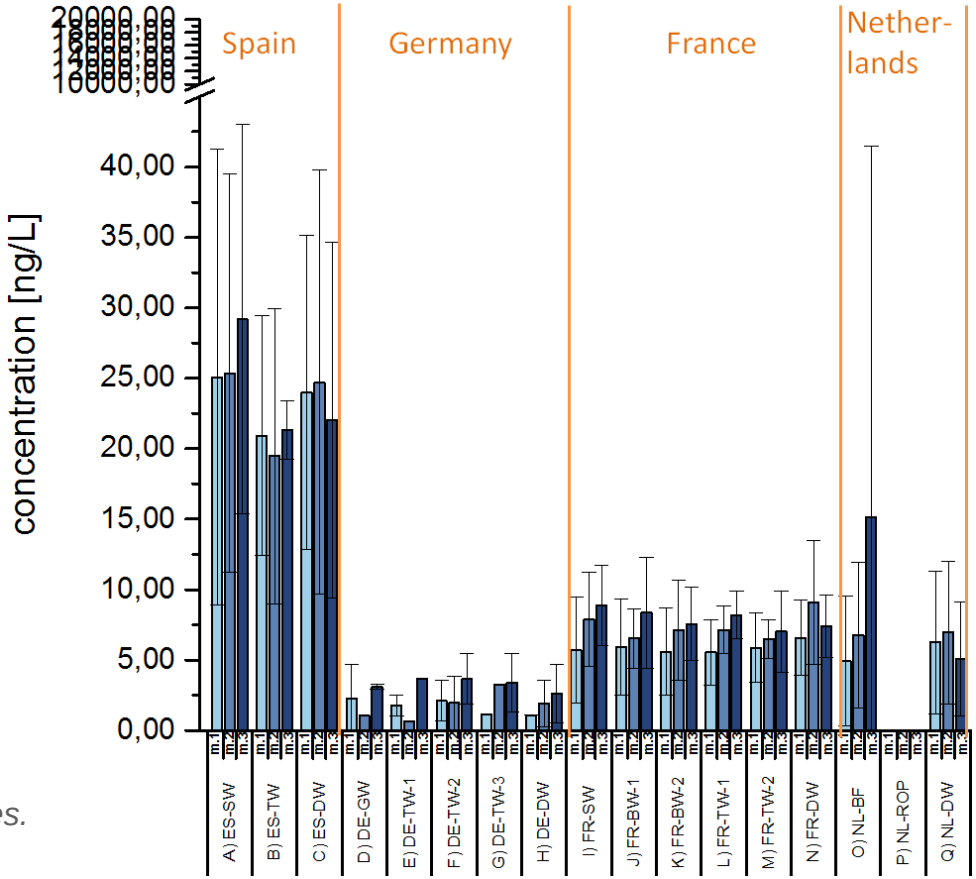


Schumann and Ruhl (2019) UBA und TUB, unpubl.

