Addressing the accumulation of trifluoracetic acid (TFA) and other very persistent, very mobile (vPvM) substances

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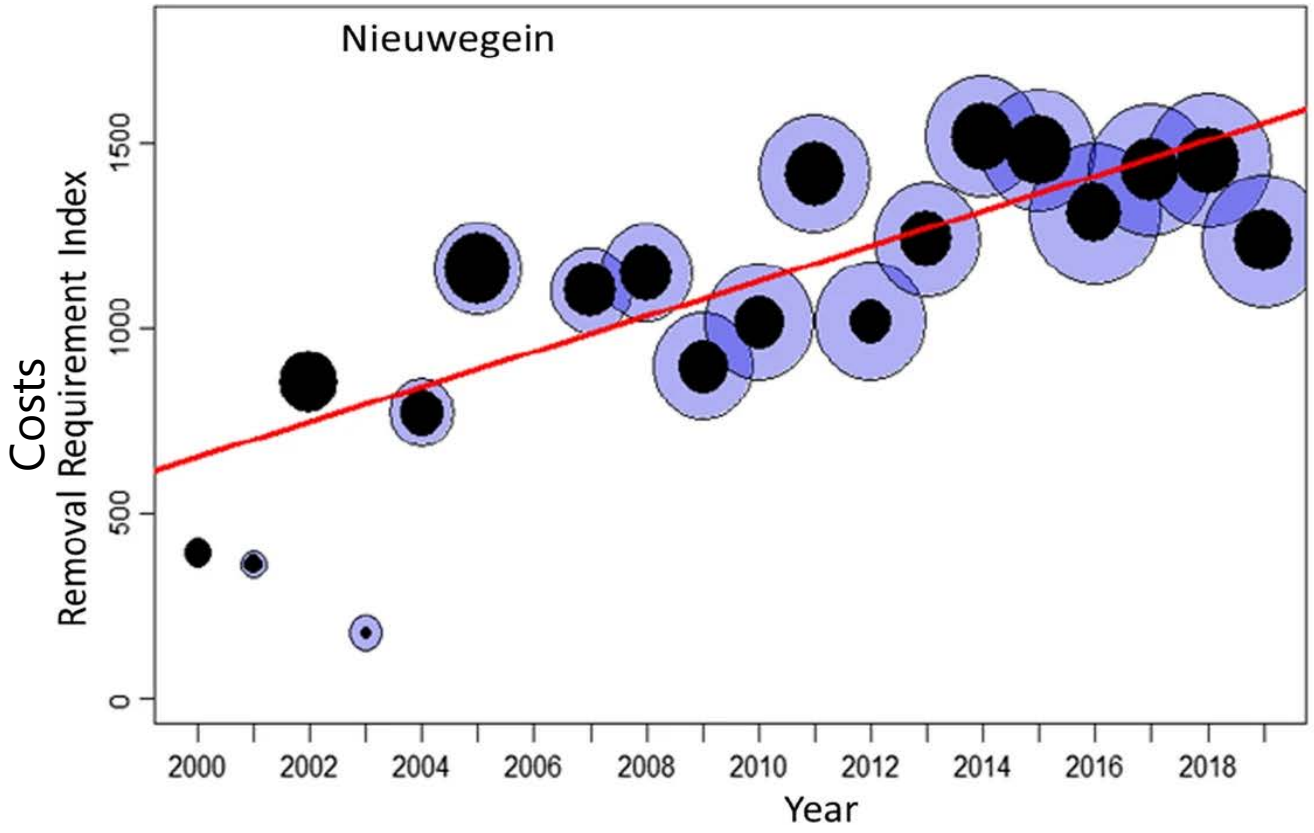
ATV Jord og Grundvand, Nyborg DK Jan 23, 2023

The hypothesis….

"The European REACH legislation will possibly drive producers to innovate their products, possibly to develop newly designed chemicals that will be less persistent, bioaccumulative or toxic. …[***T]his may result in higher mobilities of chemicals in the aqueous environment***. As a result, ***the drinking water companies may face stronger demands on removal processes*** as the hydrophilic compounds inherently are more difficult to remove."

Pim de Voogt, 2008

The results..



Lowest and highest # of persistent, mobile substances

4 parameters exceeding

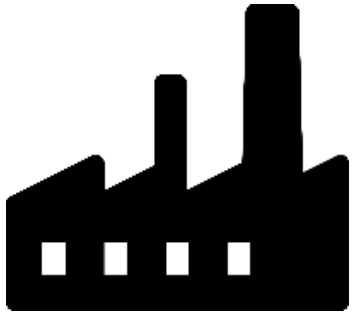
36 parameters exceeding

4 parameters reported

626 parameters reported

Pronk et al. Water Supply (2021) 21 (1): 128–145.

Properties of a drinking water contaminant



Chemical Synthesis

Persistent and Mobile

Transport through the environment or infrastructure

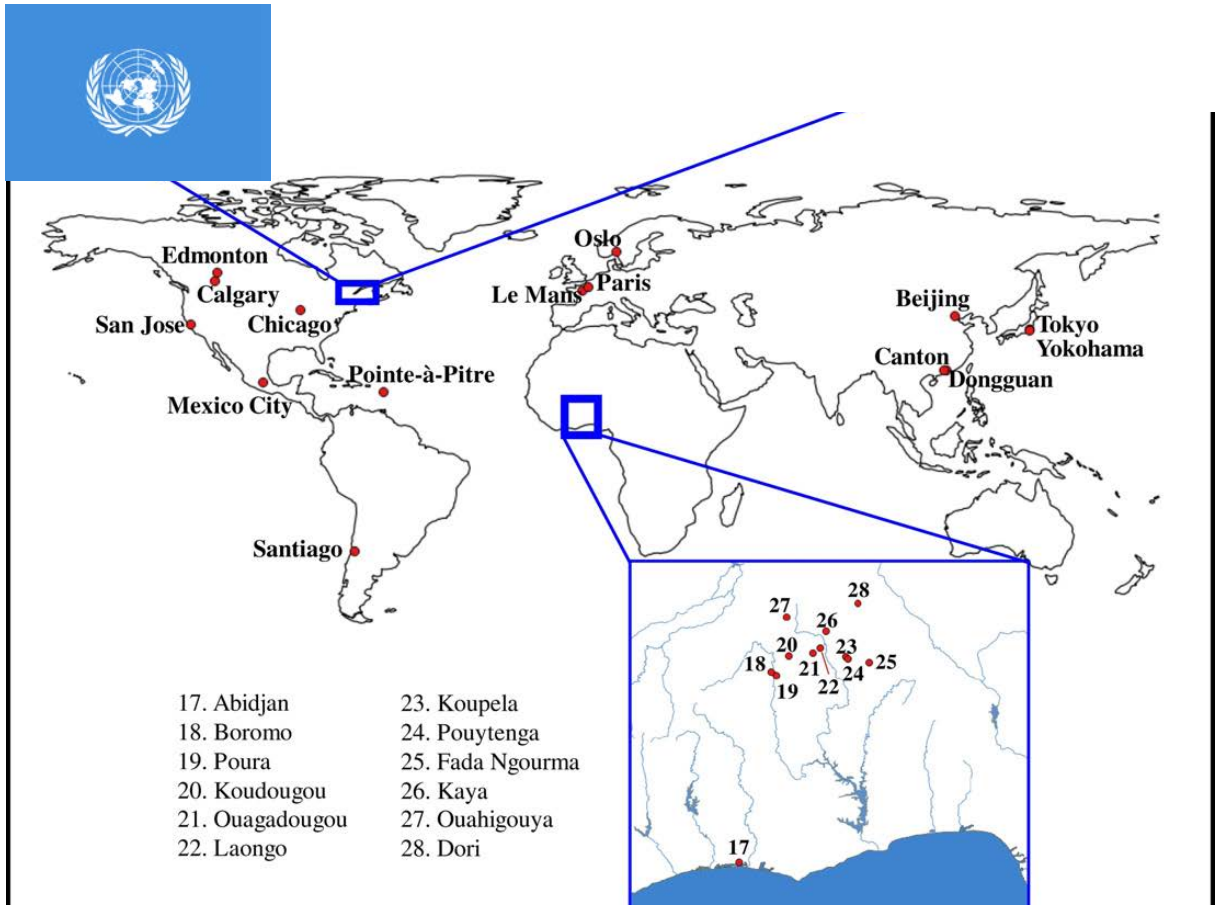
Water treatment and production

Consumption

Uses / Products

Toxic

PFAS in global tap water



- Kaboré et al. STOTEN 2018

Danish drinking water limit

Sum af PFOA, PFOS, PFNA & PFHxS	µg/L	0,002

Cities exceeding the Danish drinking water limit in 2015-2016:

Montreal, Quebec, Toronto, Chicago, Ouagadougou, Tokyo, Paris…

USA drinking limit

PFOA: 0.000004 µg/L
PFOS: 0.00008 µg/L

Cities exceeding the American drinking water limit in 2015-2016:

All of them

Trifluoracetic acid (TFA) is in water everywhere

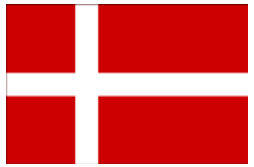
Nyt stof fundet i grundvandet

27-01-2021

Vandmiljø Vand i hverdagen Kemikalier NOVANA

Kølemidler fra klimaanlæg og drivmidler fra spraydåser kan være kilder til stoffet TFA, som i ny undersøgelse er fundet vidt udbredt i grundvandsprøver. Intet tyder på, at der er en sundhedsrisiko.

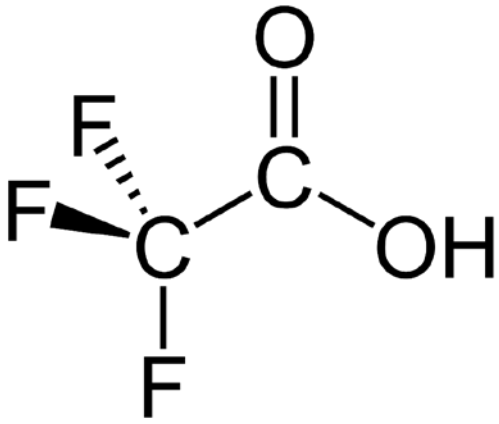
Udtagning af vandprøver fra grundvandet. Arkivfoto: Miljøstyrelsen.



