Nachweis und Auftreten von PM-Stoffen im Wasserkreislauf

~

Herausforderungen und Handlungsoptionen

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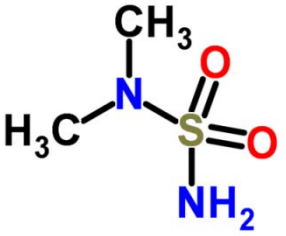
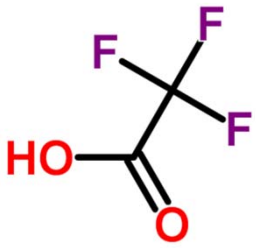
Berlin, 06.11.2018

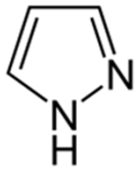
Incidental Findings in Drinking Waters

- Single very polar compounds accidentally 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





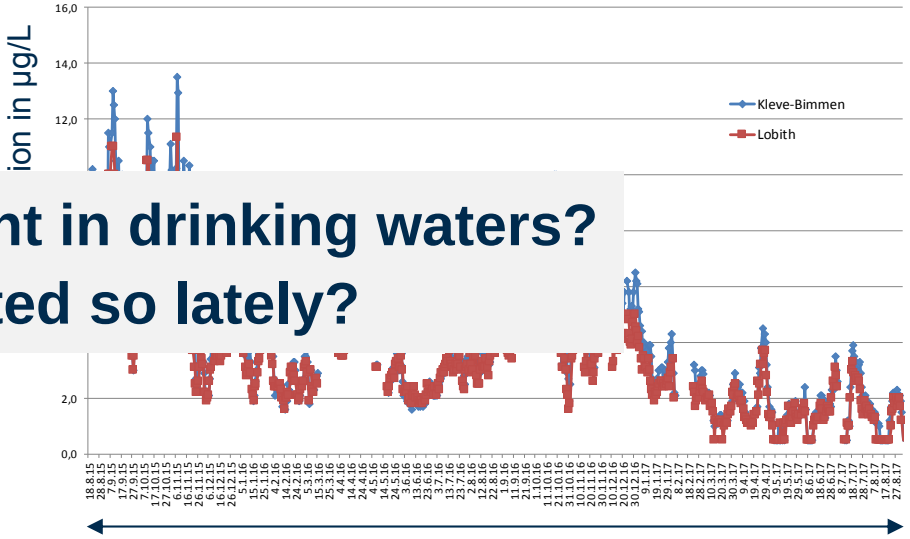
Incidental Findings in Drinking Waters



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

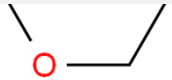
Concentration in River Rhine



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

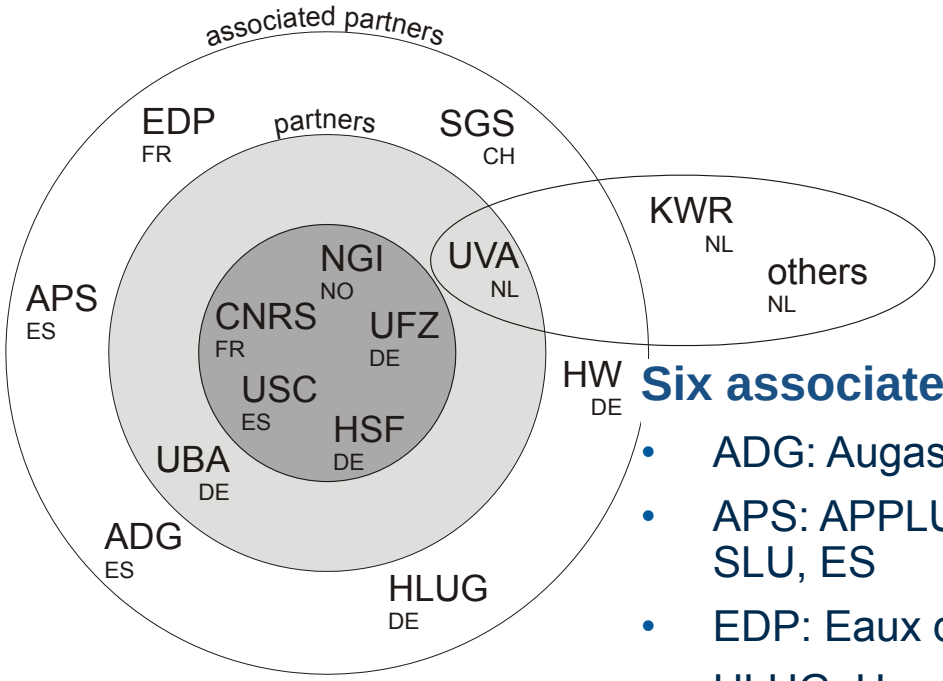


- Perfluorierte Alkylsubstanzen (PFAS)

European Project PROMOTE –
Protecting Water Resources from Mobile Trace Chemicals

Seven Partners

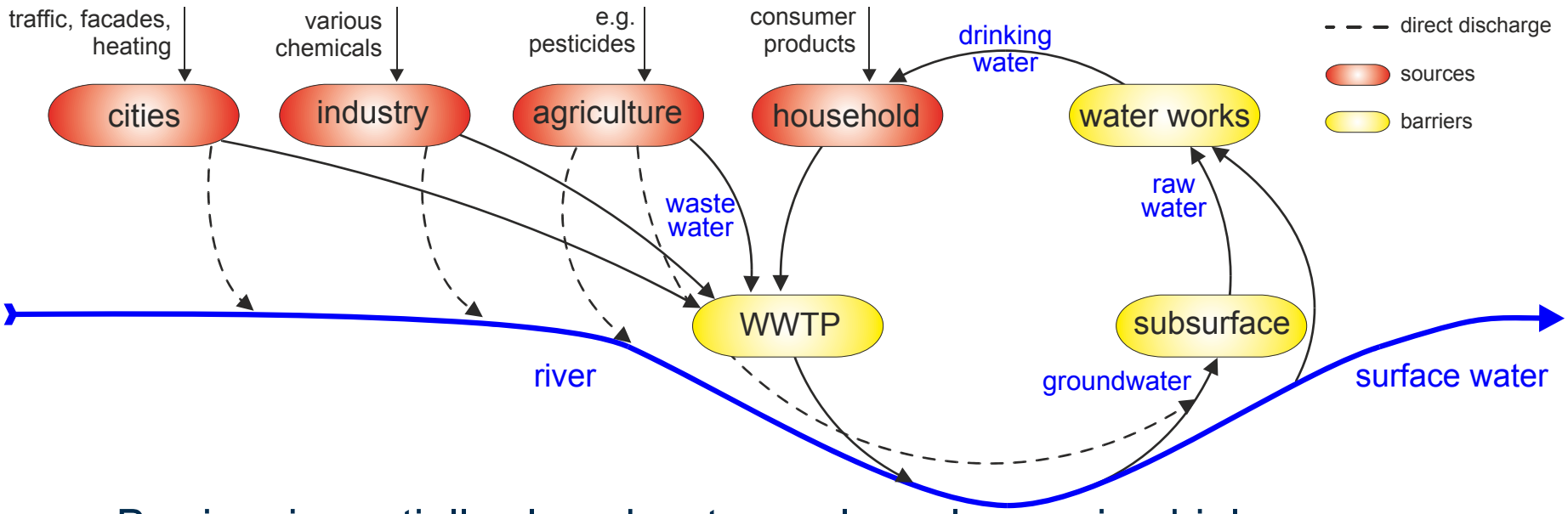
- CNRS
  Hervé Gallard
- HSF
  Thomas Knepper
- NGI
  Hans Peter Arp
- UFZ
  Urs Berger
  Thorsten Reemtsma
- UBA
  Michael Neumann
- UVA
  Pim de Voogt
- USC
  Jose Benito Quintana



