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TÜBINGEN

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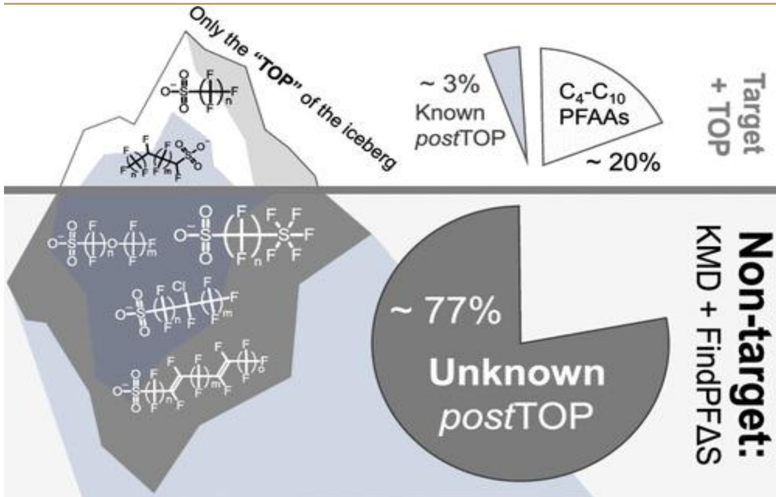


PFAS – Herausforderung für Umwelt und öffentliche Wasserwirtschaft

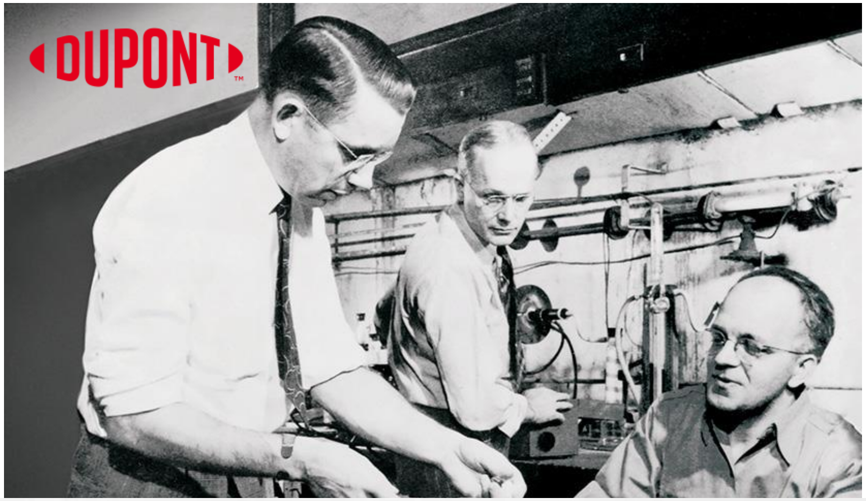
Prof. Dr. Peter Grathwohl
Hydrogeochemie
Geo-Umweltforschungszentrum (GUZ)

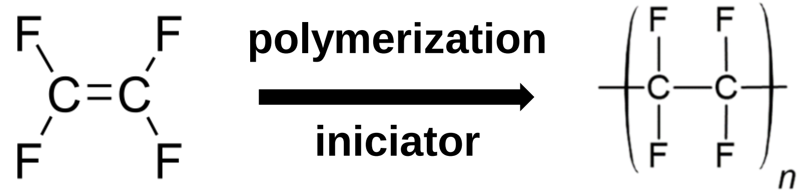
"Brief History" of (Halogenated) Solvents

1825 - 1900	Benzene (carcinogenic, weakly flammable)
1870 - 1930	Light gasoline (weakly flammable)
1900 - 1960	Heavy gasoline (flammable, less poisonous)
1880 - 1950	Carbon tetrachloride (not flammable, carcinogenic)
1930 -	**Per-, Trichloroethene (poor flammability, “non-poisonous”)**
1960 -	**CFC, Freons (non-poisonous)**
1974	**CFCs degrade ozone (Molina & Rowland)** (1985 antarctic ozone hole confirmed)
1974, 1976	Haloforms (e.g. chloroform) in drinking water
1976	VOC in river water (Rhine)
1977	**VOC in drinking water, groundwater and mineral waters, TCE carcinogenic?**
1975, 1977	Formation of HCl, Phosgene and carbon tetrachloride through photooxidation of VOCs in the atmosphere
1984, 1990	**Formation of trichloroacetic acid (through photooxidation of VOC in the atmosphere (connected to forest decline)**
1986	Utilization of CFC in textile cleaning (replacement of "per")
1987	Montreal Protocol for the banning of ozone degrading chemicals
1990	Transformation of TCE and PCE to vinylchloride in groundwater
1995	**Nobel Prize for Chemistry to Mario Molina, F. Sherwood Rowland (together with Paul Crutzen)**
1996	**End of the production of ozone degrading chemicals in industr. countries**
1996	Proof of the ubiquitous appearance of trifluoroacetate (TFA) from HFC (partially fluorinated ethane, CFC replacements, Frank et al., *Nature*, 382, 34)

................???

How it all started…

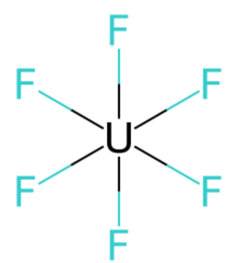


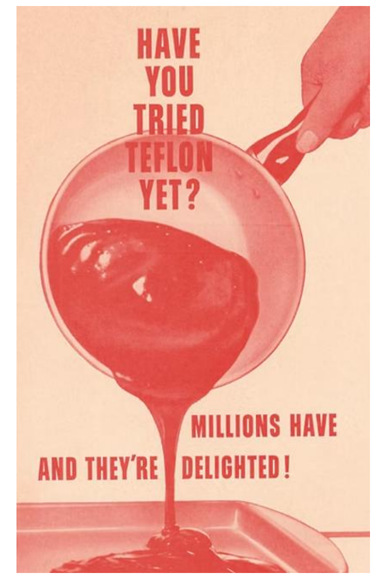


tetrafluoroethylene

polytetrafluoroethylene

MANHATTAN PROJECT
BOMB





PFOS and PFOA as emulsifiers
(chains have high affinity to PTFE)

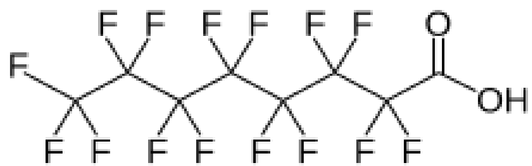
"Brief History" of Per- and Polyfluorinated Substances

- **1940s** — **PFAS were first produced and commercialized**
- **1989** — **The Montreal Protocol came into force**
- **2000** — **The 3M Company phased out C6-, C8-, and C10-based chemistries**
- **2006** — **US EPA launched 2010/2015 PFOA Stewardship Program**
- **2009** — **PFOS was listed under the Stockholm Convention on POPs**
- **2010** — **HFPO-DA was first produced**
- **2016** — **Kigali Amendment of the Montreal Protocol**
- **2019** — **PFOA was listed under the Stockholm Convention on POPs**

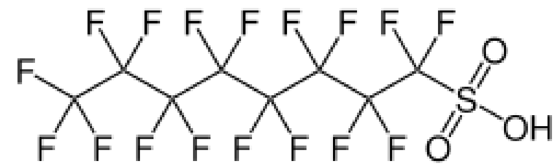
Li et al., 2026. Atmospheric transport and deposition of PFAS in East Antarctica- Evidence from snow transect measurements and a multidecadal record. Science Advances

Per- und polyfluorierte Alkylverbindungen (PFAS)

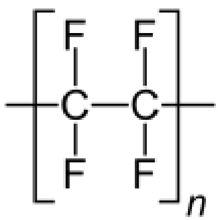
OECD: 4730, CompTox: 14735, PubChem: 7 Mio + Präkursoren