Found in 219 of 247 groundwater wells
Up to 2.4 µg/L

Tap water up to 20 µg/L
River water up to 120 µg/L

Chinese blood 97% detection
Median 8.5 µg/L

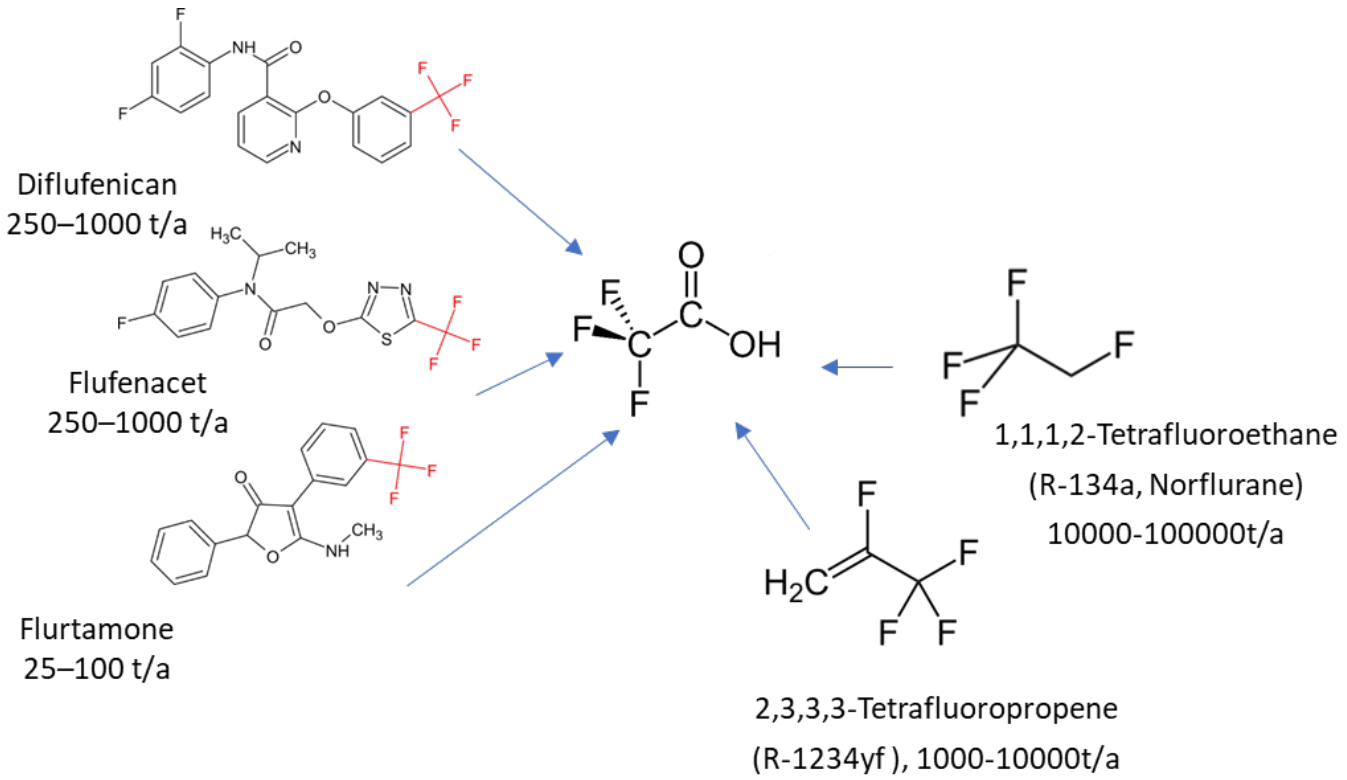


Hale et al. Environ Sci Eur 34, 22 (2022)
Duan et al. (2020)Environ Int 134:105295.

From whence the TFA?

Substance from multiple sources (Nödler & Scheurer, ES&T 2019)

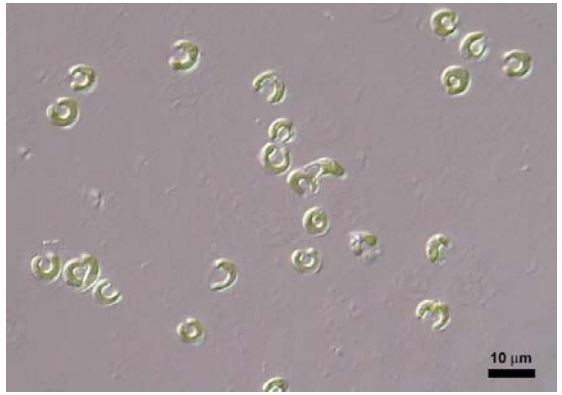
Plant protection products



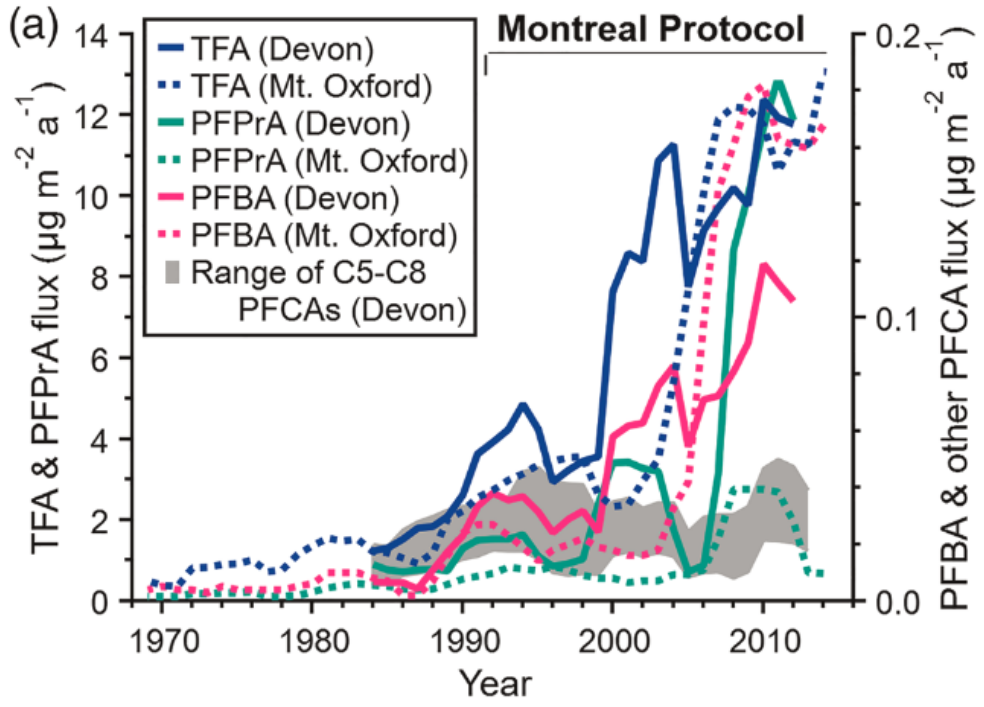
Refridgerants

There is no effective dilution to persistent global pollution

- Ice core records show accumulation of TFA and other short-chain PFAS; all evidence points to anthropogenic origin
- Lowest no-observable effect concentration **so far:** *Raphidocelis subcapitata (120 µg/L)*
- If remote levels reach threshold concentration at remote regions, there is no way of reversing this quickly
- ***Planetary Boundary Threat***

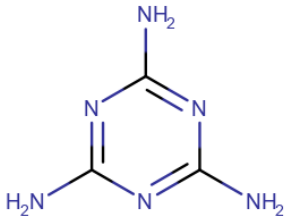


https://alchetron.com/Raphidocelis-subcapitata



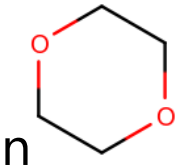
Pickard et al. Geophysical Research Letters (2020),47, e2020GL087535
Joudan (2021), ESPI 23(11), 1641-1649.
Boutonnet et al. Hum Ecol Risk Assess. 1999;5:59–124.

It is not just PFAS!



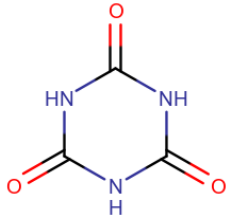
- **Melamine**

In drinking water up to 2 µg/L
Nephrotoxic in combination, especially in combination with cyanuric acid



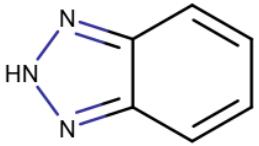
- **1,4-dioxane**

In drinking water up to 0.8 µg/L
Carcinogenic 1b



- **Cyanuric acid**

In drinking water up to 0.12 µg/L
Co-occurs with melamine

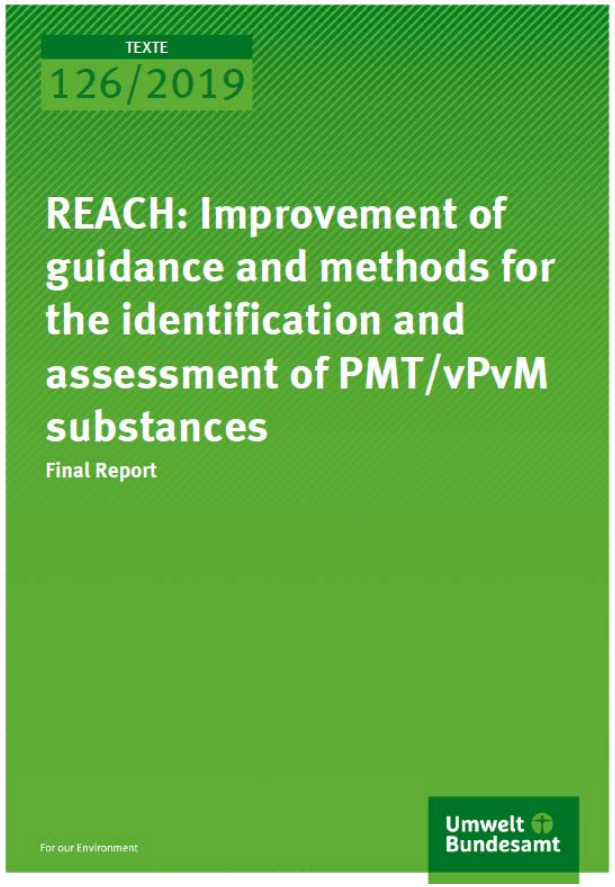


- **Benzotriazole**

In drinking water up to 0.2 µg/L
Danish limit 0.02 µg/L
suspected endocrine disruptor

Regulatory developments for persistent and mobile substances

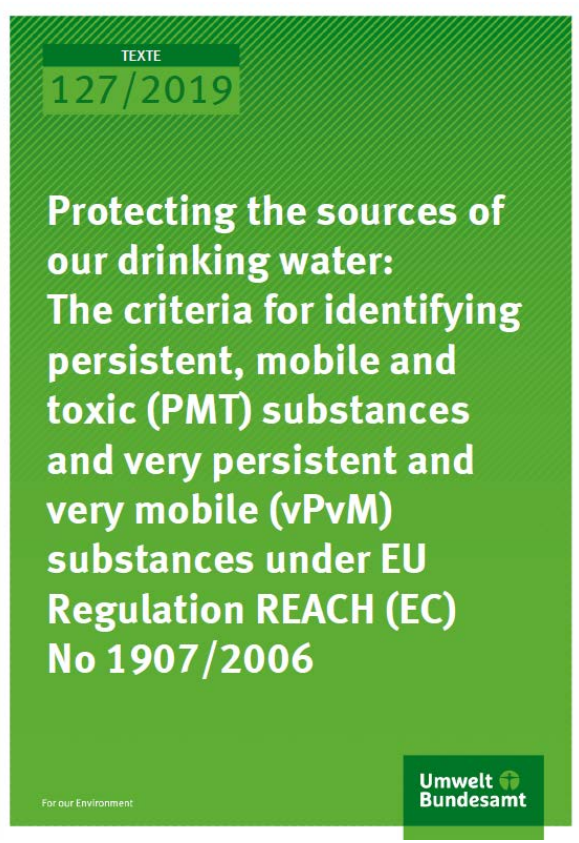
PMT/vPvM Hazard Defintion & Assessment



Scientific Background
Arp & Hale (2019)

PMT:
persistent,
mobile & toxic

vPvM:
very persistent,
very mobile



Regulatory Criteria
Neumann & Schliebner (2019)

PMT/vPvM hazard classes in the CLP regulation

EUROPEAN COMMISSION

Brussels, 19.12.2022

COM(2022) 748 final

2022/0432(COD)