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

The Protection Gap

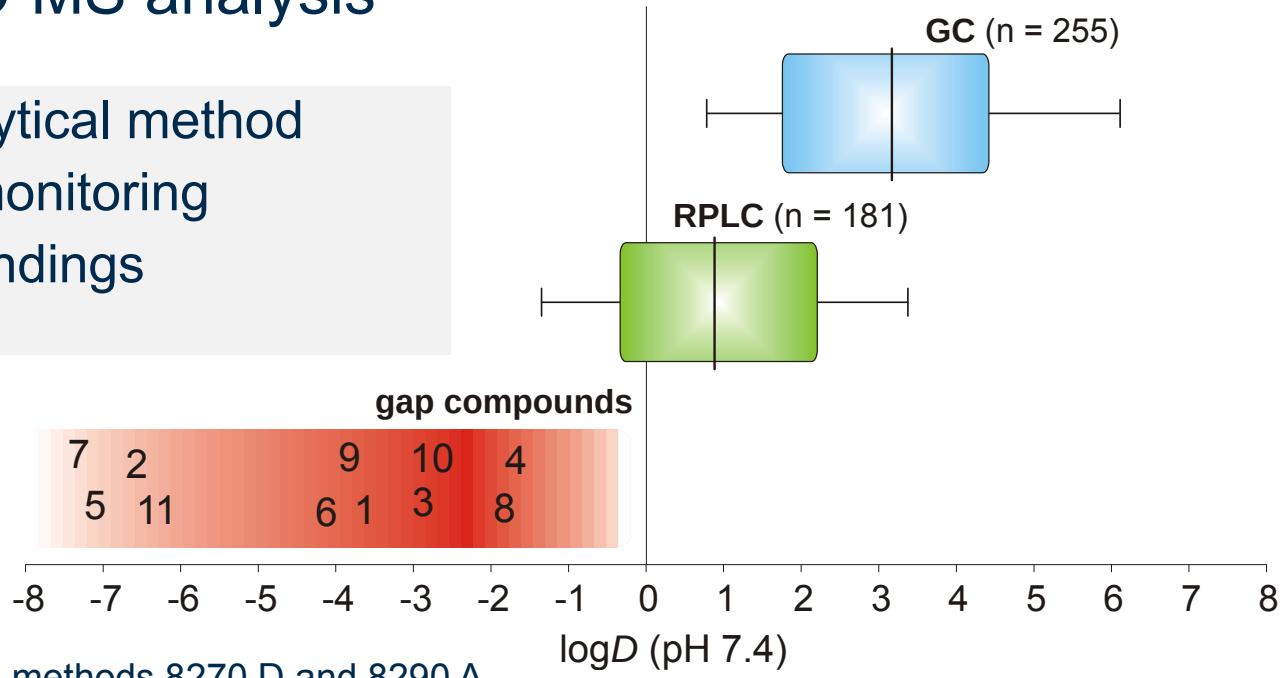


- Barriers in partially closed water cycles rely on microbial degradation and sorption processes
- For persistent (P) and very polar (mobile, M) organic compounds (PM substances) these barriers are not effective
  - water cycle may turn into a compound cycle
  - only dilution reduces concentration

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

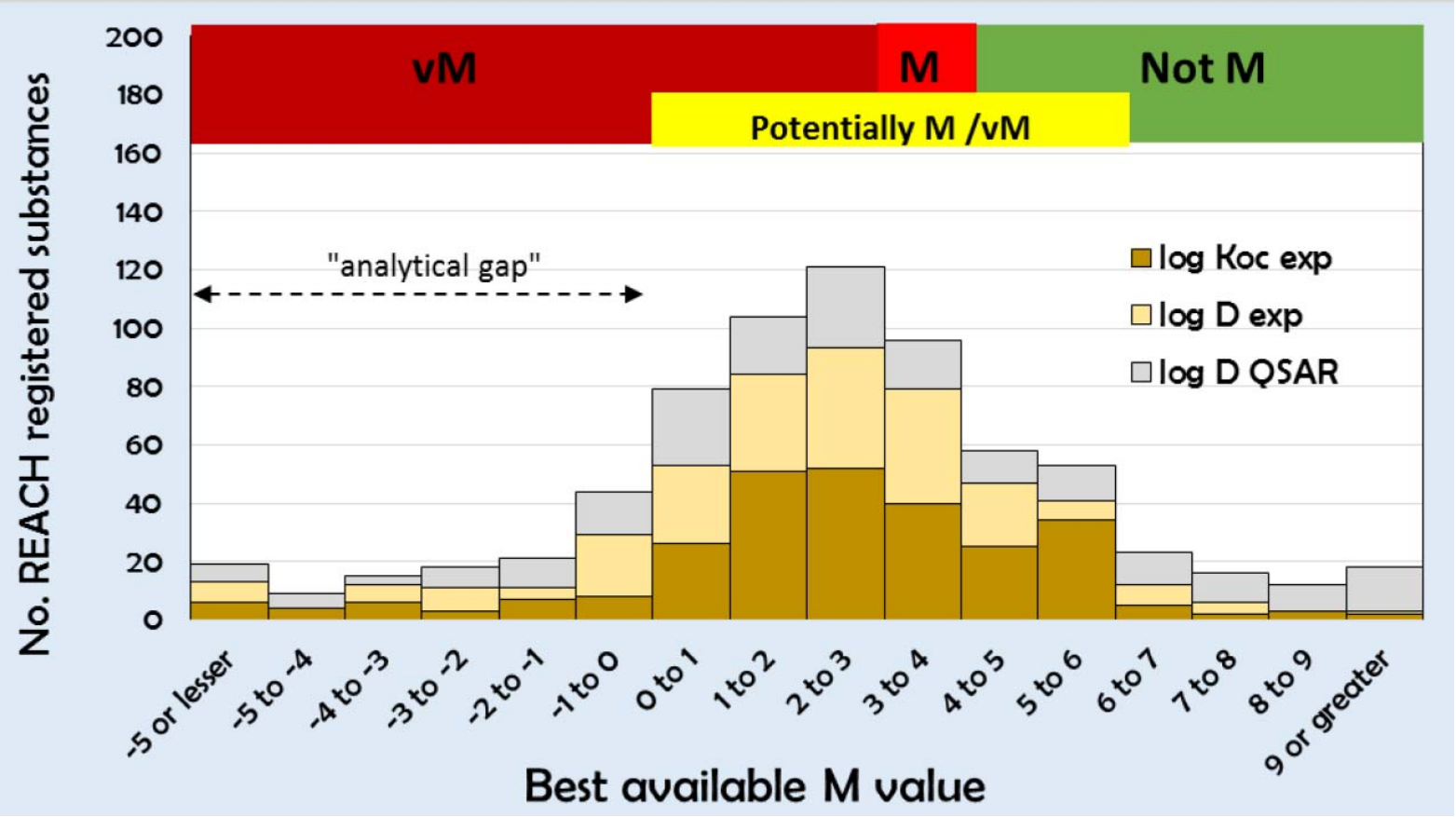
Reemtsma et al. (2016) Environ. Sci Technol. 50, 10308

Water JPI Project PROMOTE

- Fragen
  - Wie groß ist die Schutzlücke für die Wasserressourcen?
  - Wie können wir die analytische Lücke schließen?