PM Chemicals in Drinking Water Preparation

- Trifluoromethanesulfonic acid

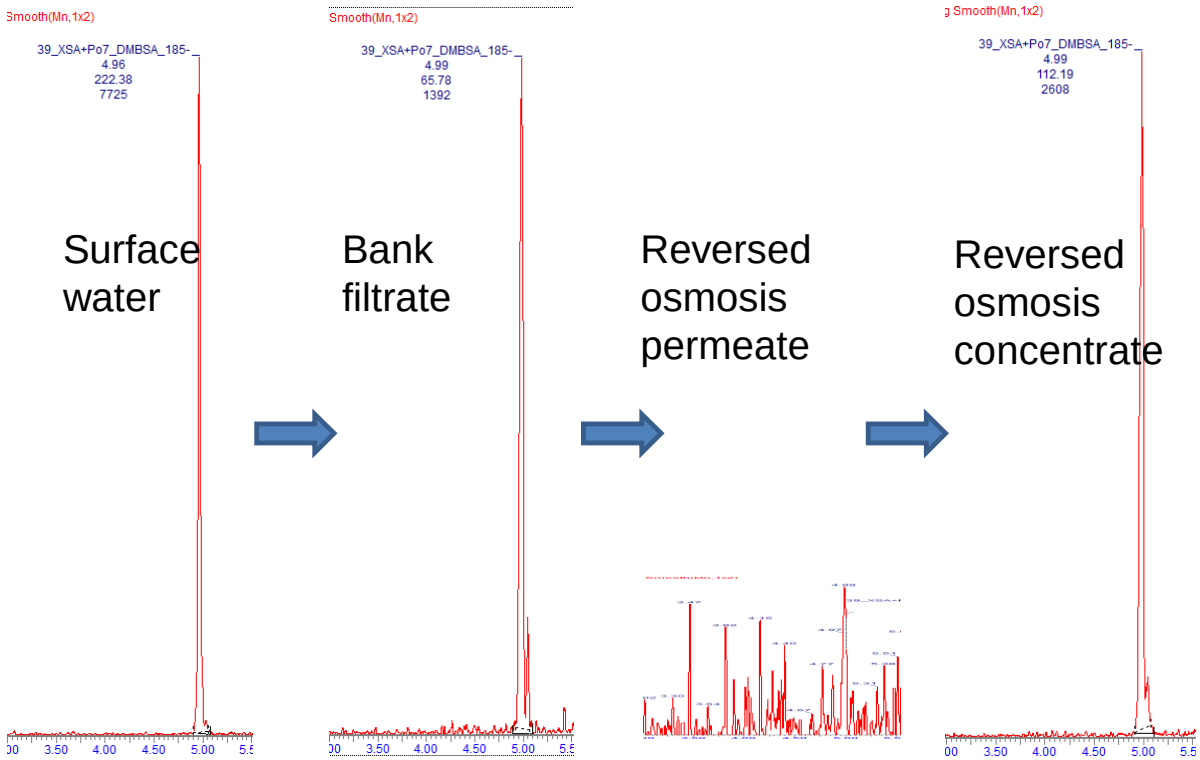




Zahn et al., (2016) Water Res.
Schulze et al., (2018) subm.

PM Chemicals in Drinking Water Preparation

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



PMT-Stoffe

- Warum ein Thema?
- Wie finden?
- Was ist da?
- Wie entfernen?
- **Wie zu bewerten?**
- Was tun?

Bewertung von PM-Stoffen

Zwei Ansätze

- A) wasserhygienischer Ansatz der Risikobewertung
  - Betrachtung von Exposition und Wirkung