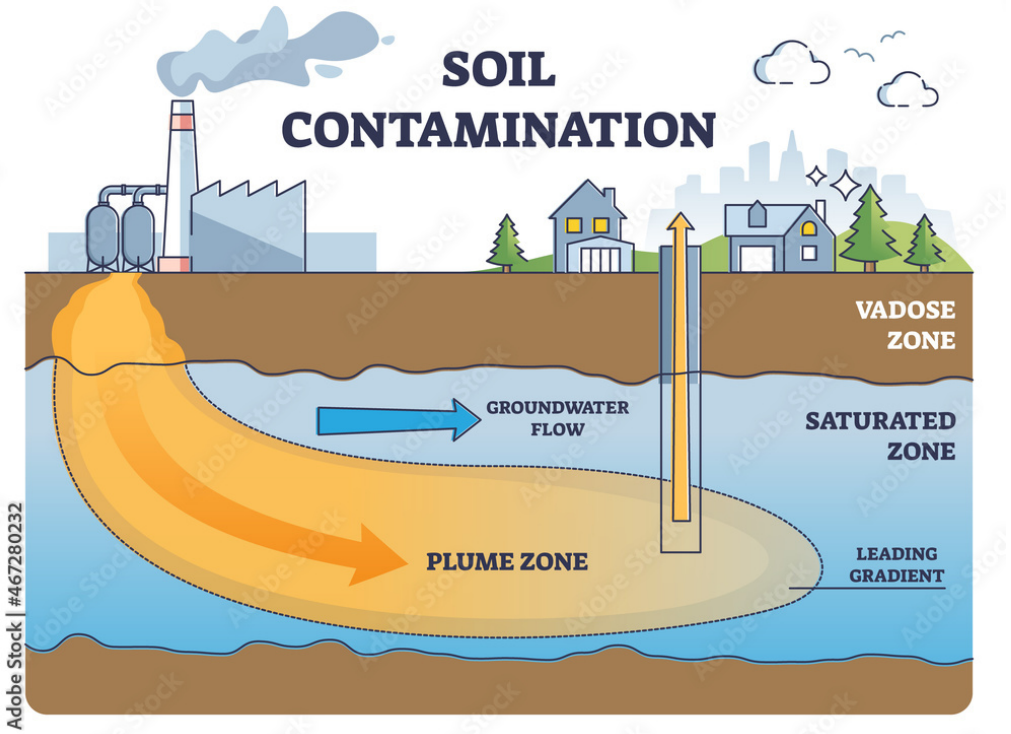
Proposal for a

REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

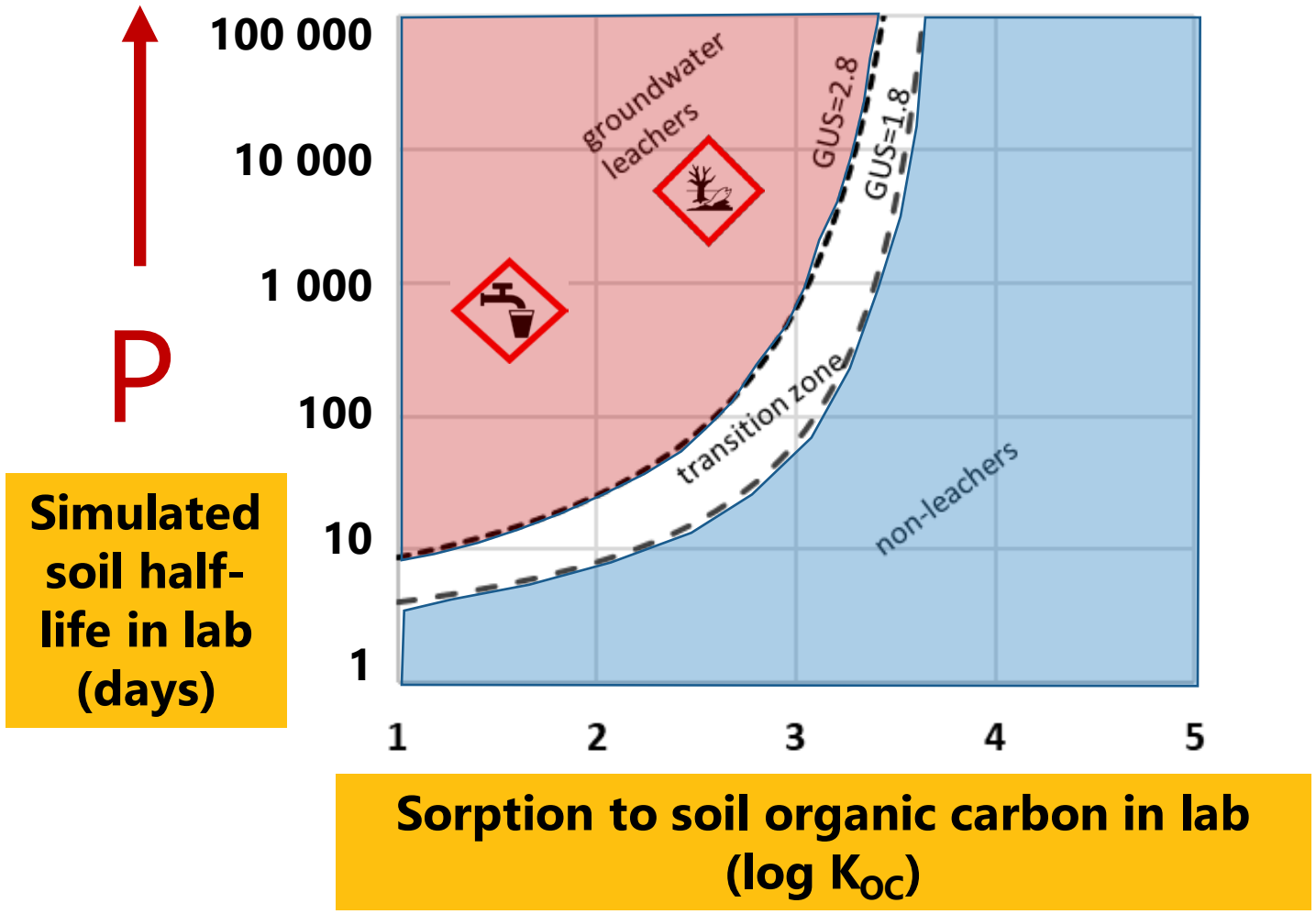
amending Regulation (EC) No 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures

..added definitions and scientific and technical criteria to enable substances and mixtures that have endocrine disrupting ('ED'), persistent, bioaccumulative and toxic ('PBT'), very persistent and very bioaccumulative ('vPvB'), ***persistent, mobile and toxic ('PMT'), or very persistent and very mobile ('vPvM') properties to be classified into established hazard classes***.

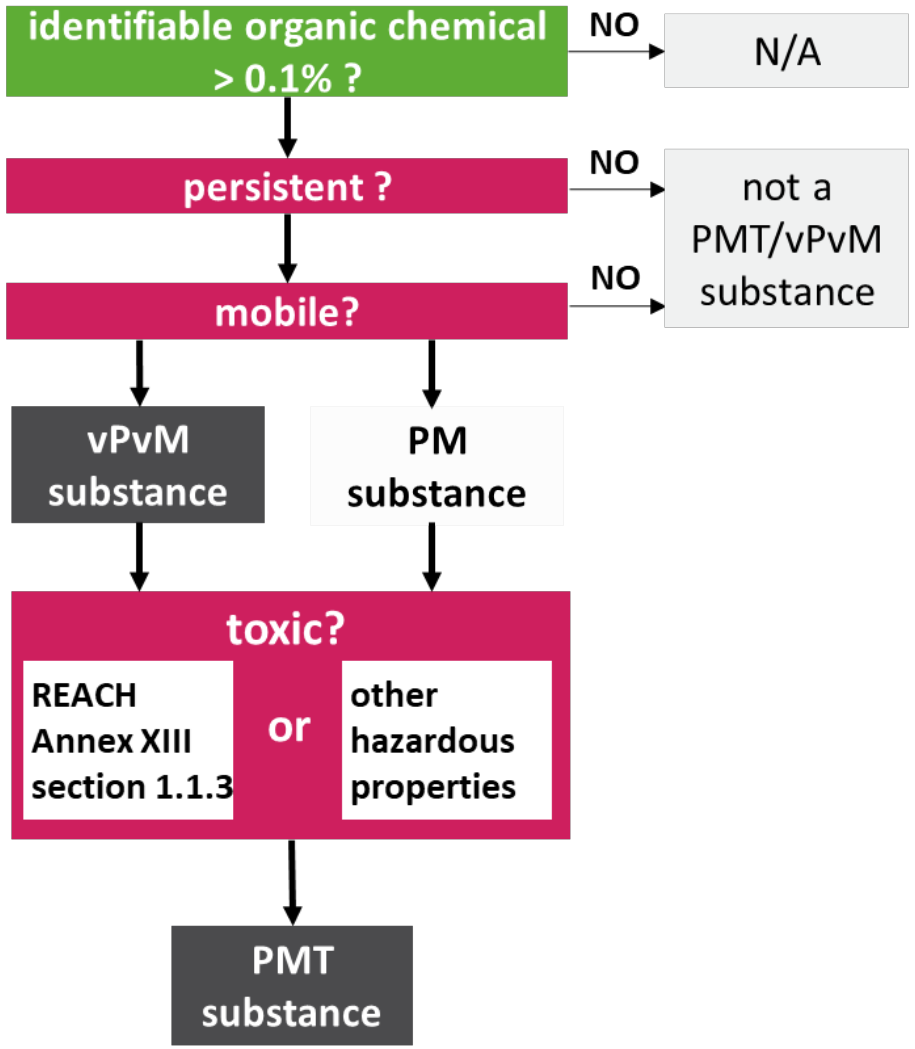
Persistence and Mobility are substance properties

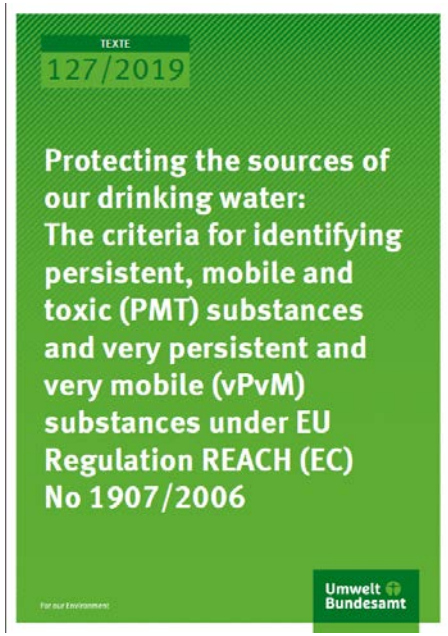


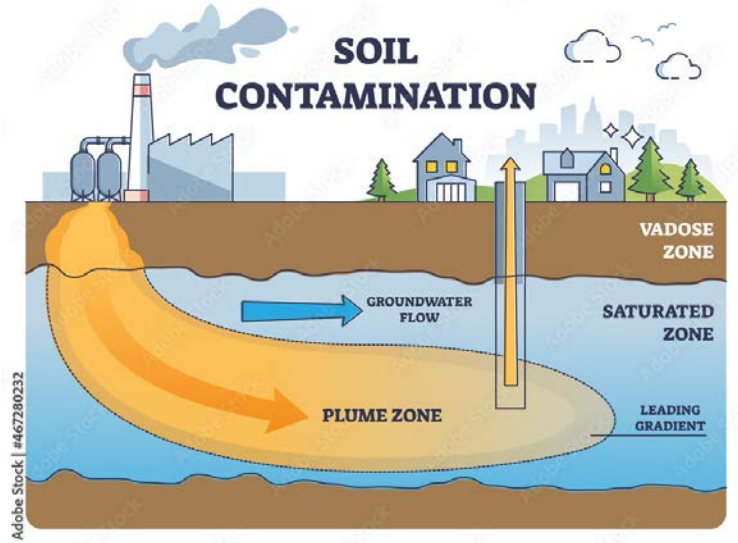
Gustafsson Ubiquity Score – GUS (1989)