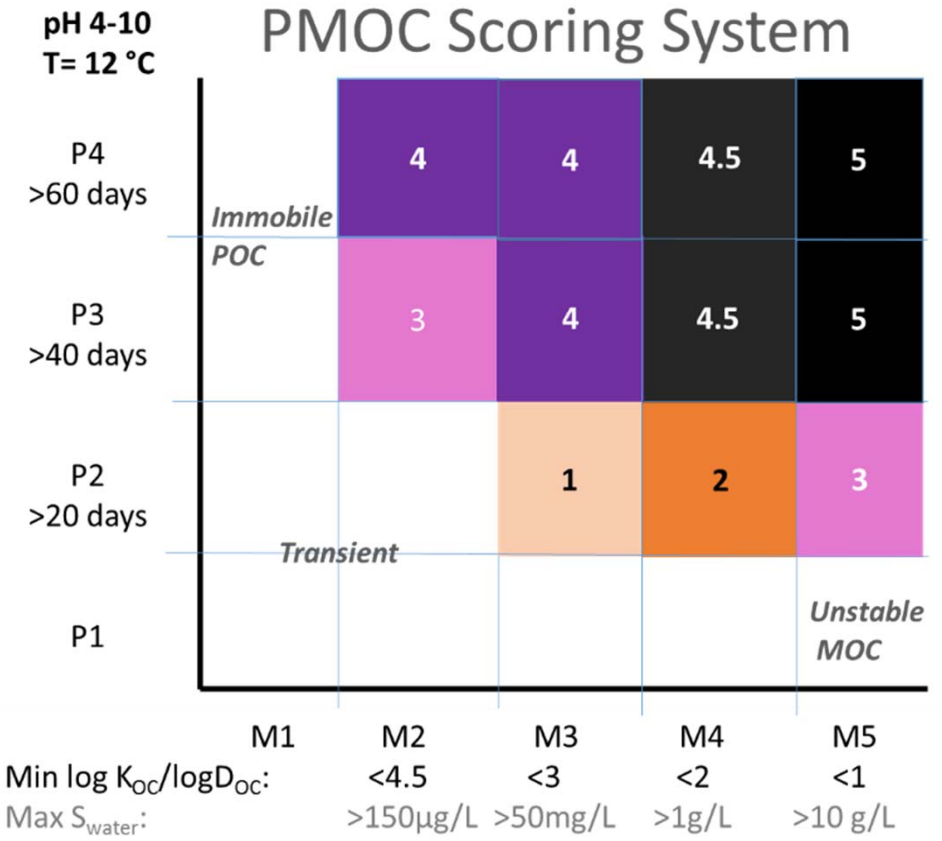
- Ansätze
  1. Suche nach PM-Stoffen in Stoffdatenbanken
     - 14.000 registrierte Stoffe (2015)
     - P (ersistence)
       - Half-life in marine water >60 days OR
       - half-life in fresh or estuarine water >40 days
     - M (obility)
       - Water solubility ≥150 µg/L AND
       - log K_{oc} ≤4.5
  2. Entwicklung neuer analytischer Methoden
  3. Suche nach unter 1. identifizierten PM-Stoffen mit diesen Methoden

Mobility of REACH Substances



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

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

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

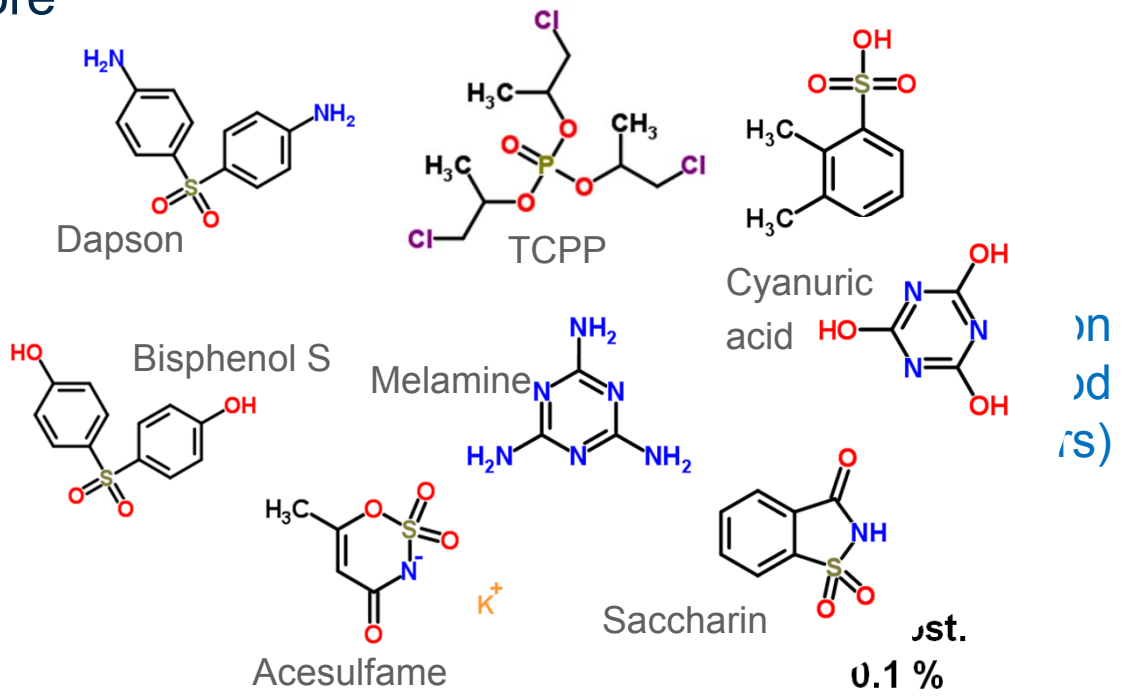
Prioritizing PM Chemicals (score 4 – 5) by Risk of Occurrence