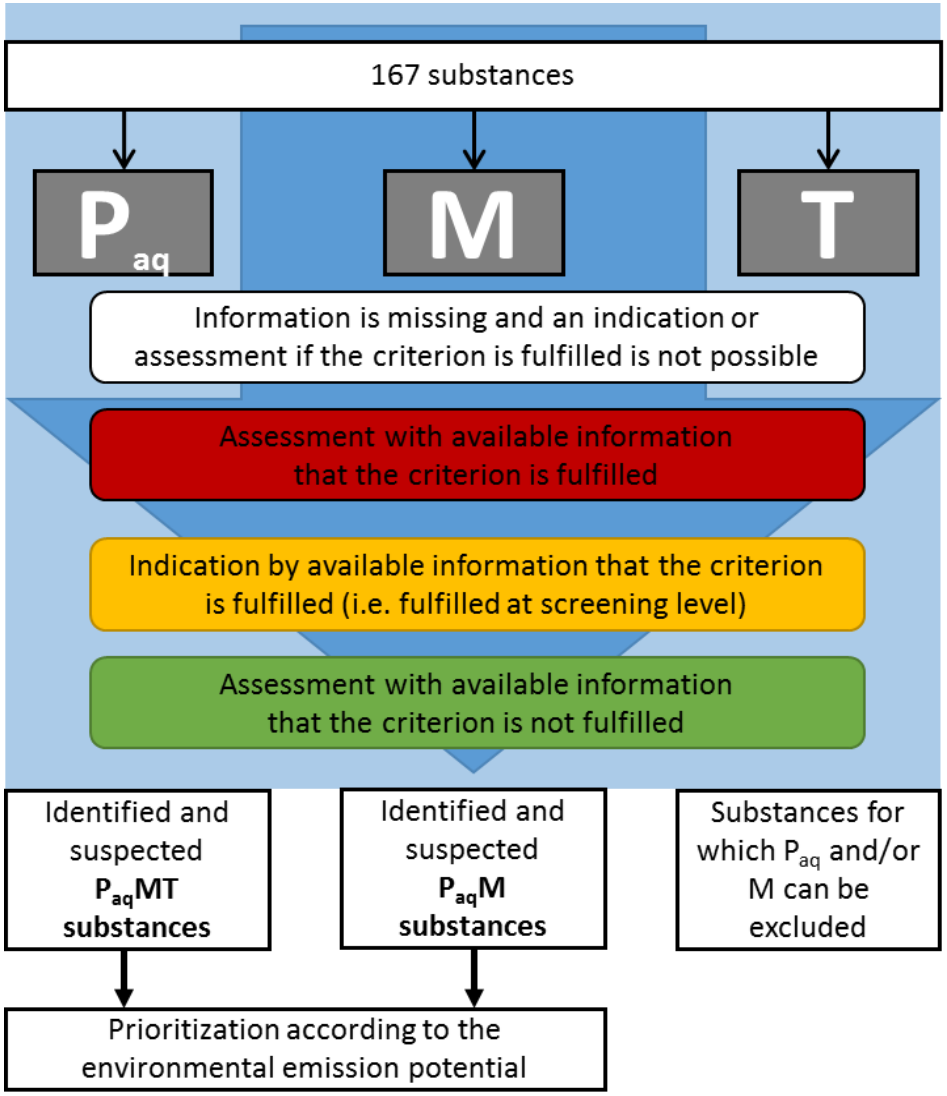
Wirkung?

- Baseline Toxicity / Narcotic Action
  - Veränderung der Membranfluidität
- Excess Toxicity
  - Decoupling
    - Zusammenbruch des Protonengradienten an den Mitochondrien
    - Dissoziierbare Stoffe (Protonenüberträger), z.B. viele Phenole
  - Receptor-mediated
  - Reactive toxicity
    - Reaktive Sauestoffspezies
    - Elektrophile

- Mobile (polare) Stoffe?

- Persistente Stoffe?

PMT Assessment Approach (traffic light)



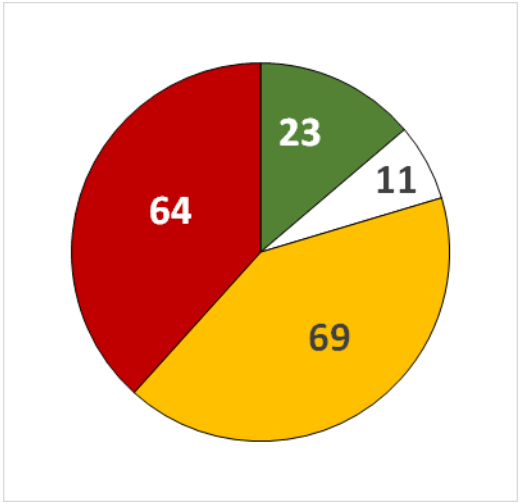
Data sources

- Public ECHA website
- The registration dossier
- Specific Chemical Safety Reports (confidential)
- Scientific literature
- QSARs