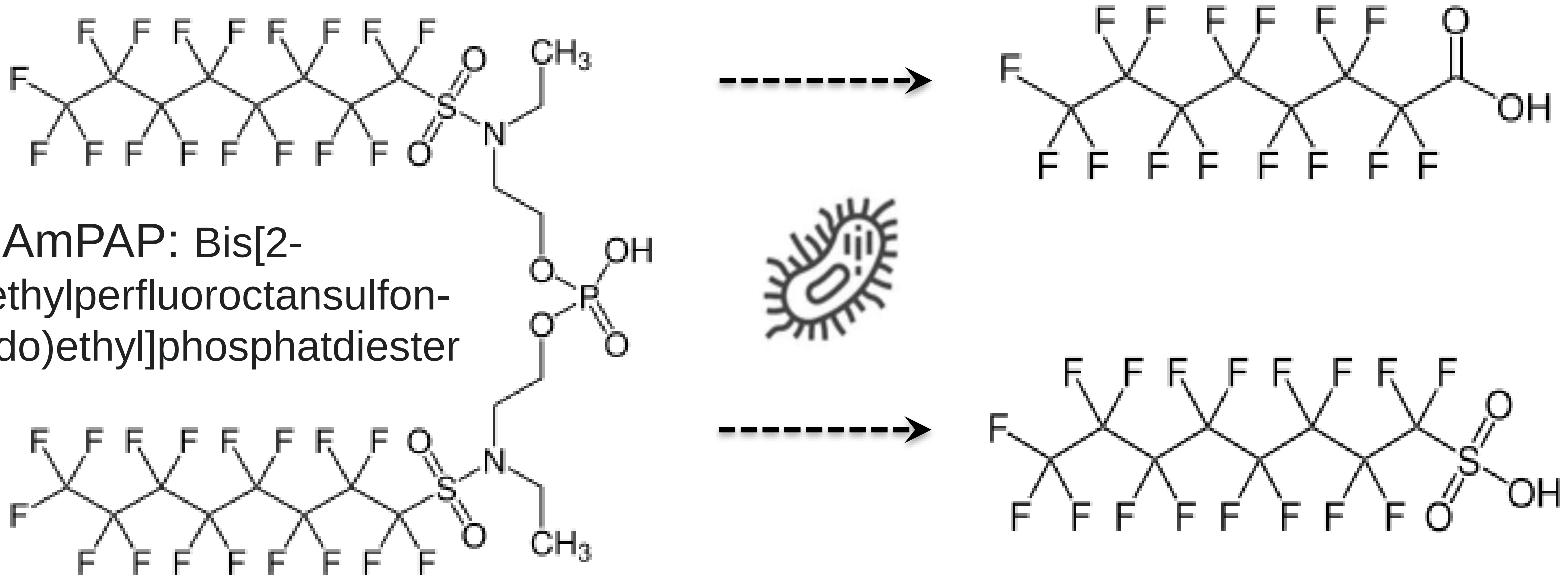
Perfluoroctansäure (PFOA)



Perfluoroctansulfonsäure (PFOS)



Polytetrafluorethylen (PTFE, Teflon)



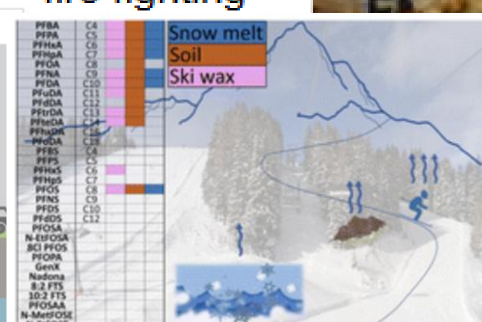
DiSAmPAP: Bis[2-(*N*-ethylperfluoroctansulfon-amido)ethyl]phosphatdiester

Anwendungsbeispiele: Per-, Polyfluoralkyl Subst. (PFAS)

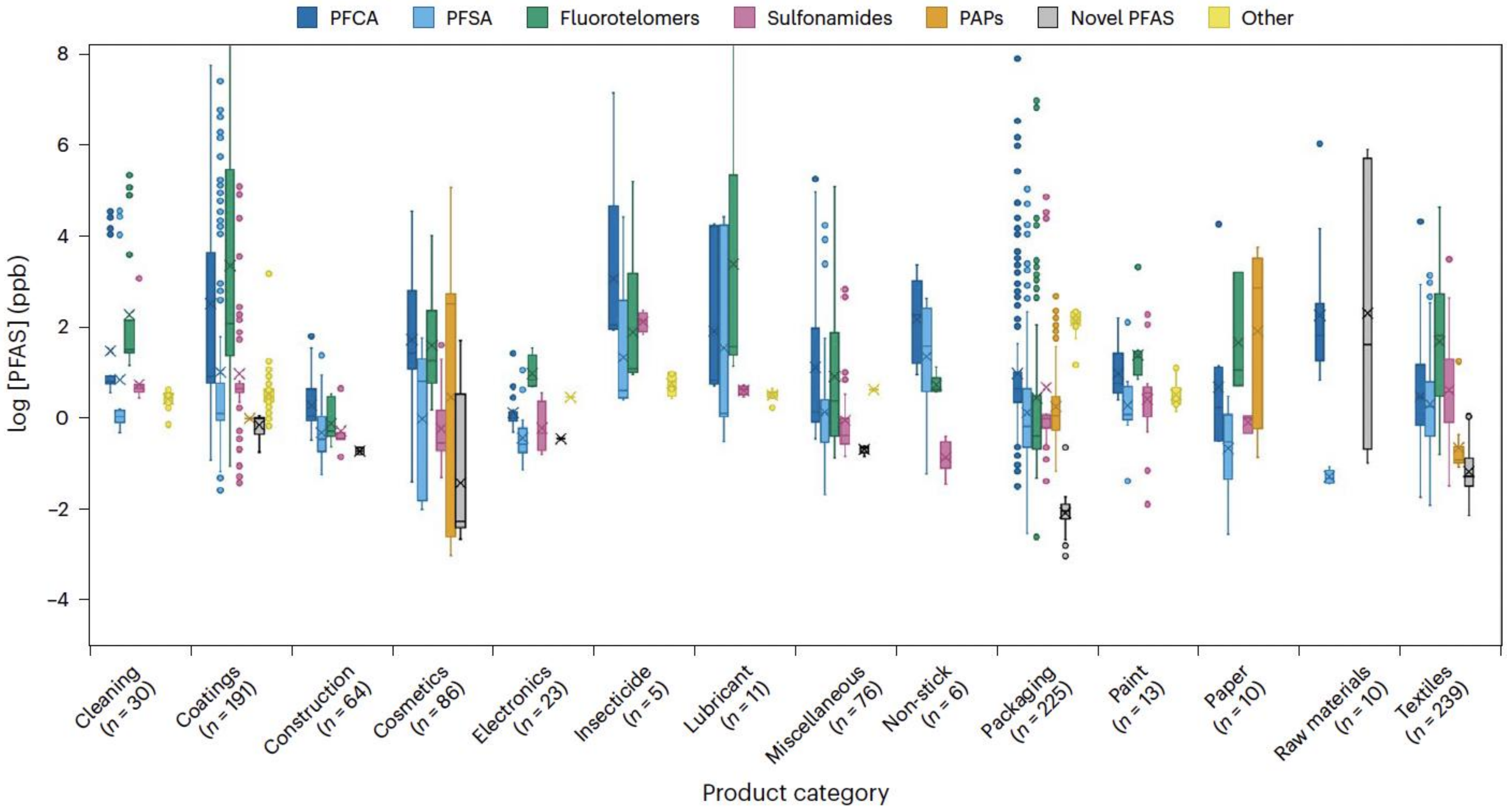
4 AECOM

Background - Where do we find PFASs?