- High emission likelyhood
- Ranking according to E-score

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

TOP 300

„Silver List“

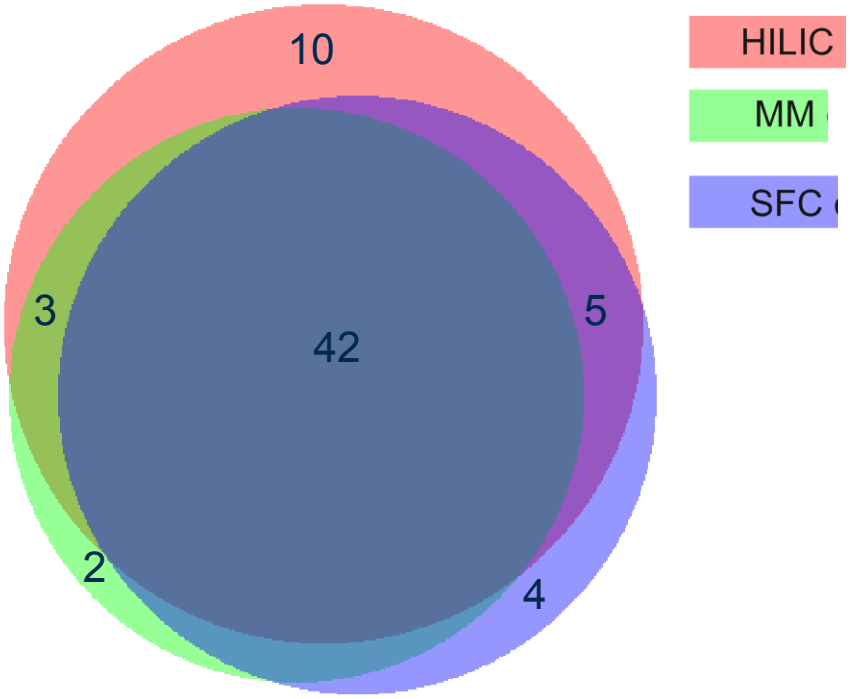


high emission likelyhood substances/precursors

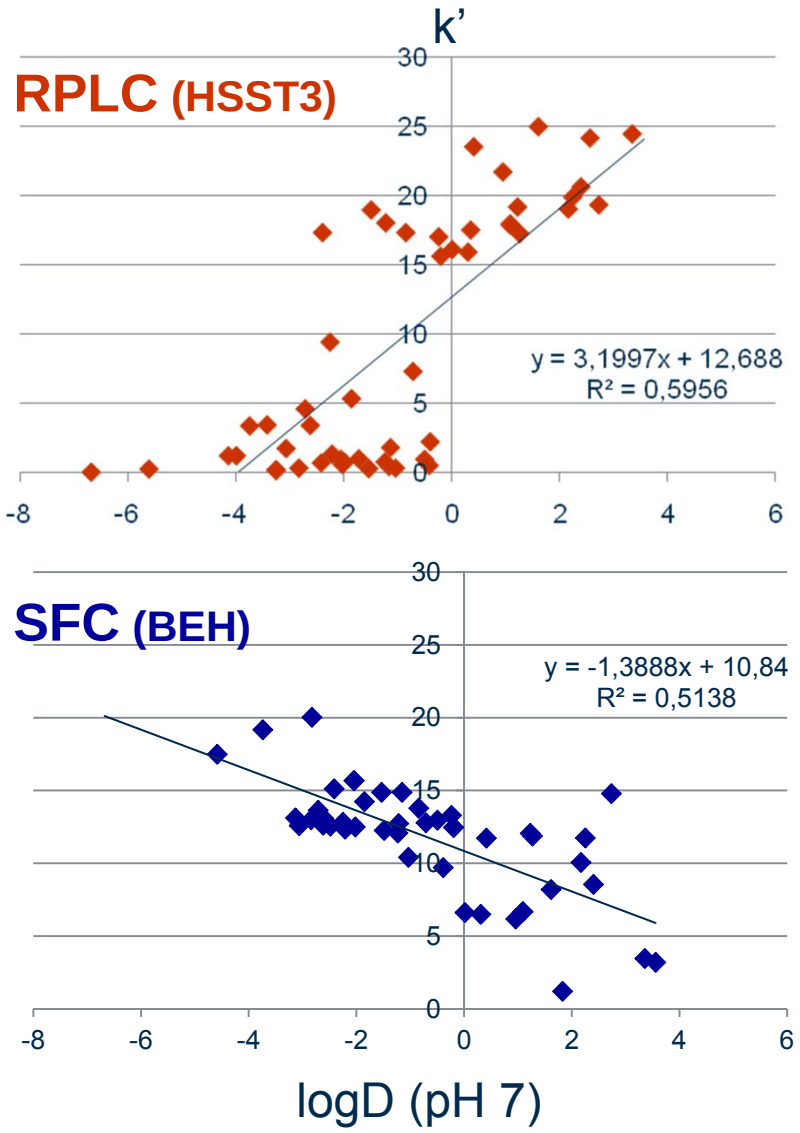
Schulze et al. (2018) Sci. Total Environ. 625, 1122–1128

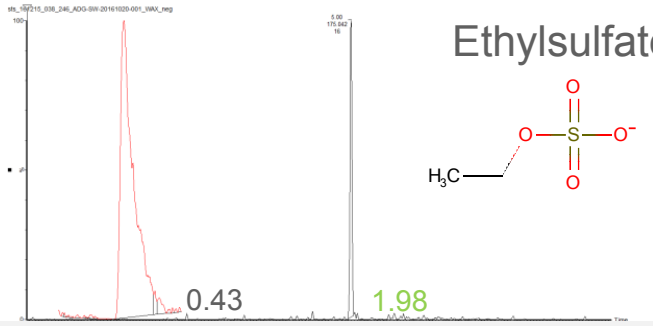
Chromatographic Approaches to Close the Analytical Gap

- 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
      - Montes et al. (2017) Environ. Sci. Technol. 51, 6250
  - Approx. 67 analytes of the "silver list"