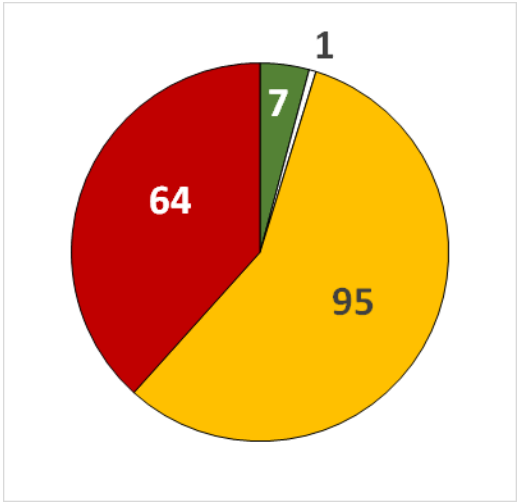
Berger et al. (2018) UBA Texte 09/2018

PMT Assessment

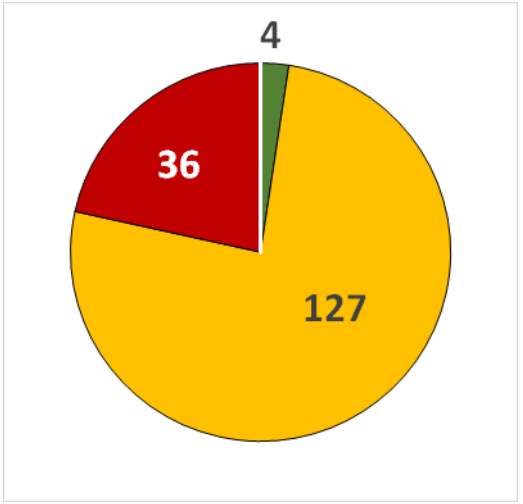
- Results for the 167 Test Compounds
  - detailed inspection of all studies available for P_{aq}, M and T