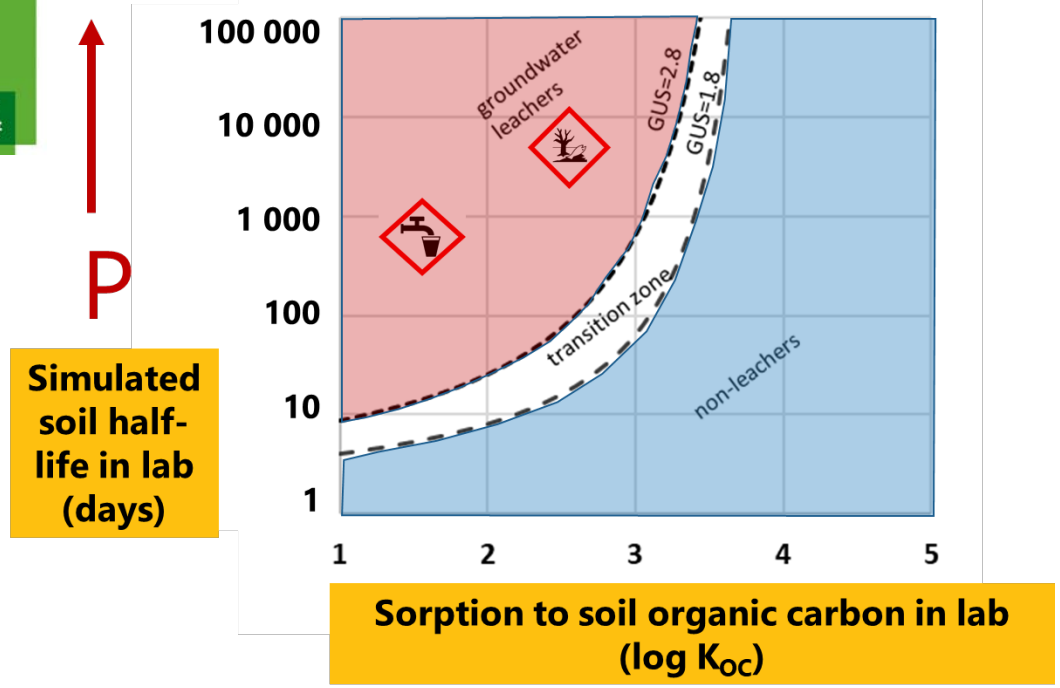
PMT/vPvM assessment



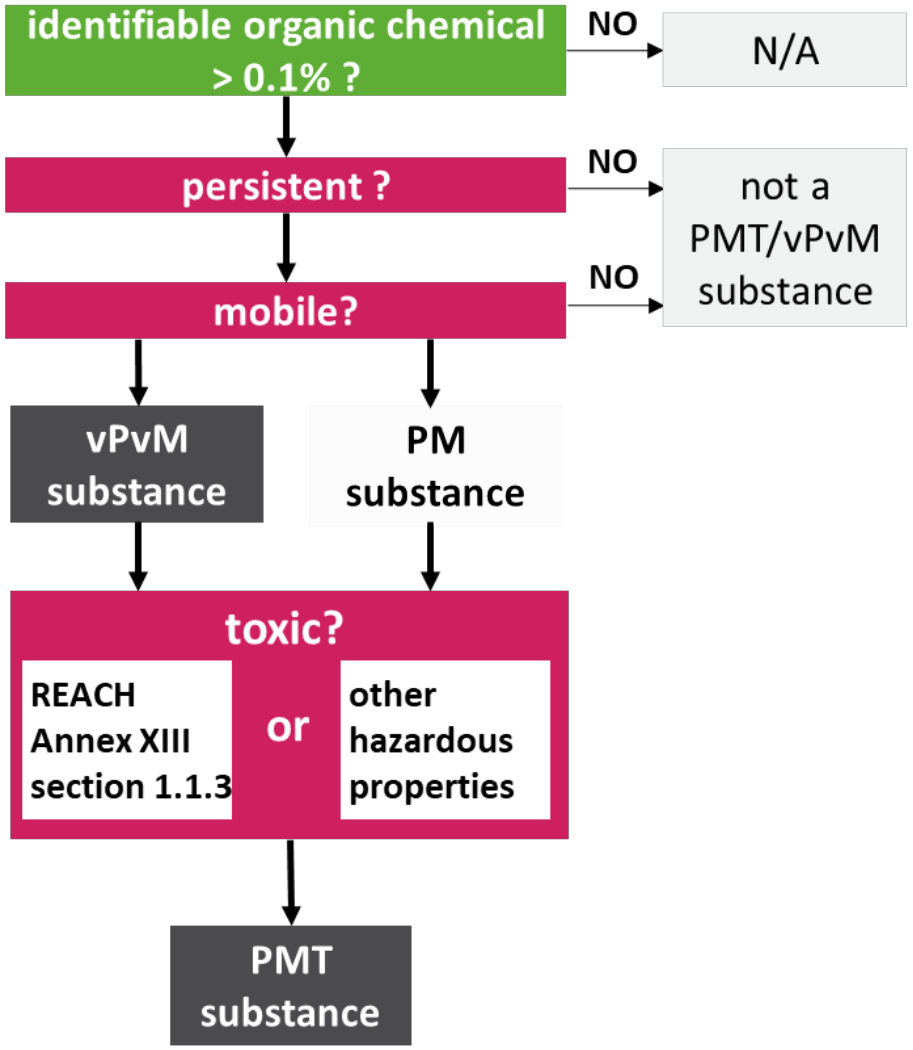




Gustafsson Ubiquity Score – GUS (1989)



Assessing persistency (P and vP)

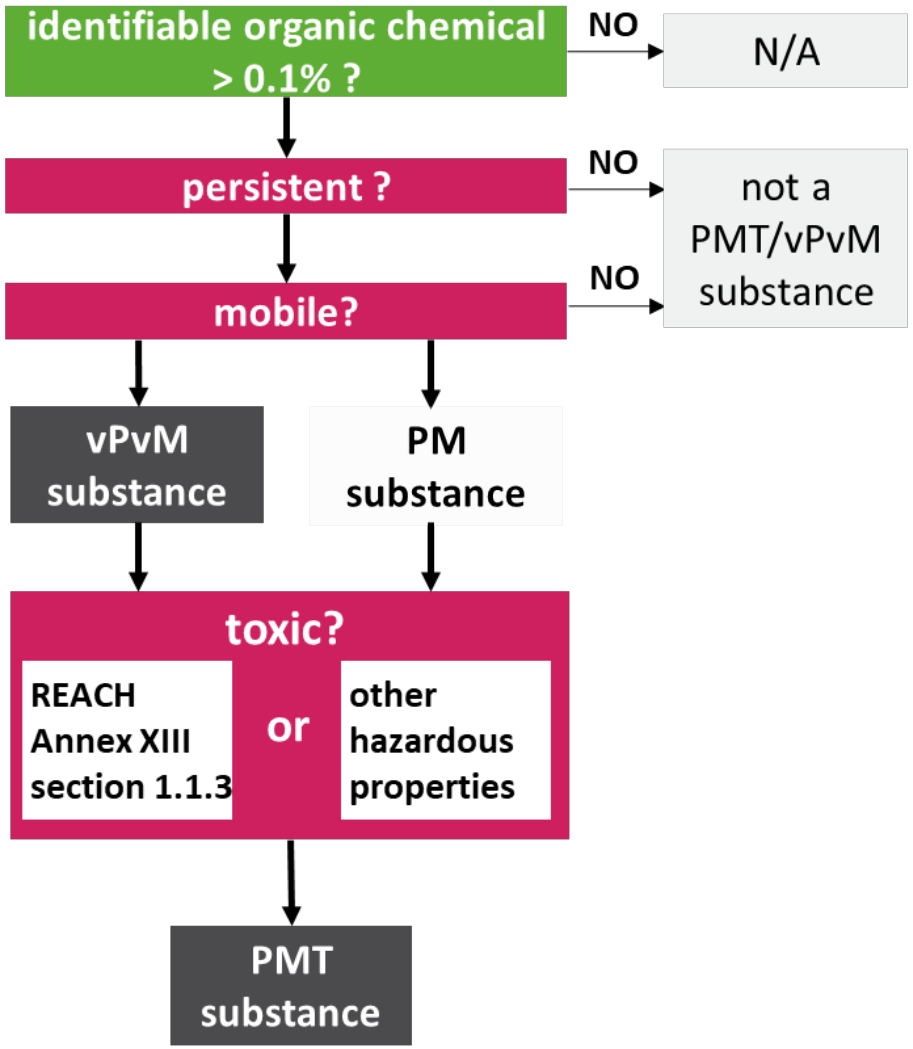


P and vP criteria identicle to Annex XIII of REACH

	persistent (P) in any of the following situations	**very persistent (vP)** in any of the following situtations
marine water	half-life > 60 days	half-life > 60 days
fresh water	half-life > 40 days	half-life > 60 days
marine sediment	half-life > 180 days	half-life > 180 days
fresh water sediment	half-life > 120 days	half-life > 180 days
soil	half-life > 120 days	half-life > 180 days

ECHA Chapter R.11. Version 3.0 (June 2017)
Neumann & Schliebner (2019)

Assessing Mobility



Mobile Criterion (M)

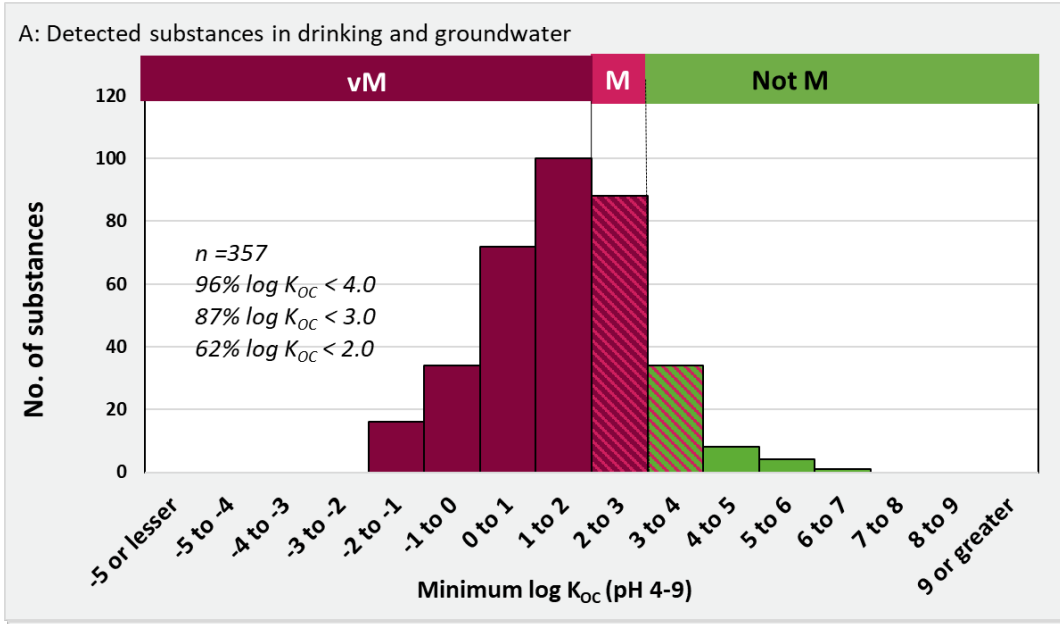
	Mobile (M) if it fulfills P or vP and the following situation	**very mobile (vM)** if it fulfills P or vP and the following situation
CLP Draft Ammendment **log K_{OC}**	< 3.0	<2.0

CLP delegated act (2022): "The classification criteria for M/vM relate, in particular, to the log Koc (soil adsorption coefficient) value. The Koc value is the organic carbon-water partition coefficient and reflects the ability of a substance to be adsorbed on the organic fraction of solid environmental compartments such as soil, sludge and sediment, and is therefore inversely related to the substances' *potential of entering into ground water*. It is therefore appropriate to assess the mobility criterion against the log Koc value of a substance, a low Koc implying a high mobility."