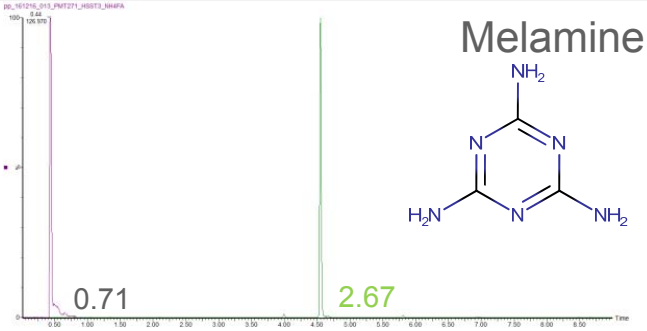


Determination of M Compounds by SFC-MS



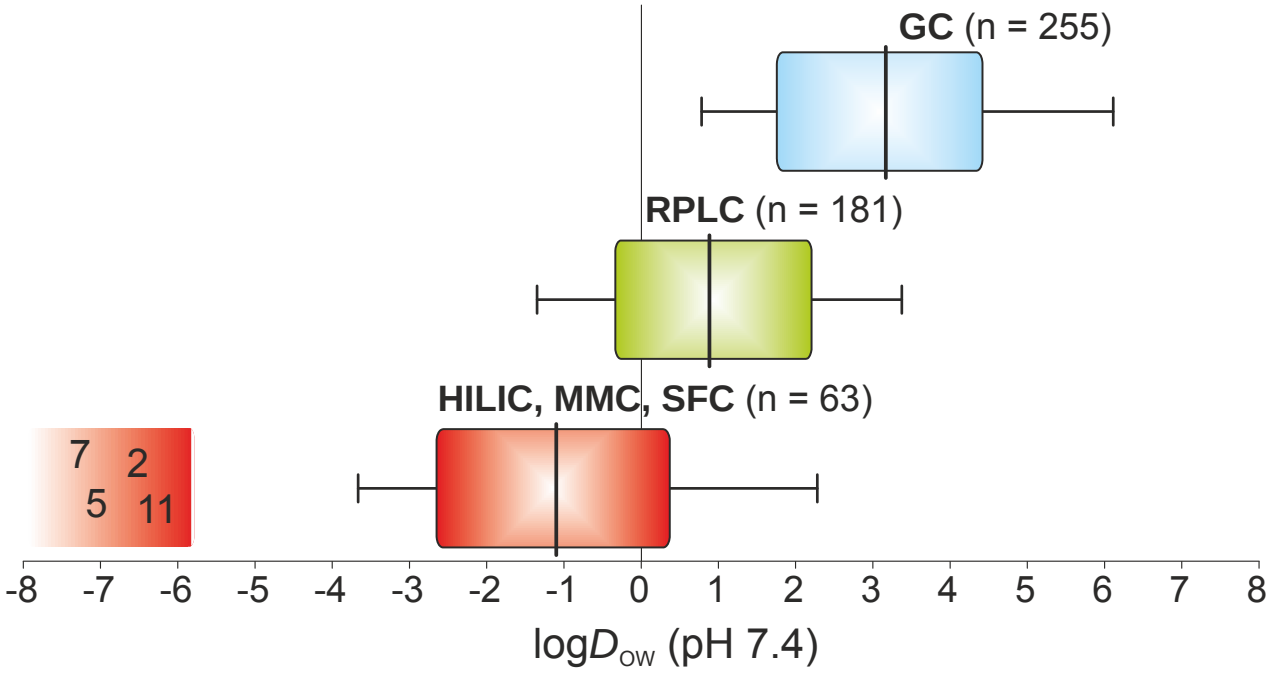


- Stronger retention of PMOC analytes
- Better peak shape
- Sensitivity increase by a factor of 4 - 5



Narrowing The Analytical Gap

- Improvement by HILIC, MMC and SFC

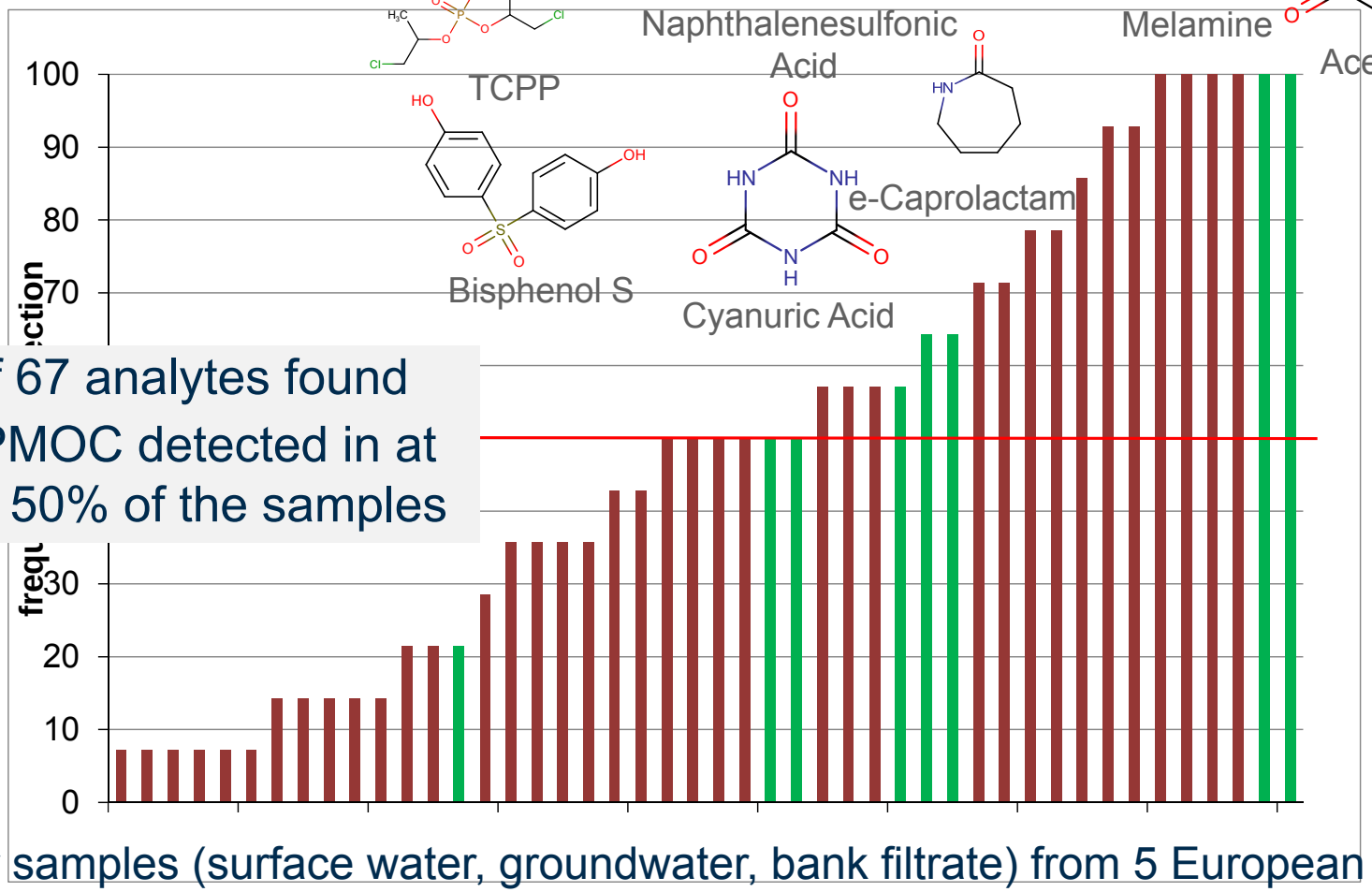


- Enrichment remains challenging

Reemtsma et al., unpubl.