P_{aq}



M

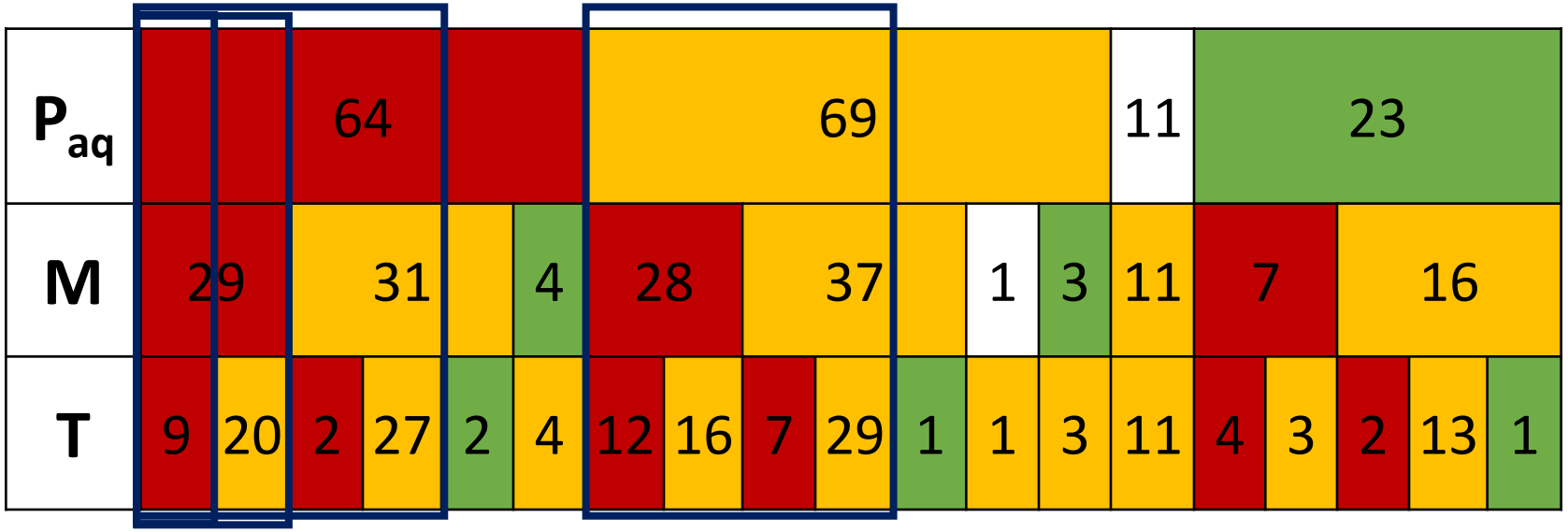


T

Berger et al. (2018) UBA Texte 09/2018

PMT Assessment

Summary of the assessment results for the 167 substances prioritized in the order P_{aq}, M and T



$P_{aq}PMT$ $_{aq}$M 122 suspected P_{aq}MT

Berger et al. (2018) UBA Texte 09/2018

Bewertung von PM-Stoffen

- **Zwei Ansätze**
- A) wasserhygienischer Ansatz der Risikobewertung
  - Betrachtung von Exposition und Wirkung

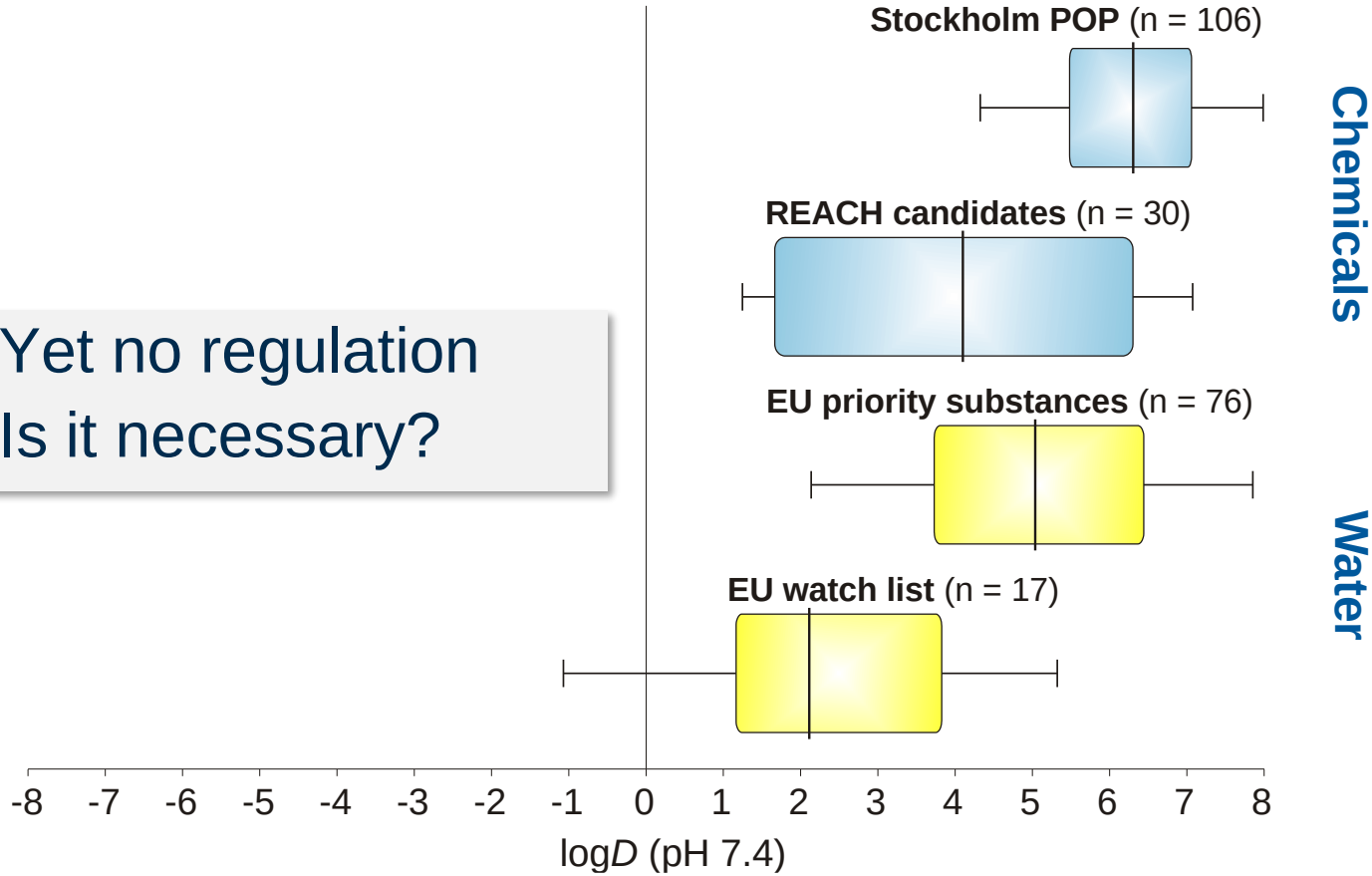
- B) umweltchemischer Ansatz
  - PMT / PBT: Persistenz, extreme Langlebigkeit in der Umwelt
  - ist ein grundsätzliches Problem und
  - widerspricht dem Konzept der Nachhaltigkeit