- Oil and water-repellent
- Stain-resistant upholstery, carpeting
- Non-stick coatings in cookware (Teflon®)
- Breathable, all weather clothing (Gore-tex®)
- Paper and packaging protectors (food packaging)
- Paints and adhesives
- Fluoro-elastomers (gaskets, O-rings, Hoses)
- Mining and oil surfactants
- Metal plating baths (chromium)
- Pesticides/Insecticides
- Aqueous film-forming foams (AFFF) for fire fighting



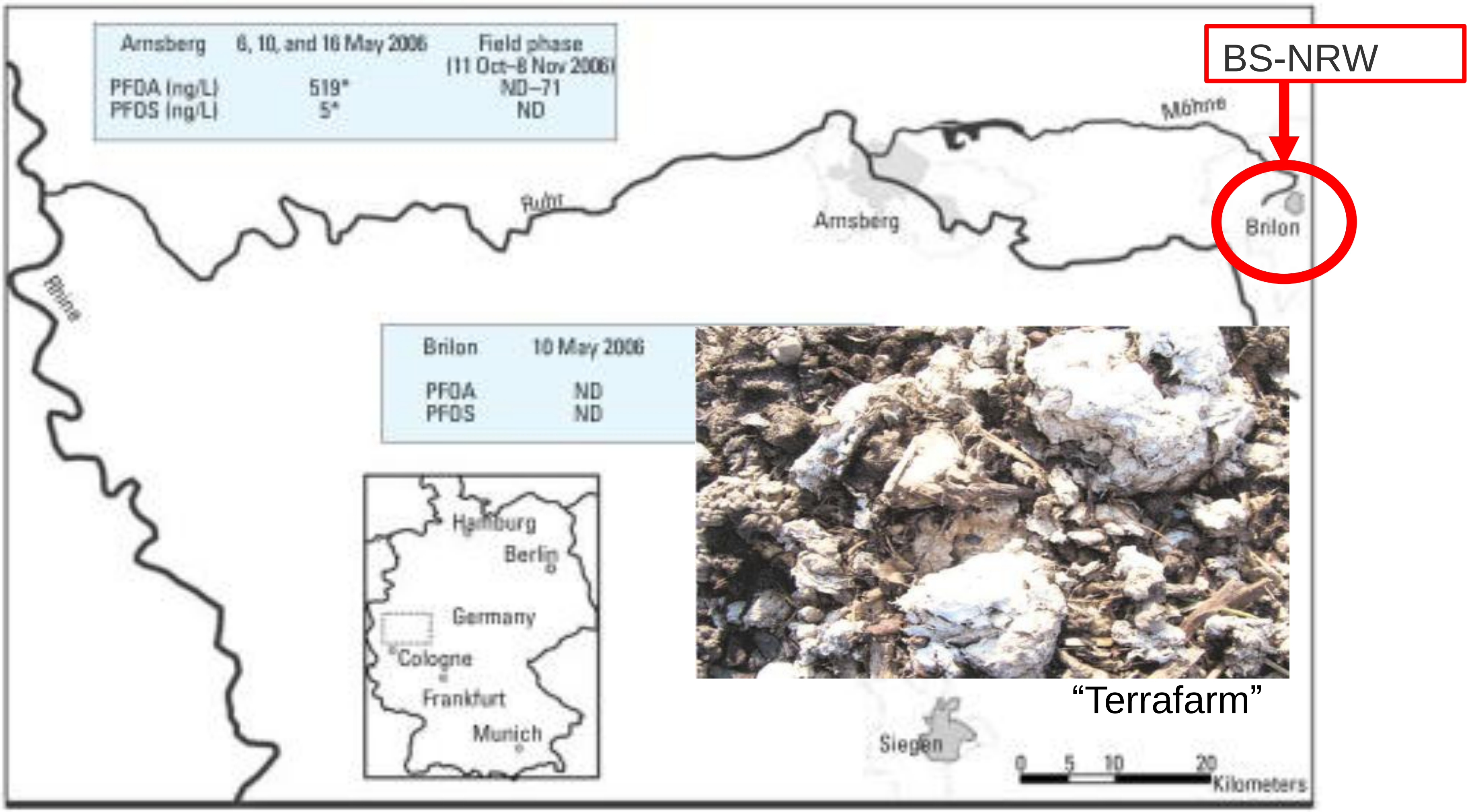
Konzentrationen in Produkten



PFAS concentration identified in various consumer and industrial product categories. Box dimensions show the span between quartiles 1 and 3 (interquartile range, IQR). Outliers are defined as values greater than 1.5Å~ the IQR. Whiskers extend from these quartiles to the largest (quartile 3) or smallest (quartile 1) non-outlier value (that is, <1.5Å~ the IQR). Y-axis units are ng ml^{-1} or µg kg^{-1} equivalent to ppb - precursors yellow and green

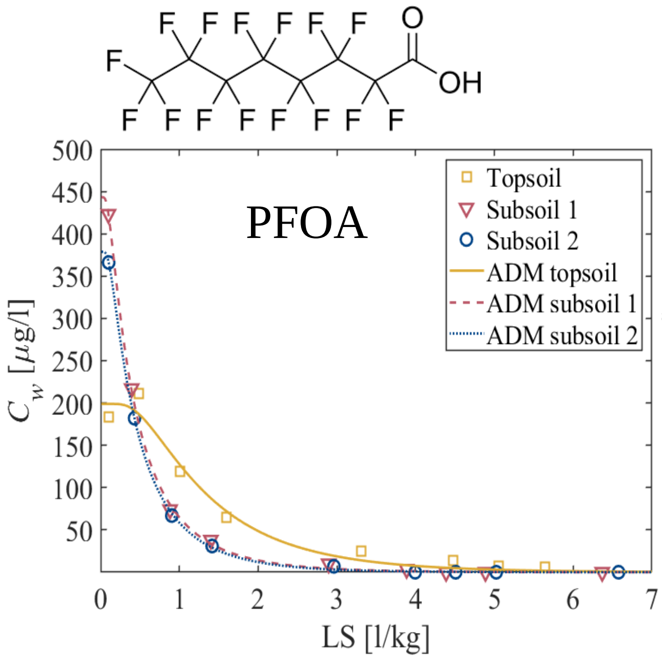
Grunfeld et al. 2023. Underestimated burden of per- and polyfluoroalkyl substances in global surface waters and groundwaters. Nature Geoscience

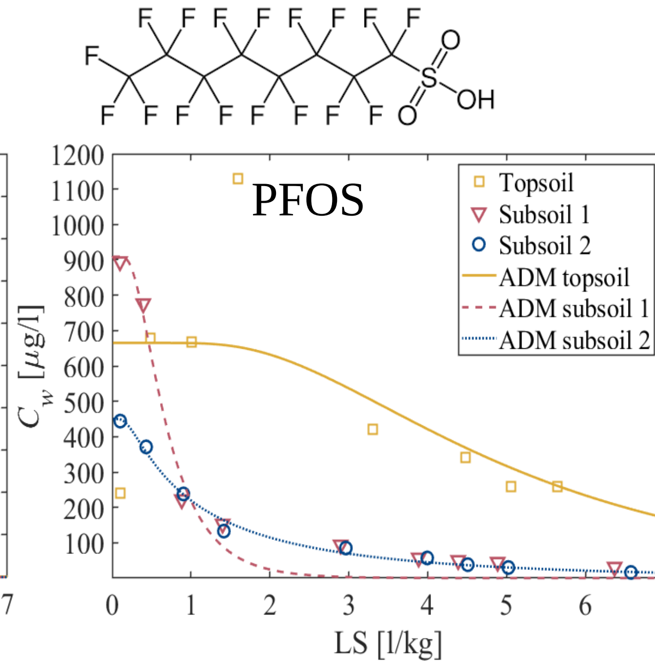
PFAS im Trinkwasser (woher?)