Screening Data for PMOC – 3 Methods

Green:
Previously known PMOC



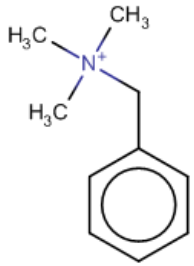
- 46 of 67 analytes found
- 25 PMOC detected in at least 50% of the samples

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

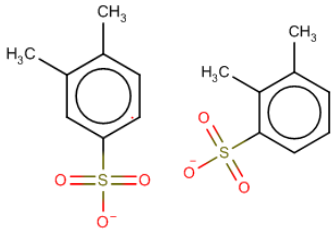
Results: Environmental monitoring

- Previously unknown PM compounds

Benzyltrimethyl ammonium

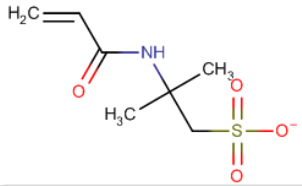


Dimethylbenzene sulfonic acid

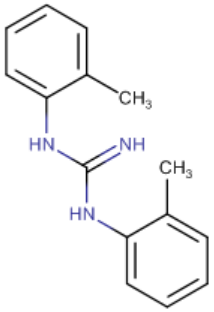


Trifluoro and Cl/Br methanesulfonic acids

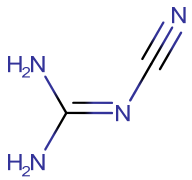
2-Acrylamido-2-methylpropane sulfonic acid