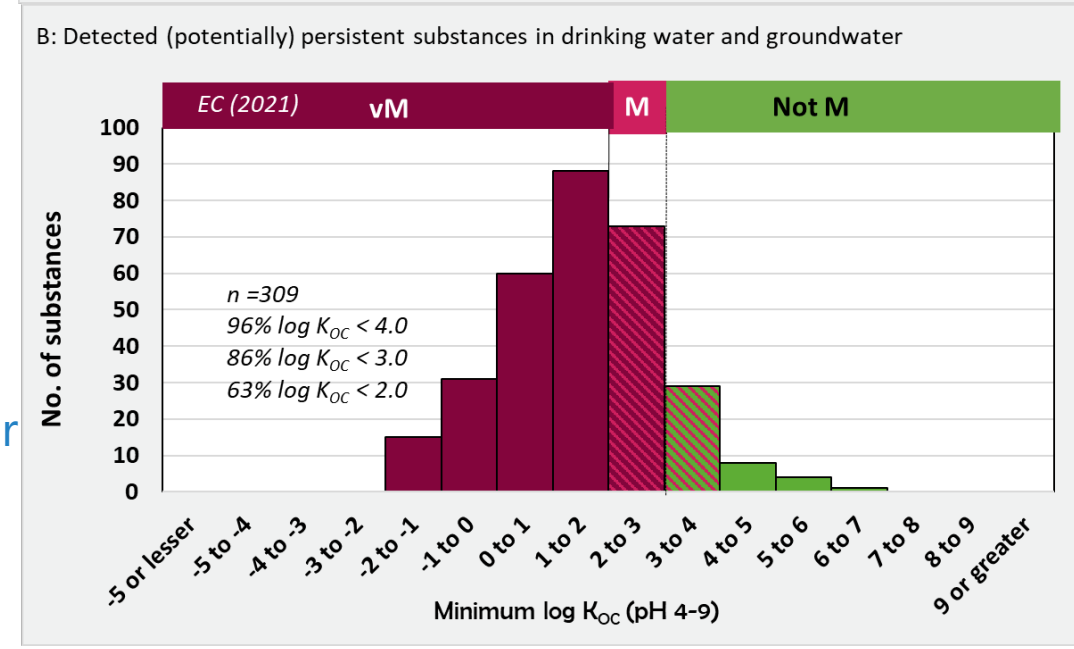
Discussion around where to set the K_{OC} threshold in CLP

- **Empirical data:**
  - Distribution of K_{OC} data for substances in drinking water
- **Other suggestions**
  - Groundwater Ubiquity Score (1989)
  - EU Common Implementation Strategy Working Group for Groundwater (log Koc < 3.0)
  - Biocide regulation (P – 20 days, log Koc < 2.7)
  - UNEP FAO (different categories)
  - Leaching tests
- **Socioeconomic impacts:**
  - Industry – extra testing, market impact
  - Health – reduced health costs/impacts
  - Environment & water supply– reduced remediation costs/impacts

Substances detected in drinking water and groundwater

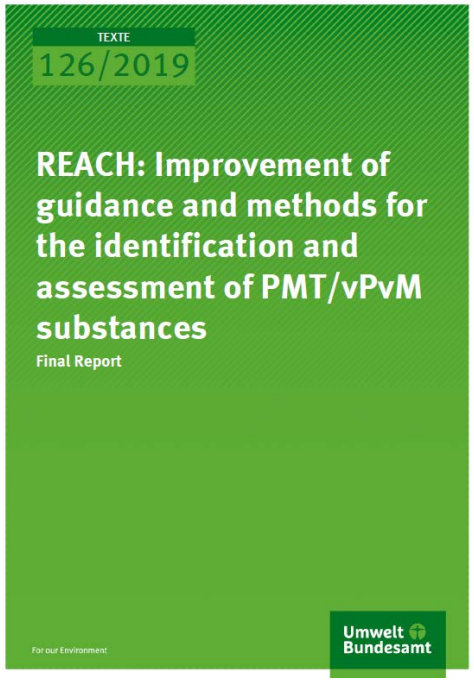


(potentially) persistent substances In drinking water and groundwater

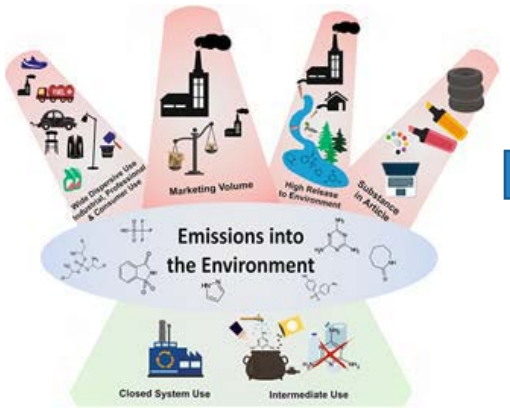


And now we go from ..

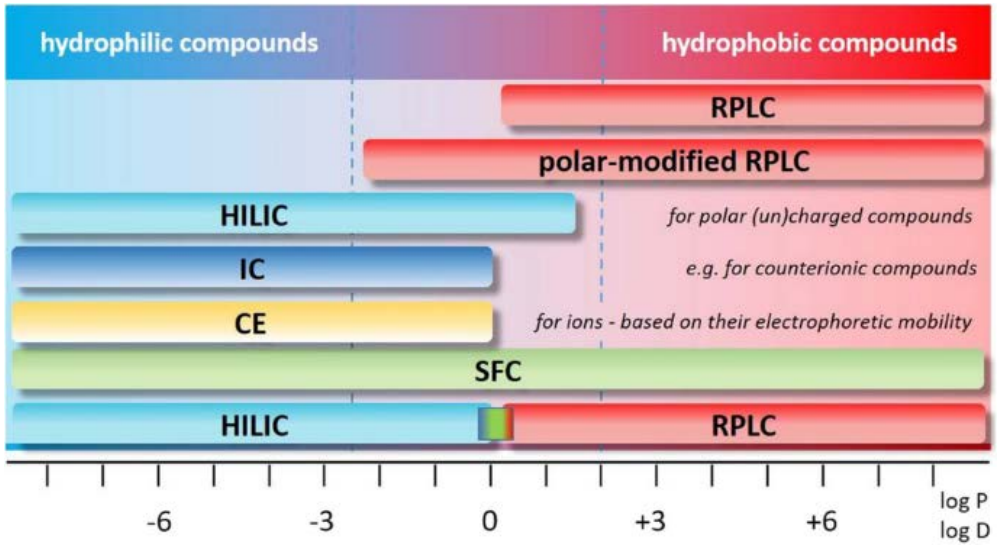
suspect screen blitz...



PMT/vPvM assessment



Emission Index Schulze et al. Science of the Total Environment, 625, 1122-1128.

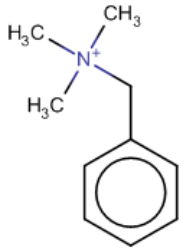


New analytical methods form mobile substances

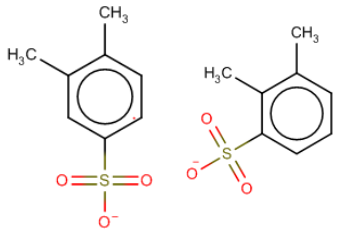
To postivie hitz!

Novel & ubiquitous drinking water contaminants identified in the past 4 years

Benzyltrimethyl ammonium

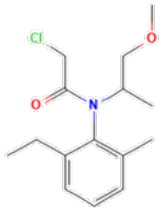


Dimethylbenzene sulfonic acid
0.01-1 µg/L

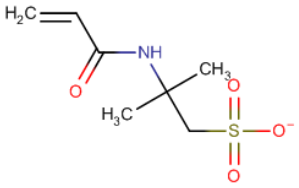


Trifluoromethane-sulfonic acid
Up to 3 µg/L

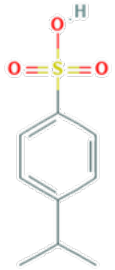
metaolachlor
Up to 0.5 µg/L



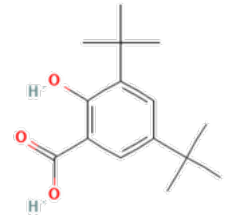
2-Acrylamido-2-methylpropane sulfonic acid
10-1000 µg/L



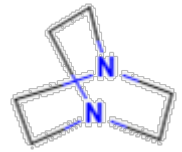
p-Cumenesulfonate



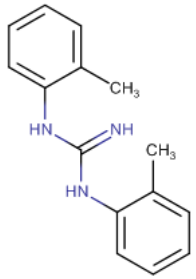
3,5-Di-tert-butylsalicyliate
0.1 – 1 µg/L



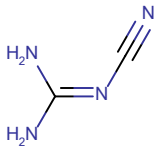
Diazabicyclooctane
0.01 – 1 µg/L



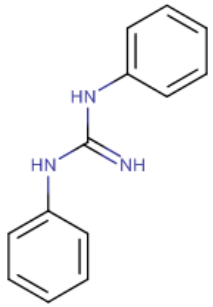
1,3-Di-*o*-tolylguanidine



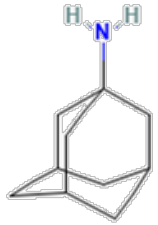
Cyanoguanidine
0.1 – 10 µg/L



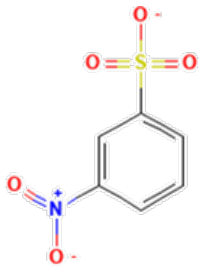
1,3-Diphenylguanidine



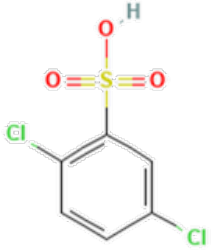
Adamantan-1-amine
Up to 0.01 µg/L



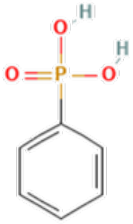
3-Nitrobenzenesulfonate
Up to 10 µg/L



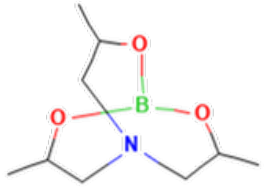
2,5-dichloro-benzenesulfonic acid
Up to 100 ng/L