From Hölzer et al. (2008)

PFAS Säulen-Elutiontests





Advection-dispersion model (ADM):

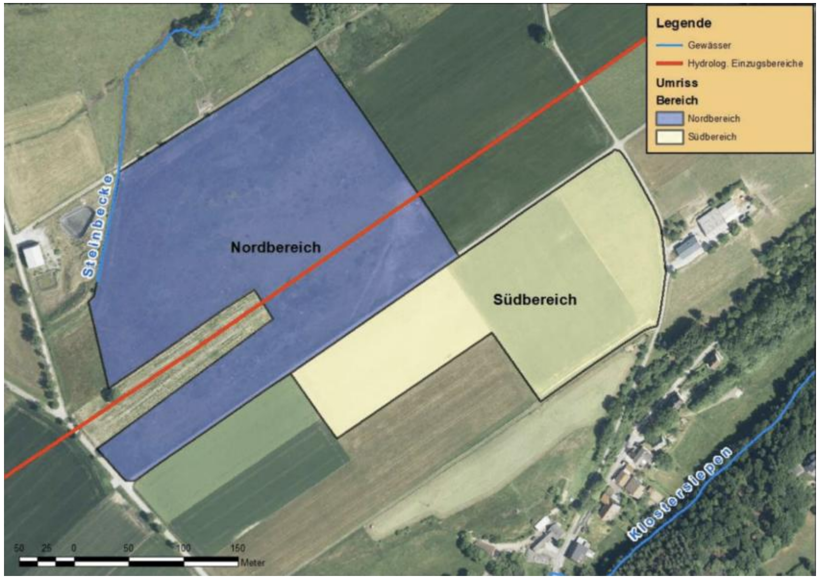
$$C_w = C_o \left\{ 1 - 0.5 \left[\mathrm{erfc}\left(\frac{K_d - LS}{2\sqrt{\frac{\alpha}{x} LS \left(\frac{n}{\rho} + K_d\right)}} \right) + \exp\left(\frac{x\left(1 - \frac{1}{R}\right)}{\alpha} \right) \mathrm{erfc}\left(\frac{K_d + LS}{2\sqrt{\frac{\alpha}{x} LS \left(\frac{n}{\rho} + K_d\right)}} \right) \right] \right\}$$

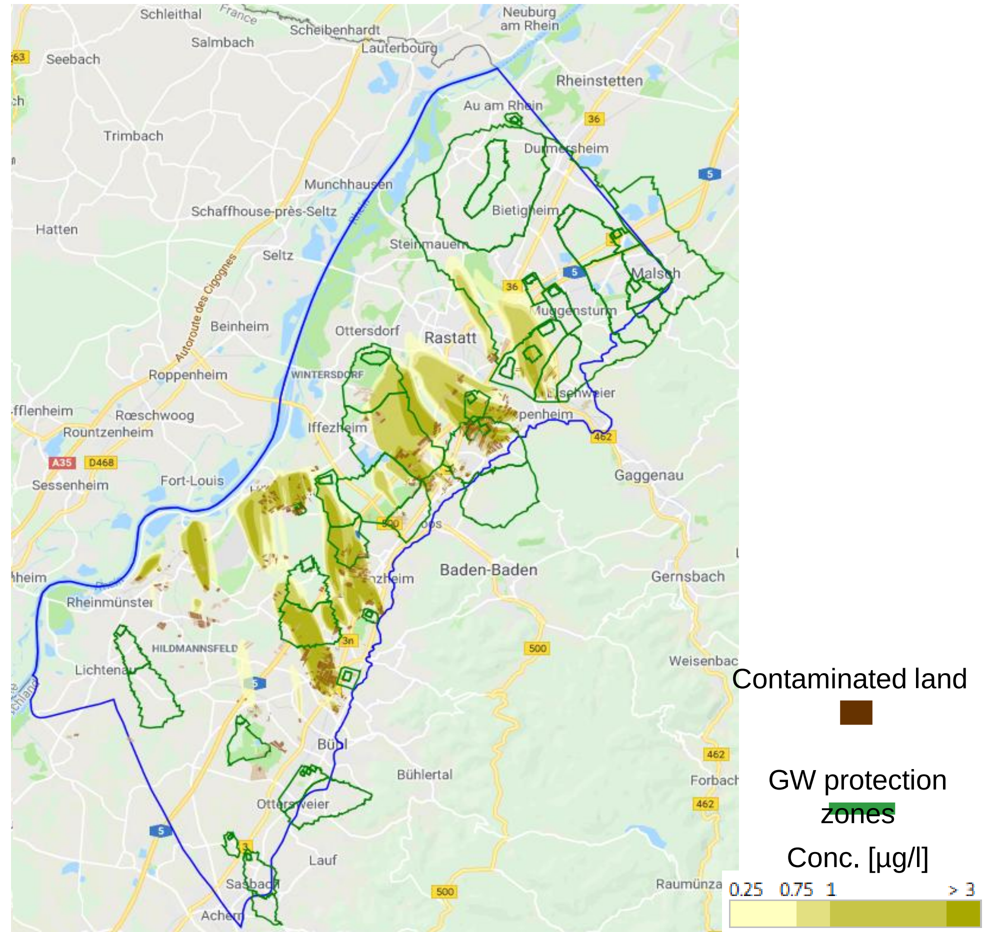
$$LS = \frac{v\ \theta\ t}{x\ \rho}$$

Röhler, K., Haluska, A.A., Susset, B., Liu, B., Grathwohl, P. (2021). Long-term leaching of PFAS from contaminated agricultural soils in Germany. J. Cont. Hydrol., 241, DOI 10.1016/j.jconhyd.2021.103812

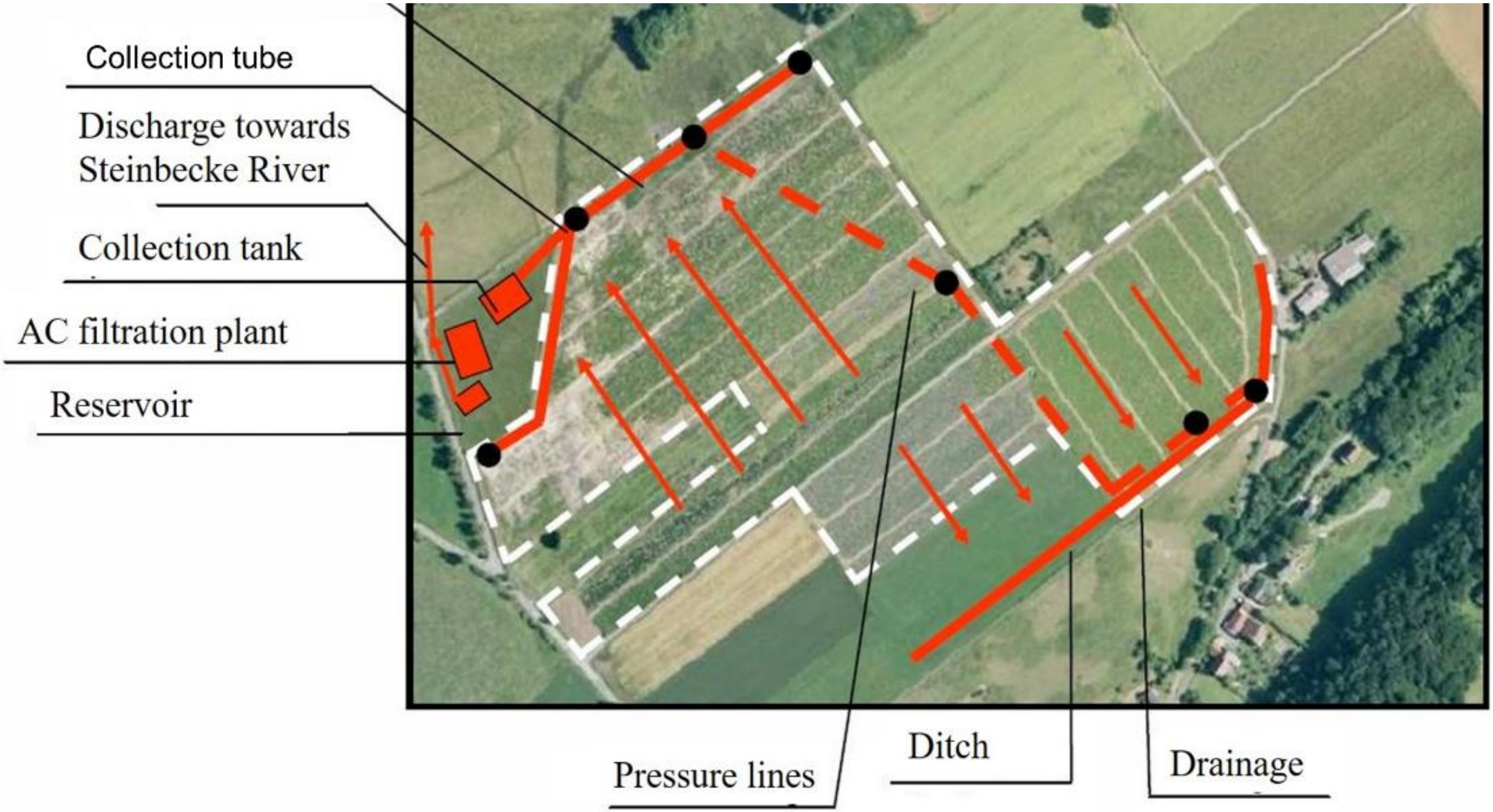
"Neue" landwirtschaftliche PFAS "Quellen"