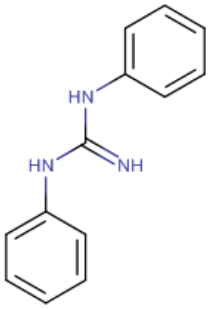
1,3-Di-*o*-tolylguanidine



Cyanoguanidine



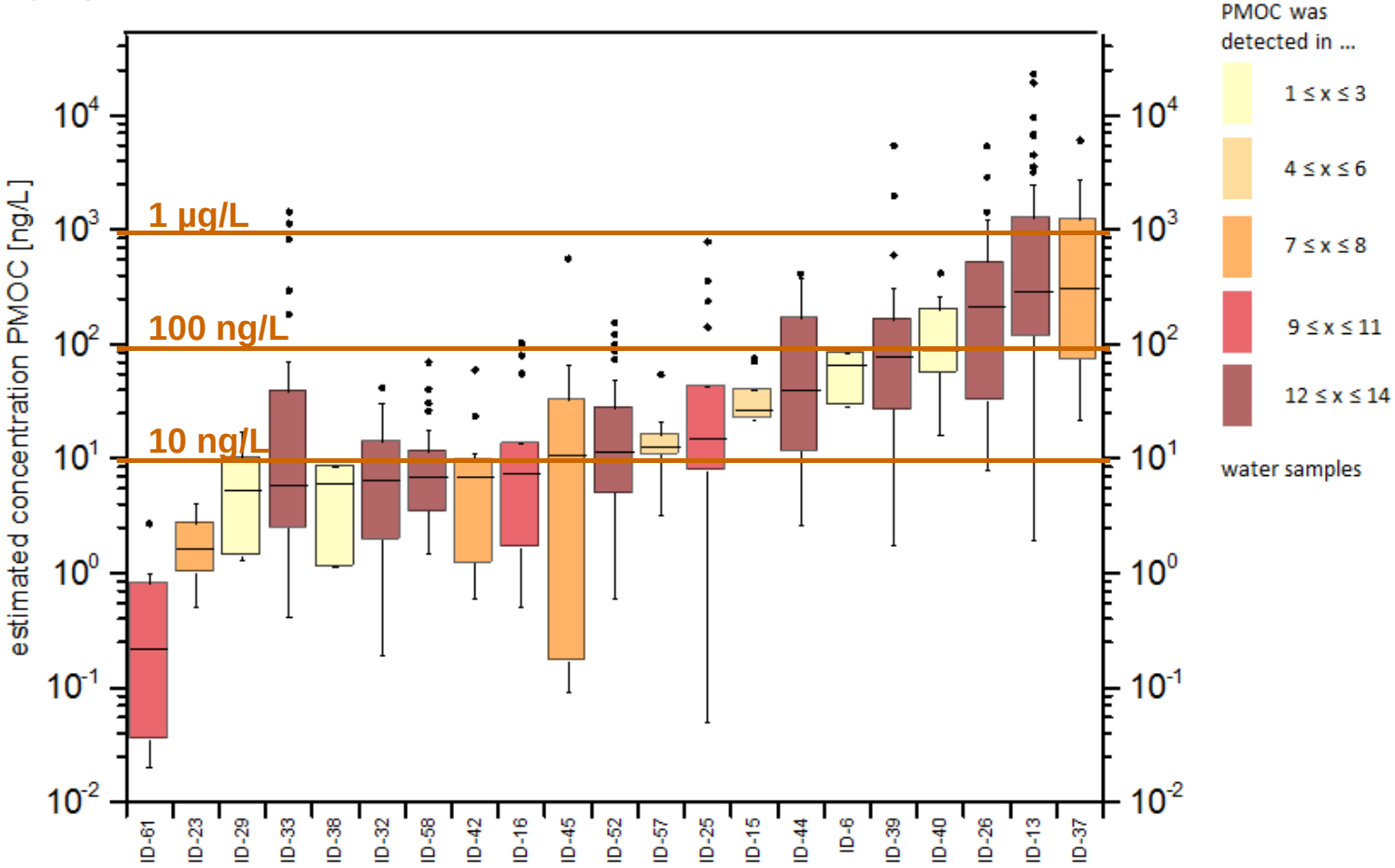
1,3-Diphenylguanidine



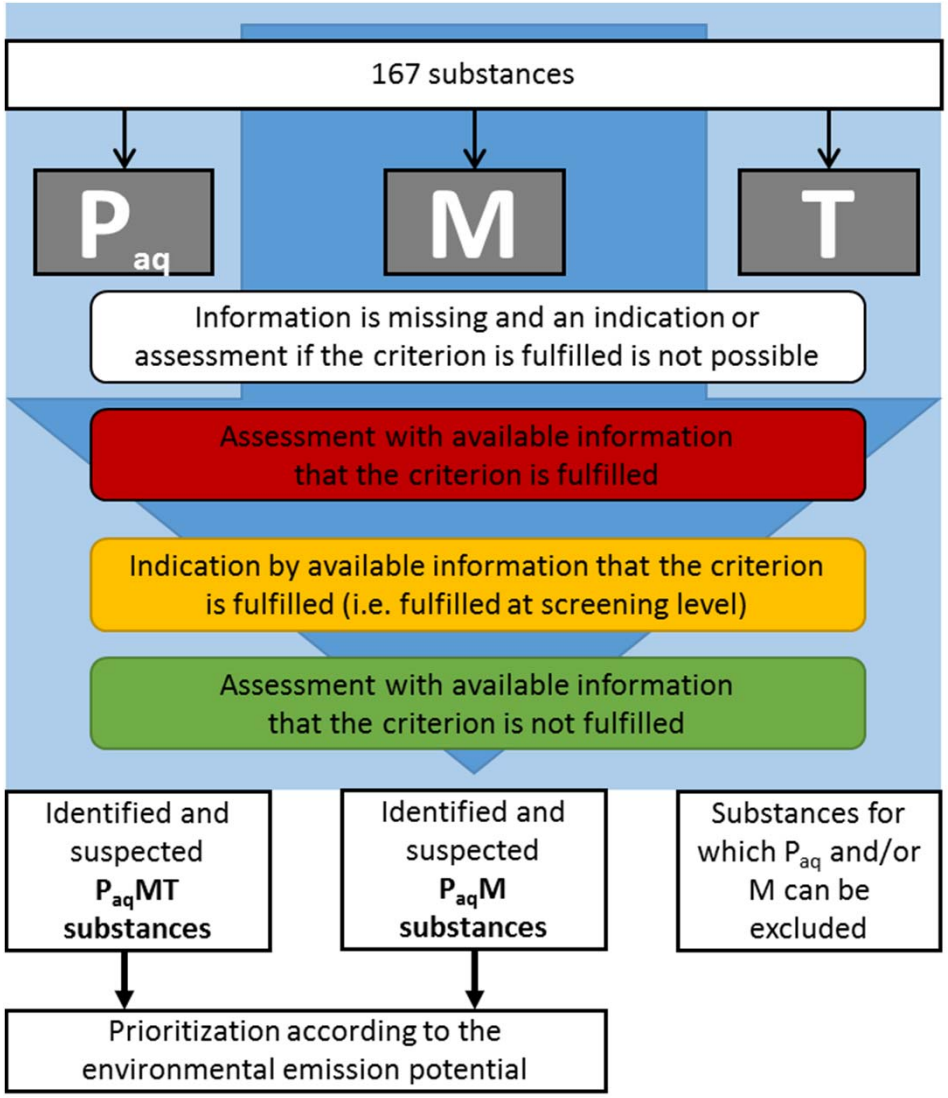
- **Processing agents in**
  - **polymerization**
  - **vulcanization**
  - **production of resins**
- **Tires and rubber**
- **Disinfectants**
- **Washing and cleaning agents**
- **Textile industrie**
- **Water treatment**
- **Fertilizer**

Monitoring of PMOCs

- Concentrations in surface water, groundwater, bank filtrate



PMT Assessment Approach (traffic light)



Data sources

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

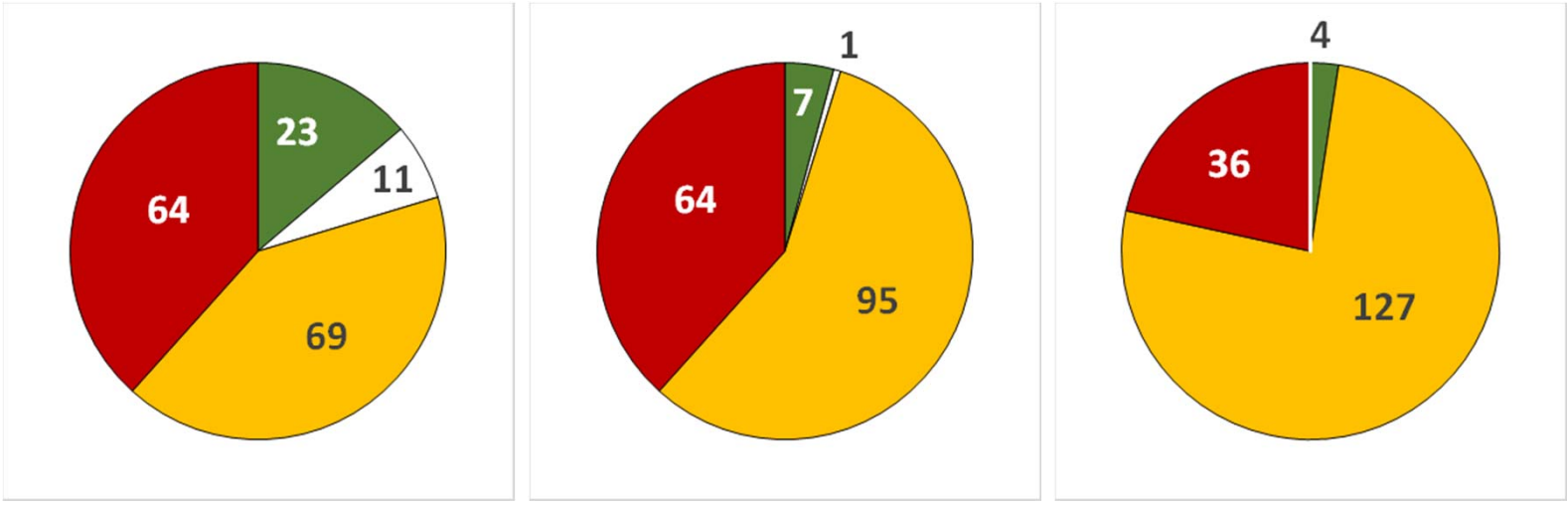
Berger et al. (2018) UBA Texte 09/2018

Criteria For Toxicity (T)

- Long-term no-observed effect concentration (NOEC) or EC_{10} for marine or freshwater organisms <0.01 mg/L OR
- CMR: Substance meets the criteria for classification as carcinogenic (category 1A, 1B or 2), germ cell mutagenic (category 1A, 1B or 2), or toxic for reproduction (category 1A, 1B or 2) OR
- Specific target organ toxicity after repeated exposure (STOT RE category 1 or 2) OR
- Effects on or via lactation (H362) OR
- Derived no-adverse effect level (DNEL) ≤9 µg/kg/d