Phenyl phosphonic acid
Up to 0.05 ng/L



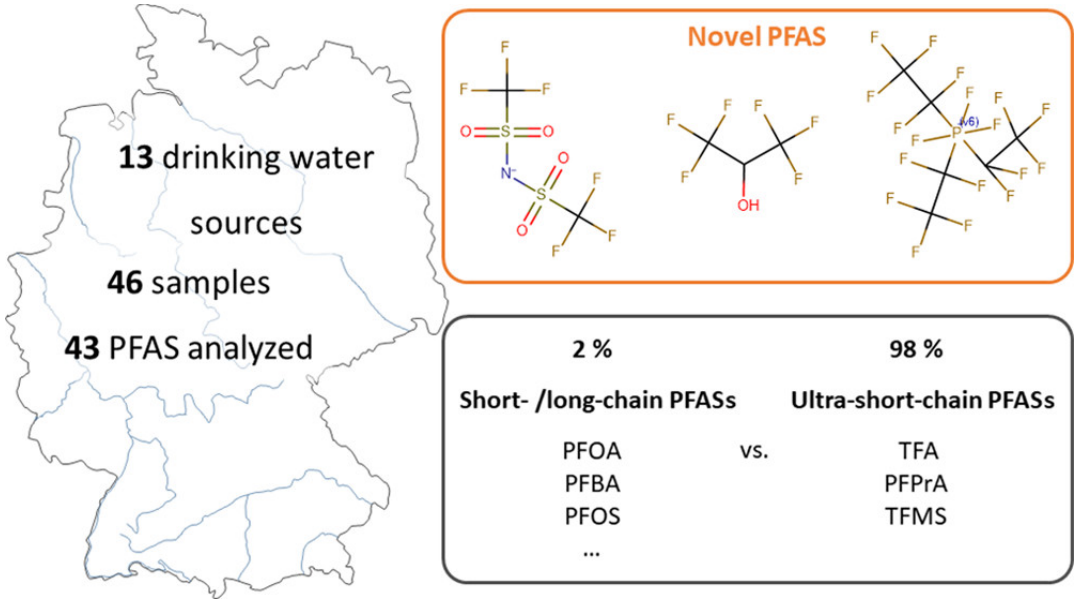
Triisopropanolamine borate
Up to 40 ng/L

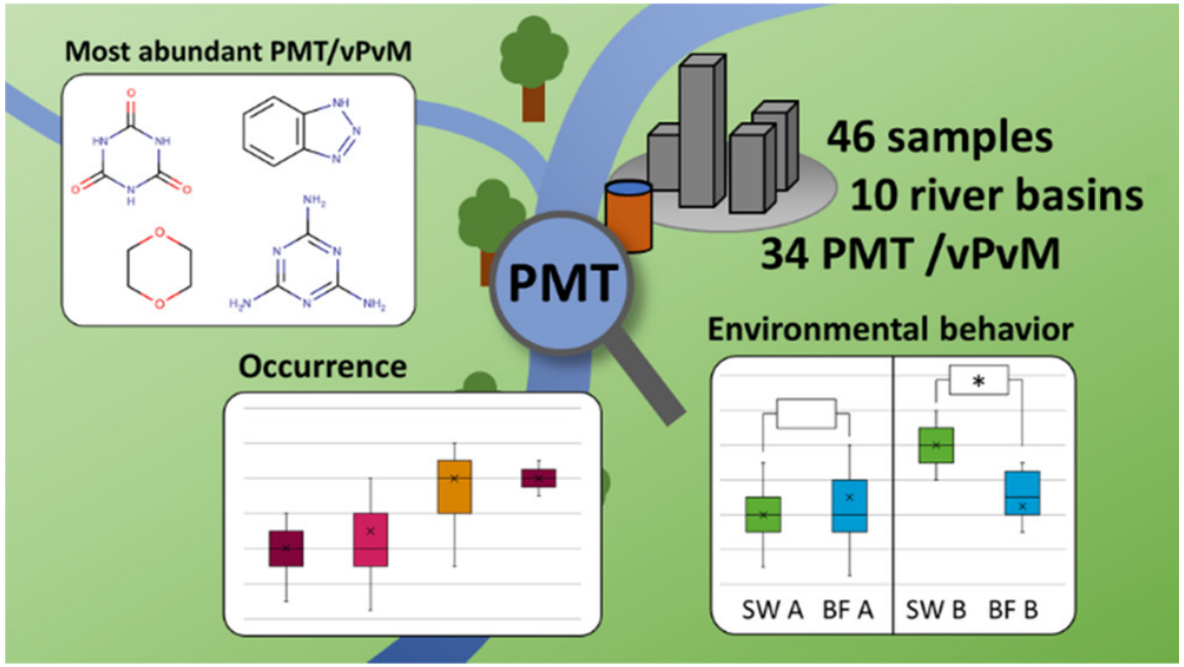


Schulze et al. Water research 153 (2019): 80-90.
Neuwald et al. Water Research 204 (2021) 117645

Neuwald et al. ES&T 2022
Kiefer et al. Water research 196 (2021) 116994

PMT/vPvM Substances in Germany's Drinking water sources





Neuwald et al.
Environ. Sci. Technol. 2022, 56, 10, 6380-6390

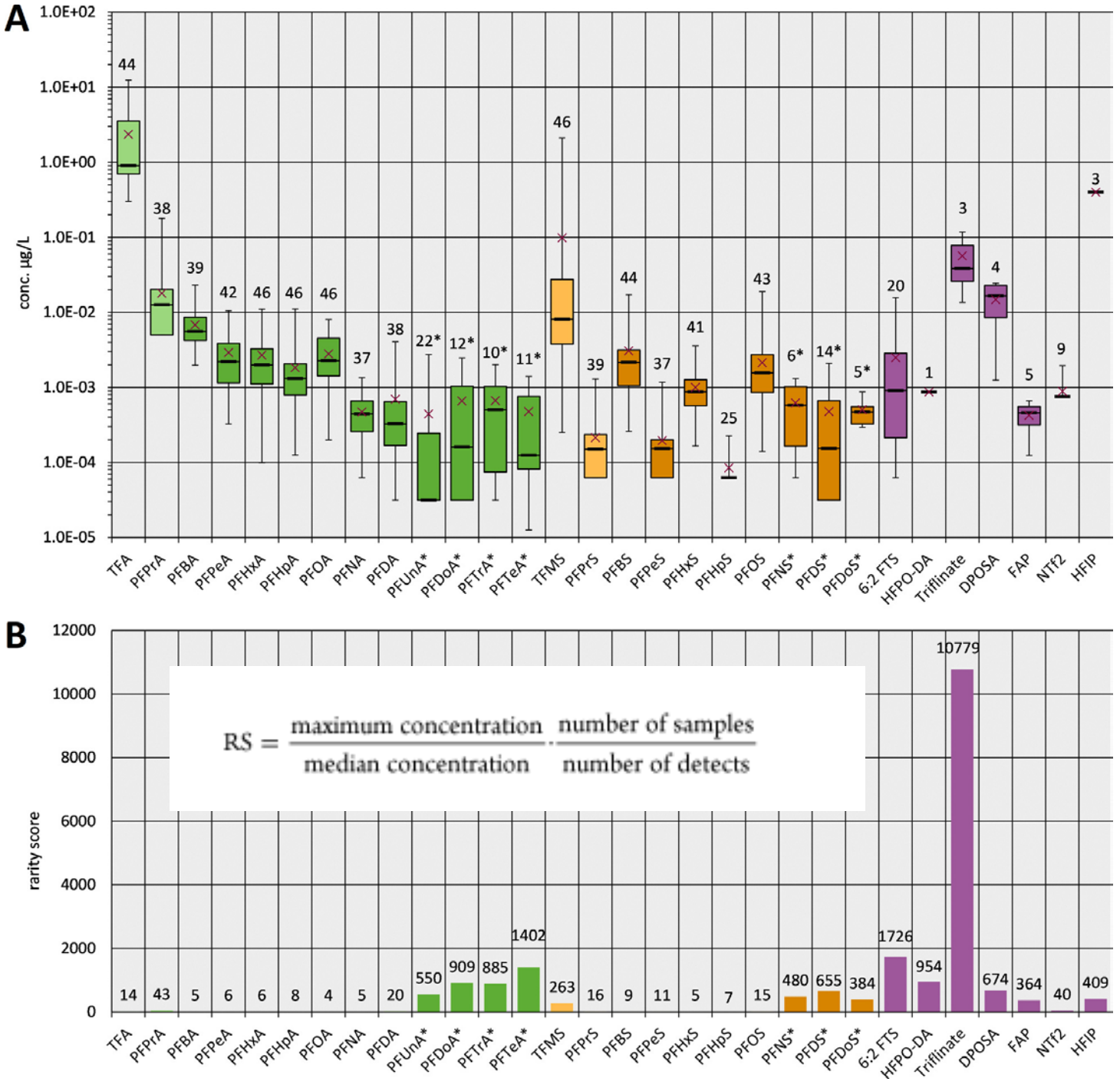
Neuwald et al.
Environ. Sci. Technol. 2022, 56, 15, 10857-10867

Concentration and ubiquity of PFAS

- TFA most abundant PFCA
- TFMSA most abundant PFSA

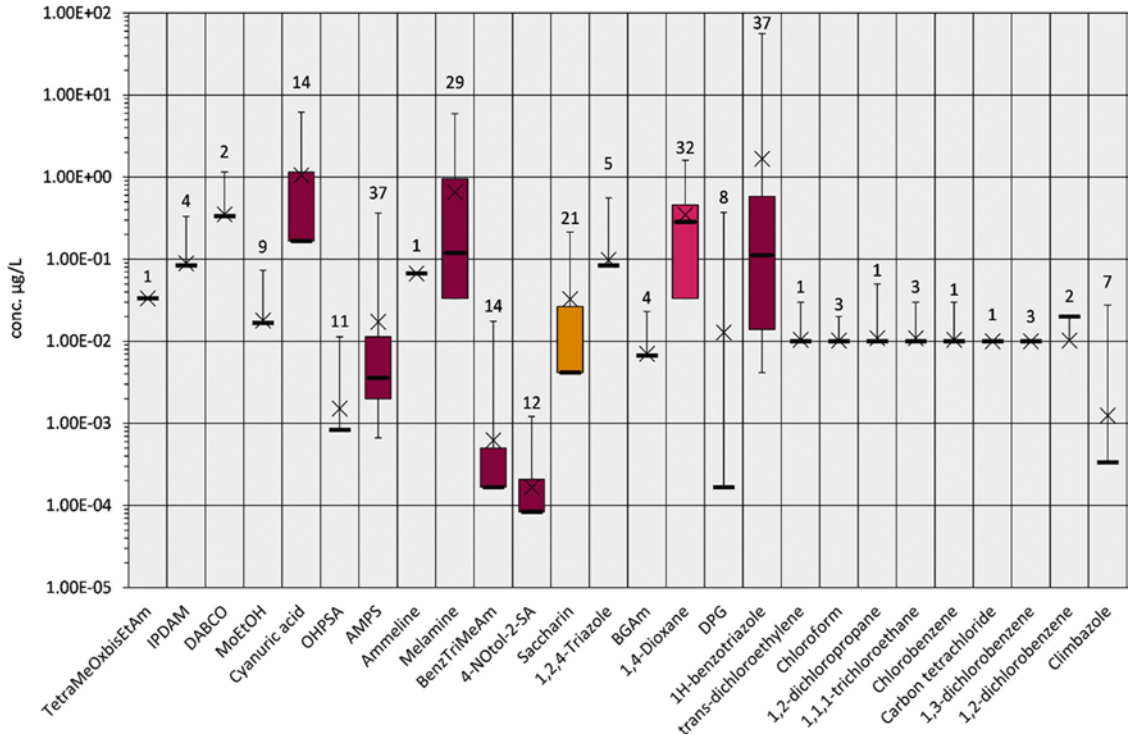
- Most PFAS ubiquitous, some PFAS local: Long-chan PFAS; 6:2 FTS; GenX, Triflinate; DPOSA; FAP*; NF2*, HFIP