Baden-Württemberg: > 600 ha landwirtschaftliche Flächen mit Kompost (Papierschlämmen)



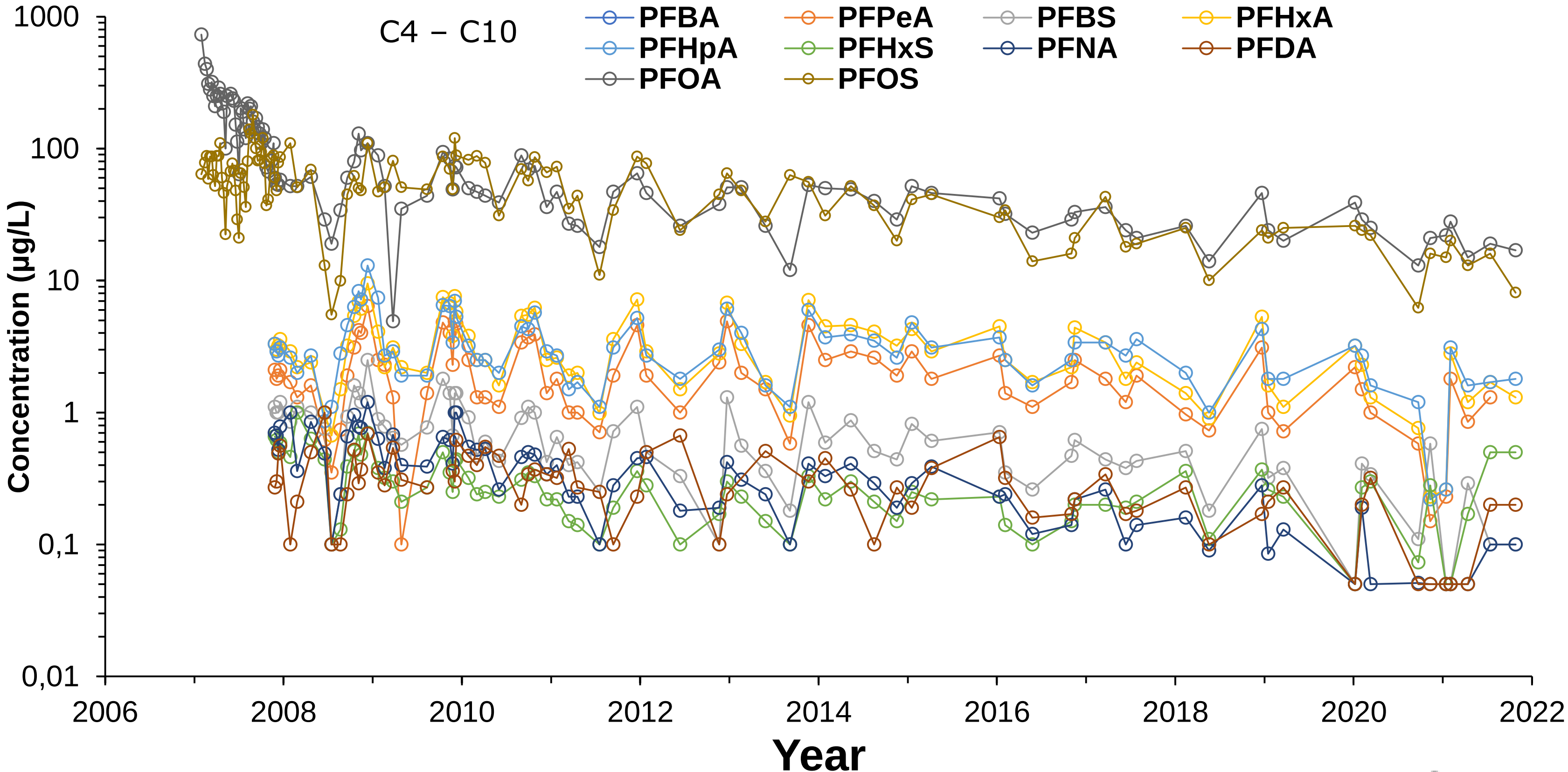


PFAS "Sanierung" (NRW)



Röhler, K., Haluska, A.A., Susset, B., Liu, B., Grathwohl, P. (2021). Long-term leaching of PFAS from contaminated agricultural soils in Germany. J. Cont. Hydrol., 241, DOI 10.1016/j.jconhyd.2021.103812

Langzeit PFAS Trends: 15 Jahre Felddaten

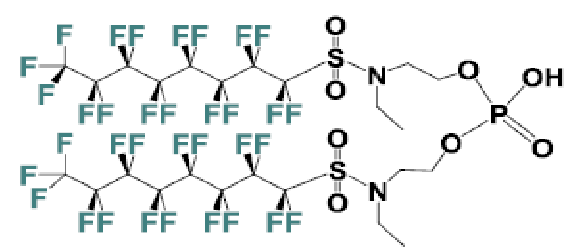


No chromatography!