PMT-Stoffe

- Warum ein Thema?
- Wie finden?
- Was ist da?
- Wie entfernen?
- Wie zu bewerten?
- **Was tun?**

PM(T) - 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

PMT - Reaktionen auf verschiedensten Ebenen

- DVGW, EurEau
  - Aktivitäten zum Schließen der Lücke hinsichtlich PMT gefordert
- UBA (FB IV)
  - Vorschlag zur Regulation von PMT als SVHC unter REACH
- Authorities in the Netherlands
  - Vorschlag zur Begrenzung von PM-Stoffen bei Abwasser-Einleitern
- ECHA, Member States Comittee
  - Anerkennung von GenX als SVHC-Stoff
- European Environment Agency
  - The European Environment - State and Outlook 2020
- European Comission – CIS
  - Working Group on Groundwater
- Kalifornische EPA
  - Initiative zur Limitierung der Gehalte an 1,4-Dioxan in verbrauchernahen Produkten

Schlussfolgerung

- Es gibt PM(T) Stoffe im Wasserkreislauf
- Erst eine begrenzte Zahl an PM-Verdachtstoffen ist analytisch zugänglich und untersucht
- Breite Screening-Methoden gibt es bisher nicht
  - Methodenkombination erforderlich, hoher Aufwand
- Transformationsprodukte fast vollständig unbetrachtet
- Möglichkeiten der Entfernung von PM-Stoffen aus Wasser begrenzt
- Viele PM Stoffe mögen nicht toxisch sein, es gibt aber auch PMT-Stoffe
- Maßnahmen darauf abstellen
  - Wissenslücken schließen
  - Entfernungsverfahren verbessern
  - Verschiedene Strategien zur Vermeidung von Emissionen verfolgen

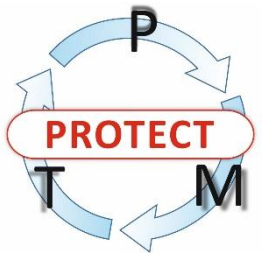
Acknowledgements

Partner

- Daniel Zahn, Thomas Knepper (HSF), Idstein
- Hervé Gallard (CNRS), Poitiers
- Jose Benito Quintana (USC), Santiago de Compostela
- Hans Peter Arp (NGI) Oslo
- Pim de Voogt (UVA, KWR), Amsterdam
- Tamara Grummt, Jochen Kuckelkorn, Michael Neumann, Aki Sebastian Ruhl (UBA), Bad Elster, Dessau, Berlin

Funding

- Water Challenges for a Changing World, Joint Program Initiative (Water JPI) Pilot Call 2013
- BMBF RiSKWa



Water JPI PROMOTE

GEFÖRDERT VOM
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Water JPI

Forskningsrådet

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