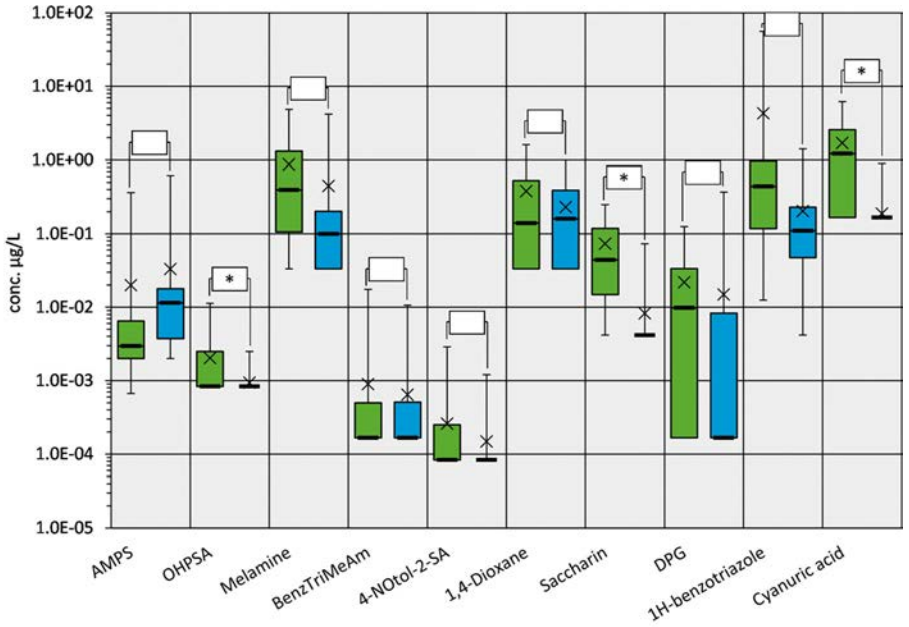
* Ionic liquids used in e.g. Li-batteries



Concentration and mobility of PMT/vPvM substances

- Ubiquitous and high concentrations: melamine, cyanuric acid, benotriazol, 1,4-dioxan, AMPS, Saccharin
- Many others detected less frequently (for now)
- Surface water concentrations were significantly similar to bankfiltrate concentrations (due to high subsurface mobility)

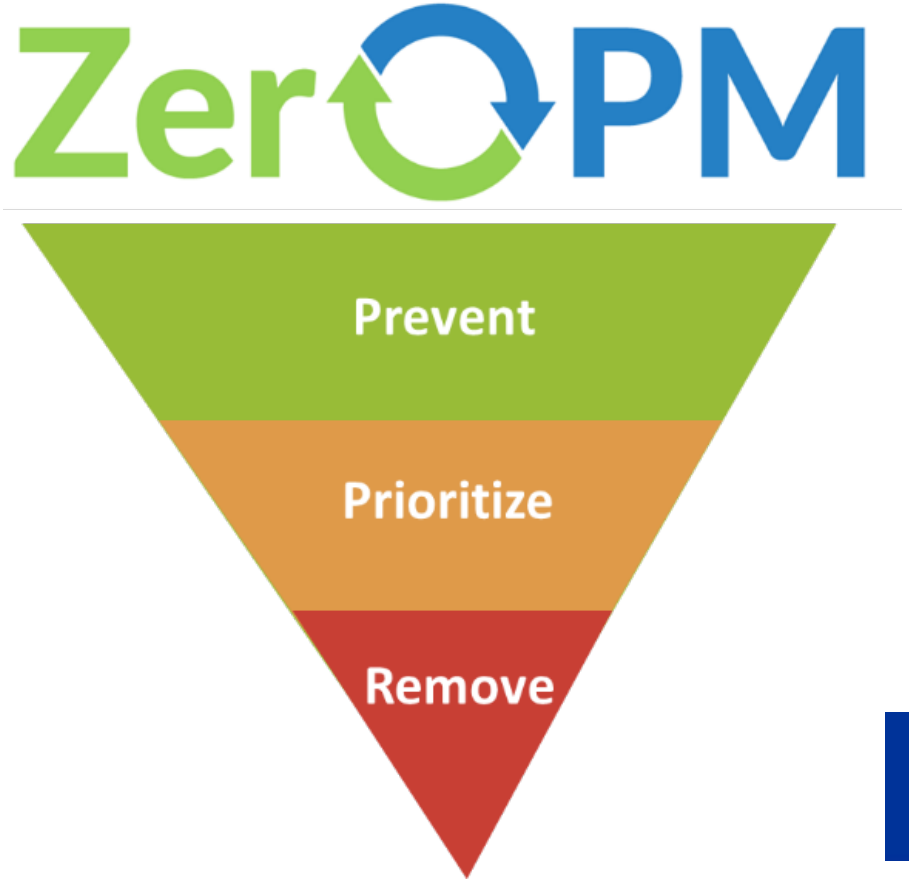




Zero pollution of persistent, mobile substances

- ZeroPM will interlink and synergize three strategies to protect the environment and human health from persistent, mobile substances:

  Prevent,
  Prioritize and
  Remove.

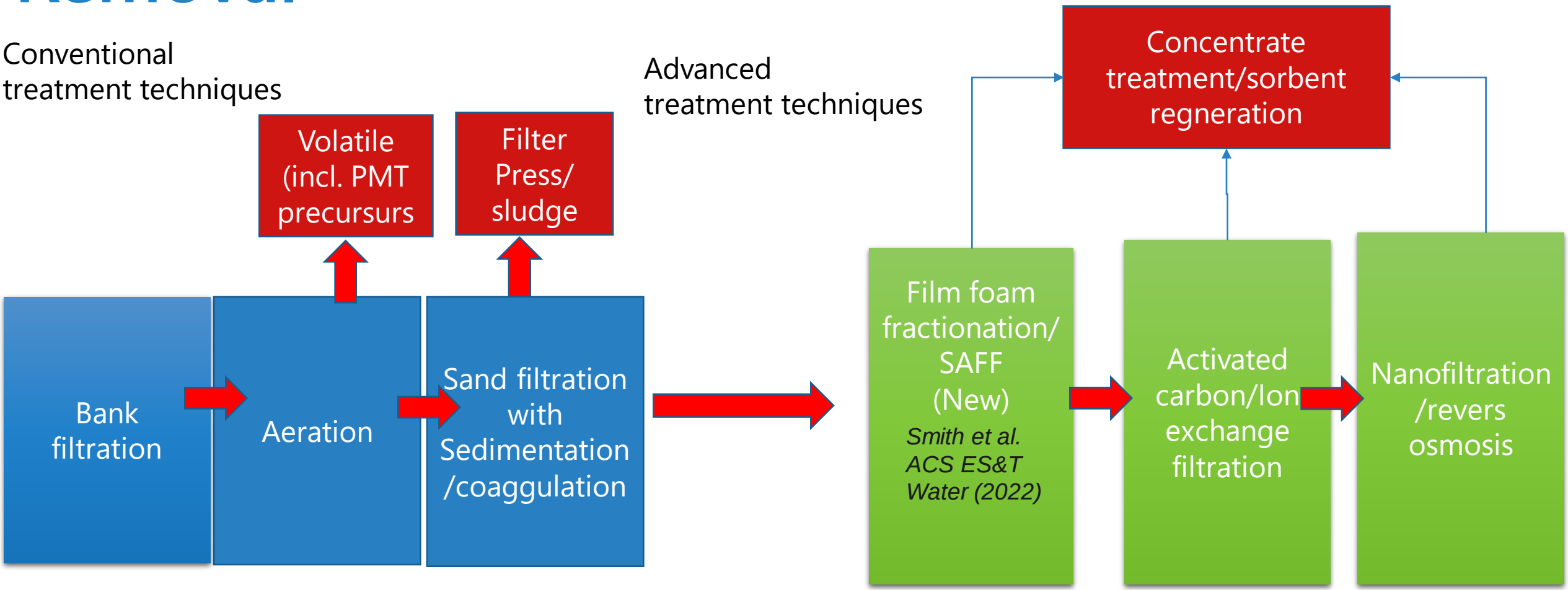


Horizon 2020 project
2021-2026

Removal

Conventional treatment techniques

Advanced treatment techniques



Least effective
0 €/m3
0 kWh/m3

1 €/m3
1 kWh/m3

PMT/vPvM substances (inc PFAS) in brines, concentrates, sorbents, soils & sludges

Solution	Concern to address**
(Catalyzed) electrolysis/oxidation	By-product formation and energy consumption
(Adsorption on AC +) incineration/pyrolysis/milling	Volatile emissions, energy consumption and scalability**
Landfilling	Long term leachate emissions

** see the NGI lead projects SLUDGEFFECT and VOW

Prioritize

PMT/vPvM hazard	REACH Emission Likelihood	Analytical & Monitoring Gaps	Remediation Gap	Exposure Level	Overall Prioritization Level
Unknown/ insufficient data	Unknown/ confidential/Not REACH registered	Unknown/ Not assessed	Remediation potential with AC and ozone unknown or difficult to estimate	No monitoring data currently available	Unknown/insufficient data
vPvM & PMT or vPvM	**Very high or High:** high E-score, detection in environment required for "very high", otherwise "high"	**Major analytical gap:** Not monitored because the substance can only be analysed by advanced / specialized methods	**No O3&AC:** Compounds that cannot be eliminated using AC or ozonation	**Ubiquitously detected and occasionally at high concentrations** in drinking water sources (greater than 0.1 µg/L or the PNEC if known)	**Highest-Priority** PMT/vPvM substance with registered under REACH > 10 tpa, very high or high emission likelihood, and at least one other
PMT		**Minor analytical gap:** Not monitored, but method development feasible	**O3 only:** Compounds that can be removed using ozonation only	**Ubiquitous but generally at low concentrations** in drinking water sources (less than 0.1 µg/L or the PNEC if known)	**High-Priority** PMT/vPvM substance, registered under REACH > 10 tpa
PM	**Medium:** low E-score or intermediate under REACH that is detected in drinking water sources	**Major monitoring gap:** Not monitored, but could be monitored using current methods	**AC only:** Compounds that can be removed using AC only	**Local contamination and occasionally at high concentrations** in drinking water sources	**Moderate-Priority** PMT/vPvM substances, but registered under REACH < 10 tpa or is suspected impurity/transformation products.
Potential PMT/vPvM		**Minor monitoring gap:** Monitored regularly, but by less than 20% of water quality labs	**Both O3&AC:** Compounds that can be removed by using both AC or ozonation	**Local contamination but generally at low concentrations** in drinking water sources	**Potential-Priority** All other cases, except if "Not PMT/vPvM"
Not PMT/vPvM	**Low:** low E-score or intermediate substance, not detected in drinking water sources	**No Monitoring gap:** Monitored regularly, but more than 20% of water quality labs	**Conventional:** Compounds that can be removed with conventional techniques	**Monitored commonly, not found:** Extensive monitoring showed no presence in sources of drinking water	**Lowest-Priority** Substance is "Not PMT/vPvM"