PMT Assessment

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

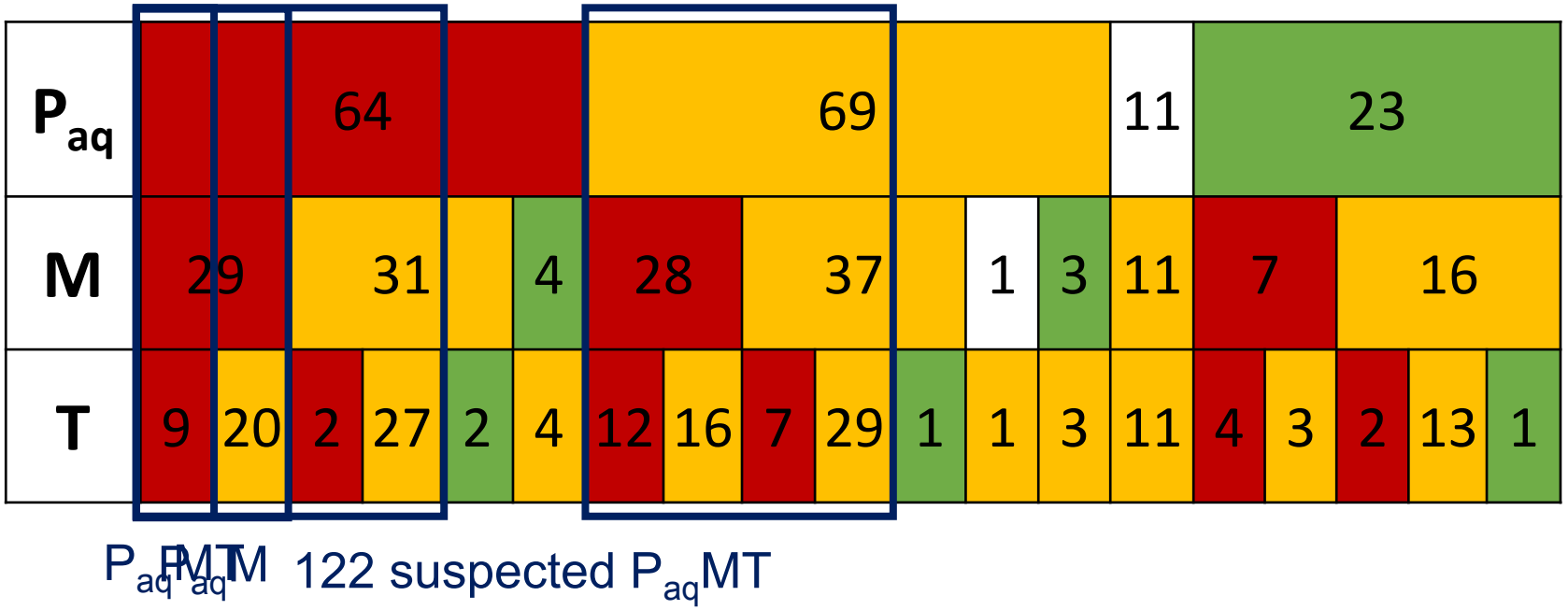


P_{aq} M T

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

PMT Assessment

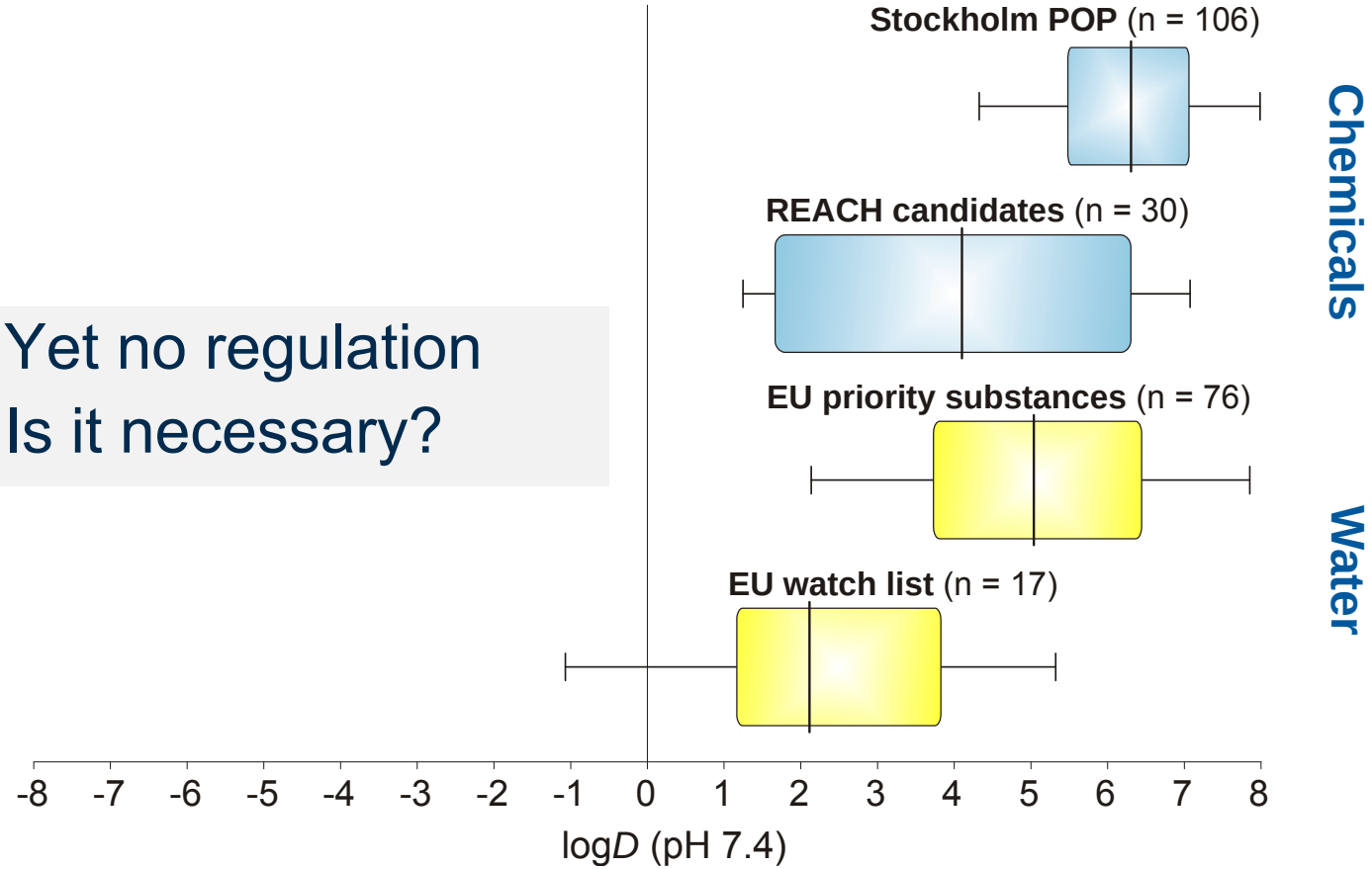
Summary of the assessment results for the 167 substances prioritized in the order P_{aq}, M and T



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

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

Treatment Options

- Conventional wastewater treatment ineffective für PM compounds
- Advanced treatment (activated carbon, ozone) likely not effective for all PM compounds
- Reversed osmosis as the only option remaining for drinking water?
  - e.g. Albergamo et al. (2019)
    - Removal of polar organic micropollutants by pilot-scale reverse osmosis drinking water treatment. Water Res. 148, 535.

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
    - Local, regional, ubiquitous
- Possible
  - Remove - Improve treatment
    - source, wastewater, drinking water
  - Reduce - Avoid discharge/release
    - Change use (open, closed systems)
    - Substitution
  - Regulate - Regulation of PMT substances

Zusammenfassung

- PM Stoffe sind ein reales Problem für die Trinkwasser-versorgung in teilweise geschlossenen Wasserkreisläufen (und die Abwasser-Wiederverwendung)
- Kenntnisse über PM-Stoffe in Rohwässern sind noch unvollständig
  - Z.B. ist ein Großteil der etwa 1000 PM-Verdachtstoffe aus REACH noch nicht untersucht
- Hohe Konzentrationen vor allem regional bei spezifischen Belastungsquellen
- Möglichkeiten der Entfernung von PM-Stoffen aus Rohwasser sind begrenzt
- Vermeidung der Belastung mit PM-Stoffen ist sinnvoll
  - PMT-Stoffe oberste Priorität
  - Regulation um zukünftige Belastungen zu vermeiden?

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  - Research Council of Norway (241358/E50)
  - French Office National de l'Eau et des Milieux Aquatiques (project PROMOTE)
  - Spanish Ministry of Economy and Competitiveness (JPIW2013-117)

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