➔ steady state

➔ input = output

Unknown precursors, known: Di-SAmPAPs

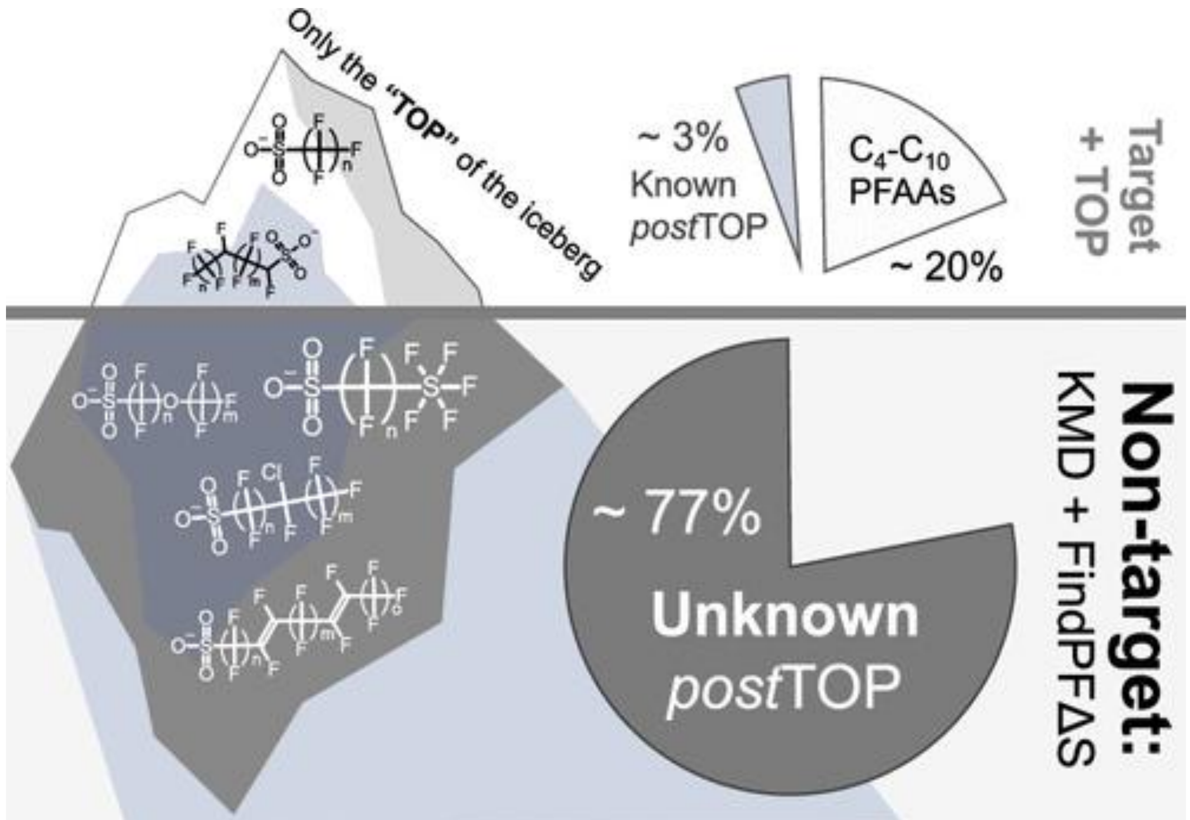


Haluska, A.A., Röhler, K., Fabregat-Palau, J., Alexandrino, D.A.M., Abramov, S., Thompson, K.J., Straub, D., Kleindienst, S., Bugsel, B., Zweigle, J., Zwiener, C. and Grathwohl, P. (2024). Complementary Field and Laboratory Batch Studies to Quantify Generation Rates of Perfluoroalkyl Acids in a Contaminated Agricultural Topsoil with Unknown Precursors. Groundwater Monit R, 44: 61-75. https://doi.org/10.1111/gwmr.12680

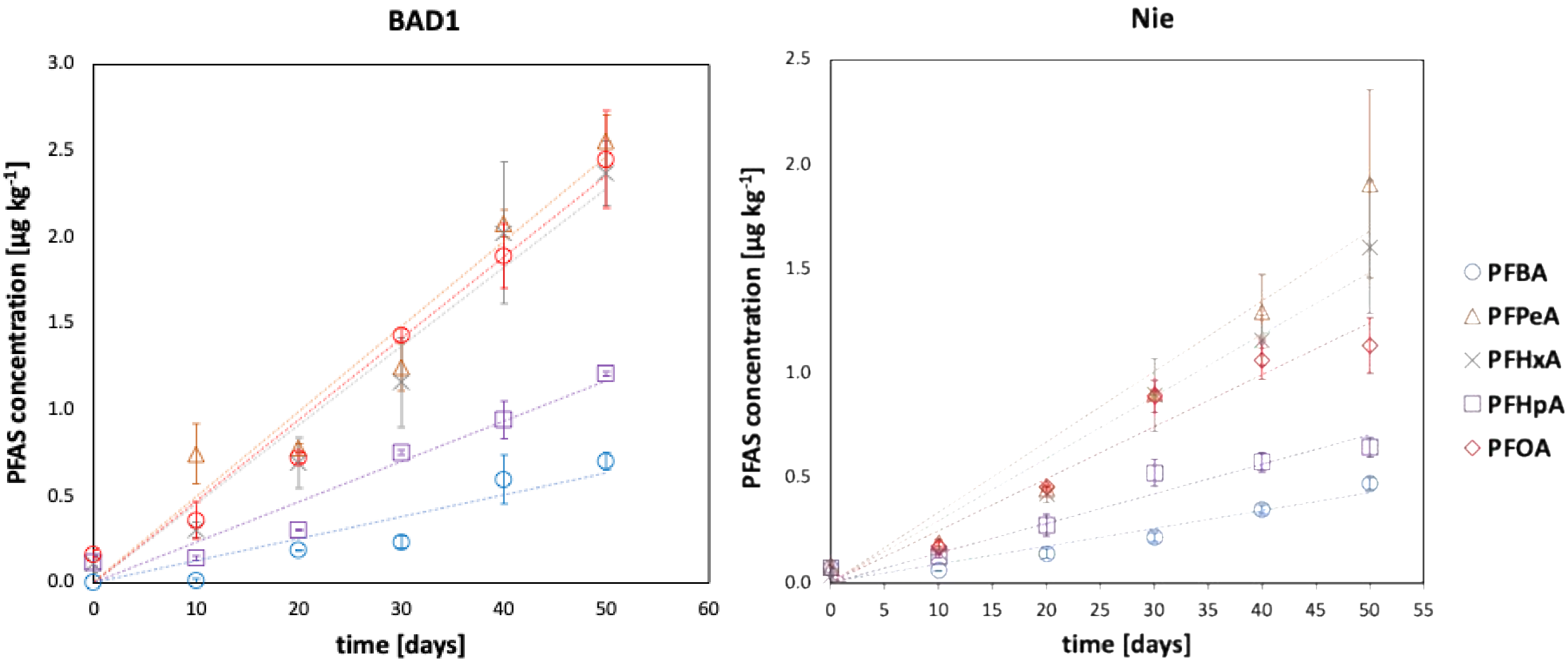
PFAS – Präkursoren und Transformationsprodukte

Per- and polyfluorinated alkyl substances (PFAS) comprise > 3000 individual compounds

Precursors forming stable end-products e.g., perfluorinated carbonic acids (PFCAs) and perflurionated sulfonic acids (PFSAs) – in the lab assessed by the TOP assay (Total Oxidizable Precursors)



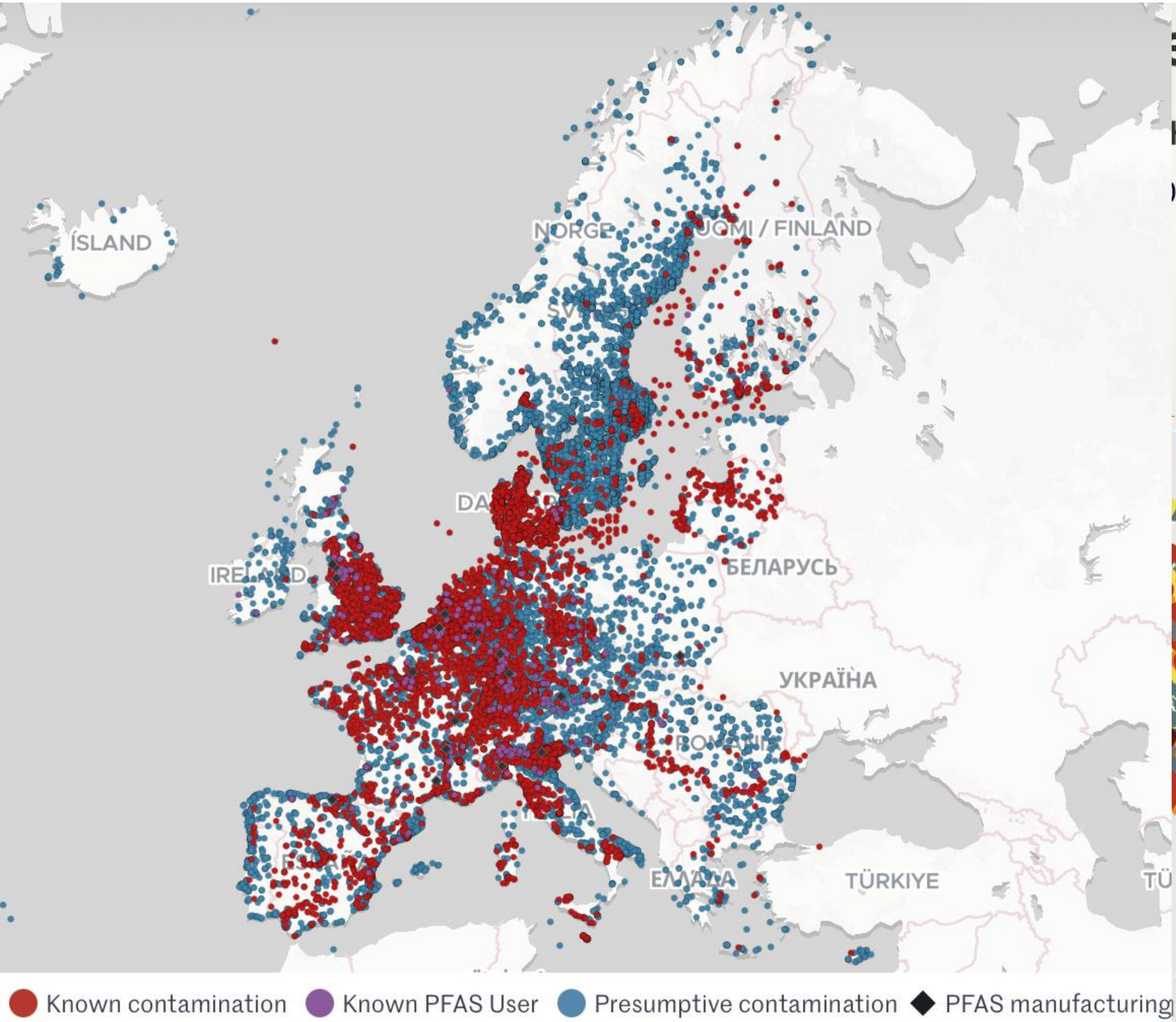
PFAS „Produktion“ in Bodenproben im Labor (terminale Transformationsprodukte)