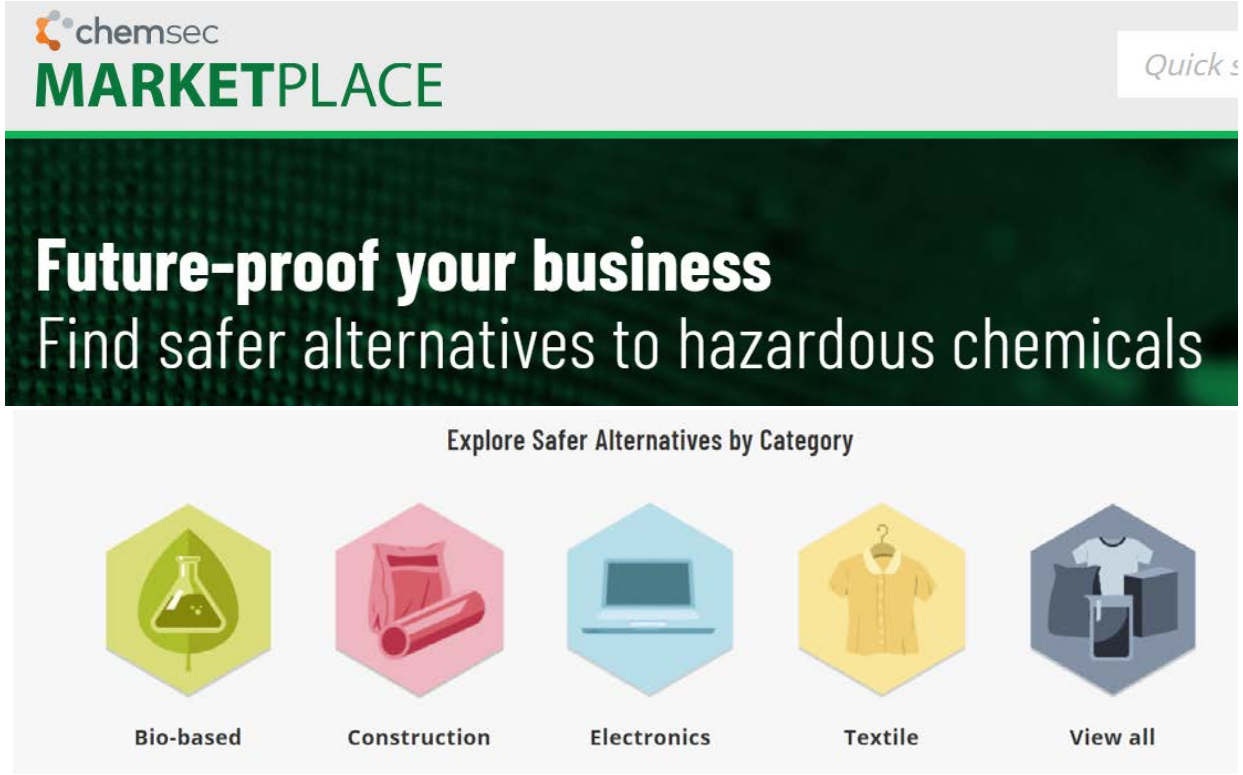
A prioritization framework for PMT/vPvM Substances under REACH for registrants, regulators, researchers and the water sector, *by Hans Peter H. Arp, Sarah E. Hale, Ulrich Borchers, Vassil Valkov, Laura Wiegand, Daniel Zahn, Isabelle Neuwald, Karsten Nödler, Marco Scheurer, UBA Texte 2023, FKZ 719 65 408 0*

Prioritized PMT/vPvM substances .....(sneak preview)

EC	CAS	Substance	PMT/vPvM hazard	Emission Index	Analytical & Monitoring Gap	Remediation Gap	Exposure level	Overall Prioritization Level
203-618-0	108-80-5	cyanuric acid	vPvM & PMT	very high	Minor monitoring gap	No O3&AC	Ubiquitous, high conc	Highest-priority
203-615-4	108-78-1	Melamine	vPvM & PMT	very high	Monitored frequently	No O3&AC	Ubiquitous, high conc	Highest-priority
249-616-3	29420-49-3	PFBS	vPvM & PMT	very high	Monitored frequently	No O3&AC	Ubiquitous, low conc	Highest-priority
204-661-8	123-91-1	1,4-dioxane	vPvM & PMT	very high	Monitored frequently	No O3&AC	Ubiquitous, high conc	Highest-priority
202-394-1	95-14-7	Benzotriazole	vPvM & PMT	very high	Monitored frequently	Both O3&AC	Ubiquitous, high conc	Highest-priority
244-479-6	21615-47-4	Ammonium undecafluorohexanoate (PFHxA)	vPvM & PMT	very high	Minor monitoring gap	No O3&AC	Ubiquitous, low conc	Highest-priority
200-929-3	76-05-1	Trifluoroacetic acid	vPvM	very high	Monitored frequently	No O3&AC	Ubiquitous, high conc	Highest-priority
200-300-3	56-93-9	Benzyltrimethylammonium chloride	vPvM	very high	Major monitoring gap	No O3&AC	Ubiquitous, low conc	Highest-priority
222-823-6	3622-84-2	N-butylbenzenesulphonamide	vPvM	very high	Major monitoring gap	No O3&AC	Ubiquitous, low conc	Highest-priority
204-445-3	121-03-9	4-nitrotoluene-2-sulphonic acid	vPvM	very high	Major monitoring gap	No O3&AC	Ubiquitous, low conc	Highest-priority
248-580-6	27619-97-2	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanesulphonic acid	vPvM	very high	Monitored frequently	No O3&AC	Ubiquitous, low conc	Highest-priority
200-087-7	51-28-5	2,4-dinitrophenol	vPvM & PMT	very high	Minor monitoring gap	No O3&AC	Local, high conc	Highest-priority
200-915-7	75-91-2	tert-butyl hydroperoxide	vPvM & PMT	high	Major monitoring gap	No O3&AC	no detections known	Highest-priority
203-444-5	106-93-4	1,2-dibromoethane	vPvM & PMT	very high	Monitored frequently	No O3&AC	Local, high conc	Highest-priority
201-152-2	78-87-5	1,2-dichloropropane	vPvM & PMT	very high	Monitored frequently	No O3&AC	Local, high conc	Highest-priority
202-808-0	99-99-0	4-nitrotoluene	vPvM & PMT	high	Monitored frequently	No O3&AC	monitored commonly, not found	Highest-priority
203-639-5	109-01-3	1-methylpiperazine	vPvM & PMT	very high	Major monitoring gap	No O3&AC	no detections known	Highest-priority
200-864-0	75-35-4	1,1-dichloroethylene	vPvM & PMT	very high	Monitored frequently	No O3&AC	Local, high conc	Highest-priority
200-663-8	67-66-3	Chloroform	vPvM & PMT	very high	Monitored frequently	No O3&AC	Local, high conc	Highest-priority
200-927-2	76-03-9	Trichloroacetic acid	vPvM & PMT	high	Minor monitoring gap	No O3&AC	no detections known	Highest-priority
204-500-1	121-82-4	Perhydro-1,3,5-trinitro-1,3,5-triazine	vPvM	very high	Minor monitoring gap	No O3&AC	Local, high conc	Highest-priority

Prevent

- **Expand Green chemistry** => Biodegradable, non-toxic chemistry
- **Safe design** => No use or emissions of PMT/vPvM substances in products unless **essential use**



EUROPEAN COMMISSION

Brussels, 19.12.2022
C(2022) 9383 final

ANNEXES 1 to 4

ANNEXES

to the

Commission Delegated Regulation

amending Regulation (EC) No 1272/2008 as regards hazard classes and criteria for the classification, labelling and packaging of substances and mixtures

With PMT/vPvM hazard classes in the CLP legislation:

Recognize the hazard before the risk (i.e. high volume production / emissions)

Conclusions for PFAS and PMT/vPvM substances

- Do we have knowledge about future pollution threats?
  - -> Big data approaches to develop early warnings of PFAS and PMT/vPvM substances. Focus on data repositories (hazard, production, use, emissions)

- How can we investigate early warnings and how do we monitor?
  - -> Yes, through suspect screening, non-target analysis
  - -> UBA Suspect list of 344 PMT/vPvM substances

- How do we communicate in an uncertain world?
  - -> Planetary Boundary Threats,
  - -> Prevention is healthier (and cheaper) than the cure

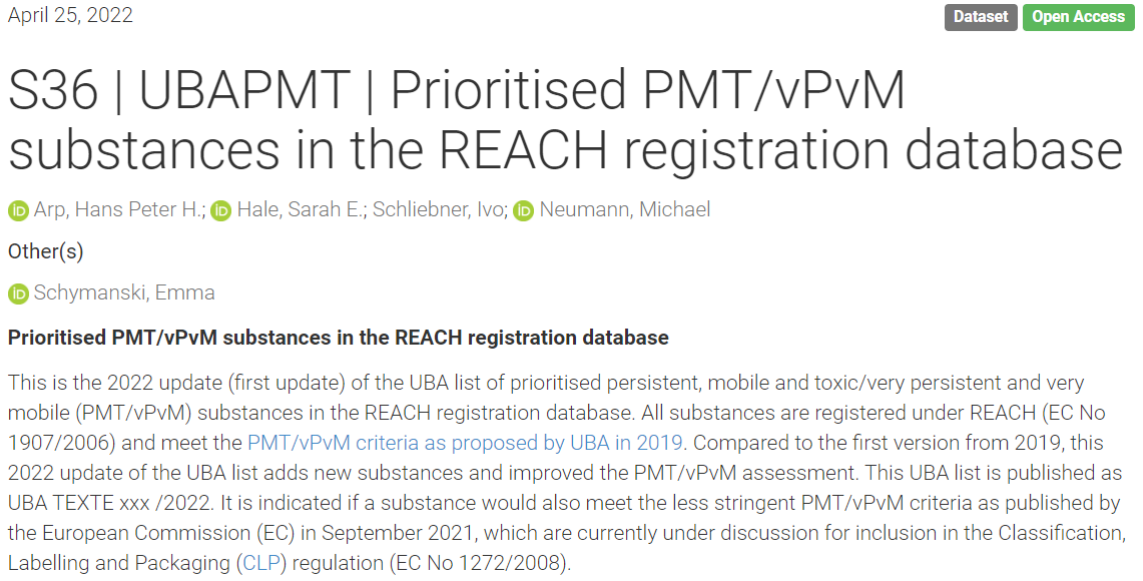
Suspect lists

Repository for all outputs of ZeroPM on Zenodo

- https://zenodo.org/communities/zeropm-h2020/

Suspect lists published via the Norman SLE
https://zenodo.org/communities/norman-sle
S36 – UBA PMT/vPvM substances
S90 – ZeroPM Box 1 substances
S100 –PFAS identified in REACH 2019

Four UBA Texte reports
-- coming within weeks



April 25, 2022

Dataset Open Access

S36 | UBAPMT | Prioritised PMT/vPvM substances in the REACH registration database

Arp, Hans Peter H.; Hale, Sarah E.; Schliebner, Ivo; Neumann, Michael

Other(s)

Schymanski, Emma

Prioritised PMT/vPvM substances in the REACH registration database

This is the 2022 update (first update) of the UBA list of prioritised persistent, mobile and toxic/very persistent and very mobile (PMT/vPvM) substances in the REACH registration database. All substances are registered under REACH (EC No 1907/2006) and meet the PMT/vPvM criteria as proposed by UBA in 2019. Compared to the first version from 2019, this 2022 update of the UBA list adds new substances and improved the PMT/vPvM assessment. This UBA list is published as UBA TEXTE xxx /2022. It is indicated if a substance would also meet the less stringent PMT/vPvM criteria as published by the European Commission (EC) in September 2021, which are currently under discussion for inclusion in the Classification, Labelling and Packaging (CLP) regulation (EC No 1272/2008).

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https://www.umweltbundesamt.de/en/PMT-substances

2021-2026

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www.zeropm.eu
https://twitter.com/ZeroPM_H2020
Youtube: ZeroPM – H2020

WPs and partners

- WP1: Project management
- WP2: Alternatives Assessment
- WP3: Policy
- WP4: Market transition
- WP5: Substance grouping
- WP6: Risk assessment
- WP7: Technical solutions
- WP8: Communication and dissemination