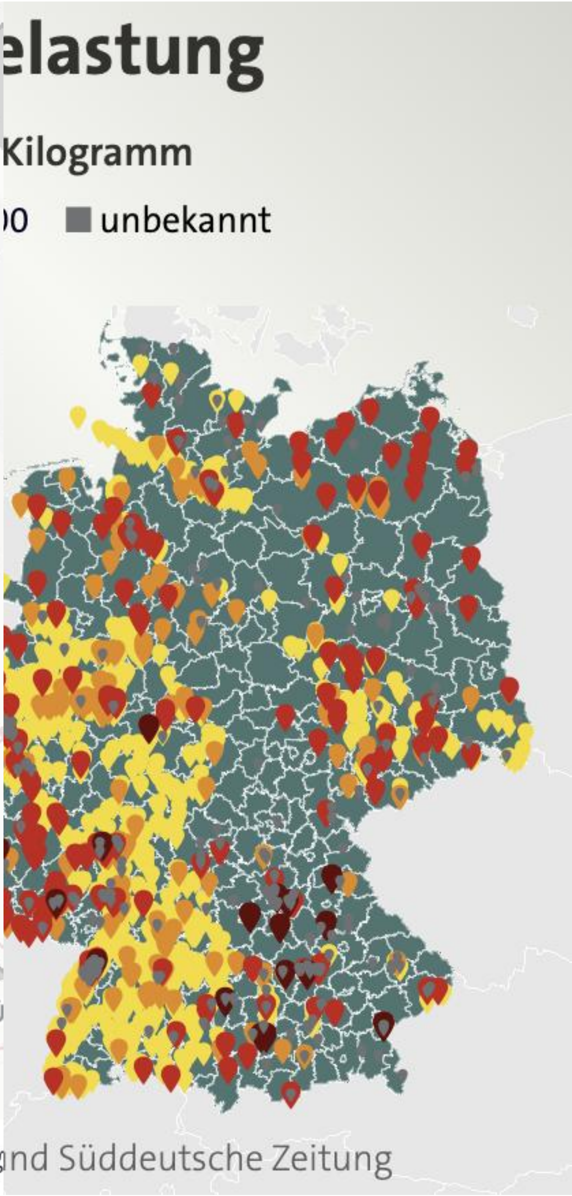


$$C_w = F/Q$$

Röhler, K., Susset, B., Grathwohl, P. (2023). Production of perfluoroalkyl acids (PFAAs) from precursors in contaminated agricultural soils: Batch and leaching experiments. Science of The Total Environment, 902, 166555, https://doi.org/10.1016/j.scitotenv.2023.166555

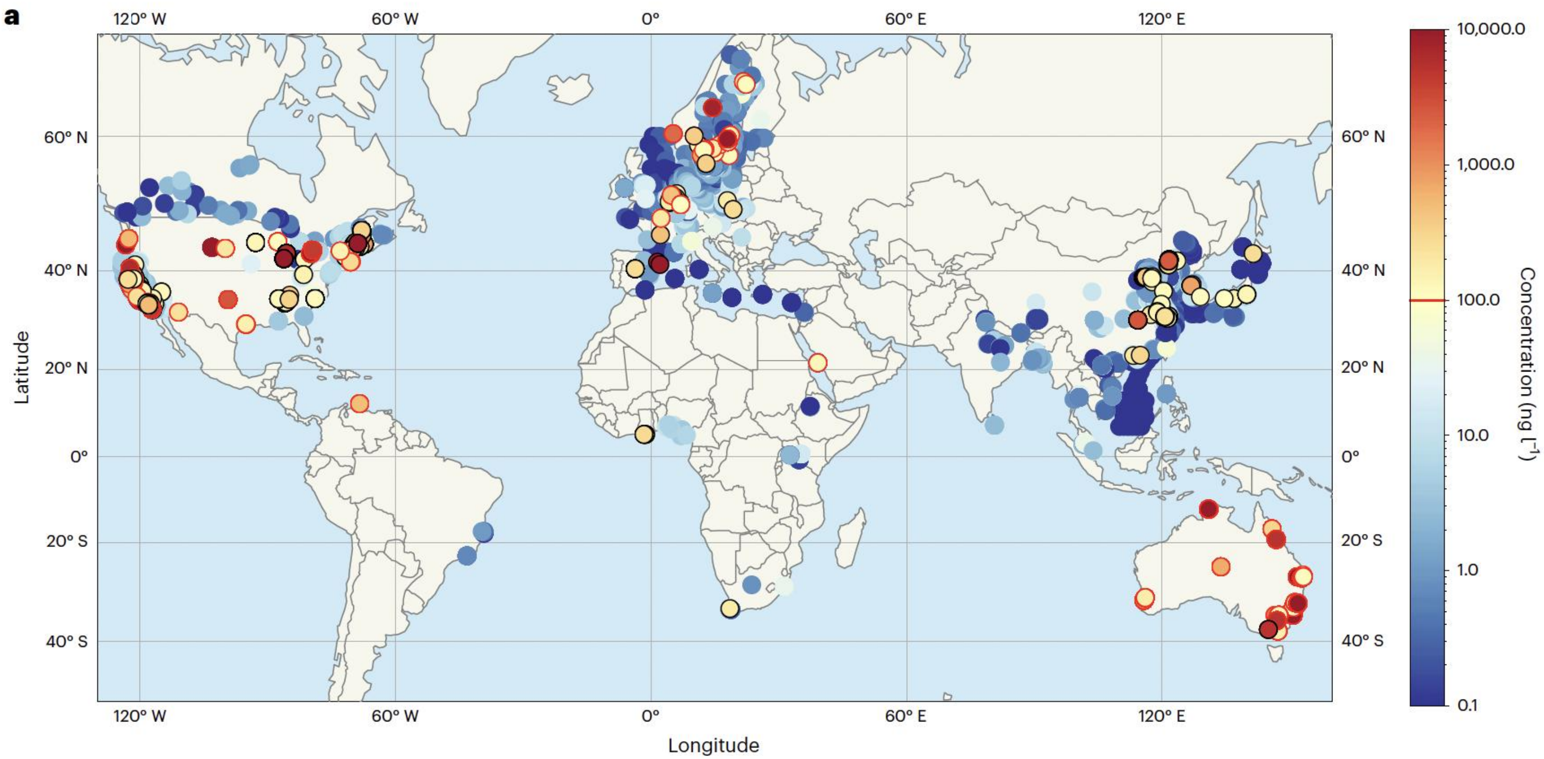
Dimension des Problems





Source: Forever Pollution Project

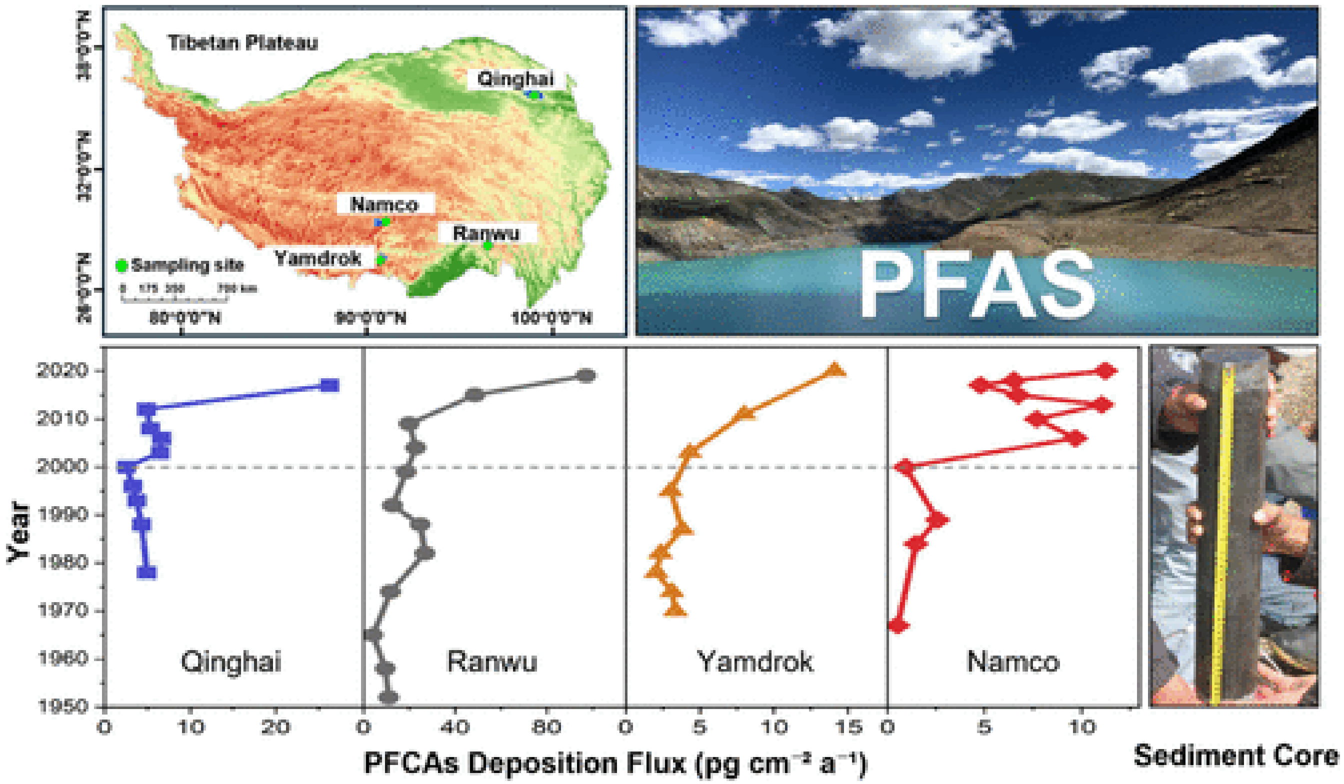
Auftreten im Oberflächengewässern und Grundwasser



Global map of PFAS concentration in water: Sum of concentration of 20 PFAS subject to EU guidance in surface water, groundwater and drinking water samples. Those above the EU drinking water limit of 100 ng l^{-1} (marked red on scale bar) are circled in red (for known contamination sources (for example, AFFF or non-AFFF)) or black (unknown sources)

Grunfeld et al. 2023. Underestimated burden of per- and polyfluoroalkyl substances in global surface waters and groundwaters. Nature Geoscience

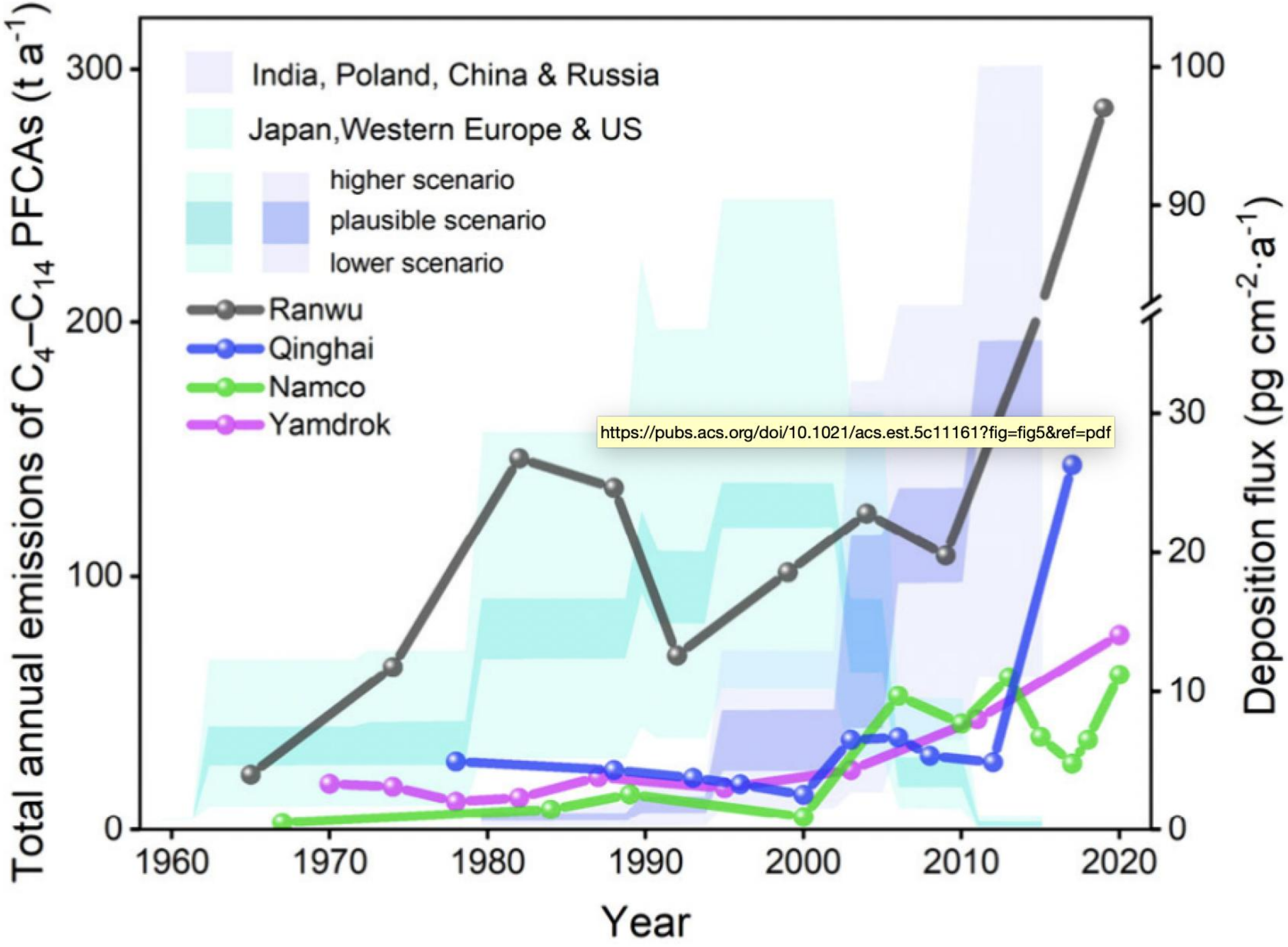
Long range transport and deposition



- Since 2000 shift from PFOS to PFBA
- Strong increase of short chain PFAS (PFBA) since 2000
- Doubling rates 7 – 15 year

Cui et al. 2026. Temporal Trends of Per- and Polyfluoroalkyl Substances (PFASs) in Tibetan Plateau Sediment Cores (1952−2020)- Tracking Global Emission History and Industrial Transformation in PFAS Production. ES&T.pdf

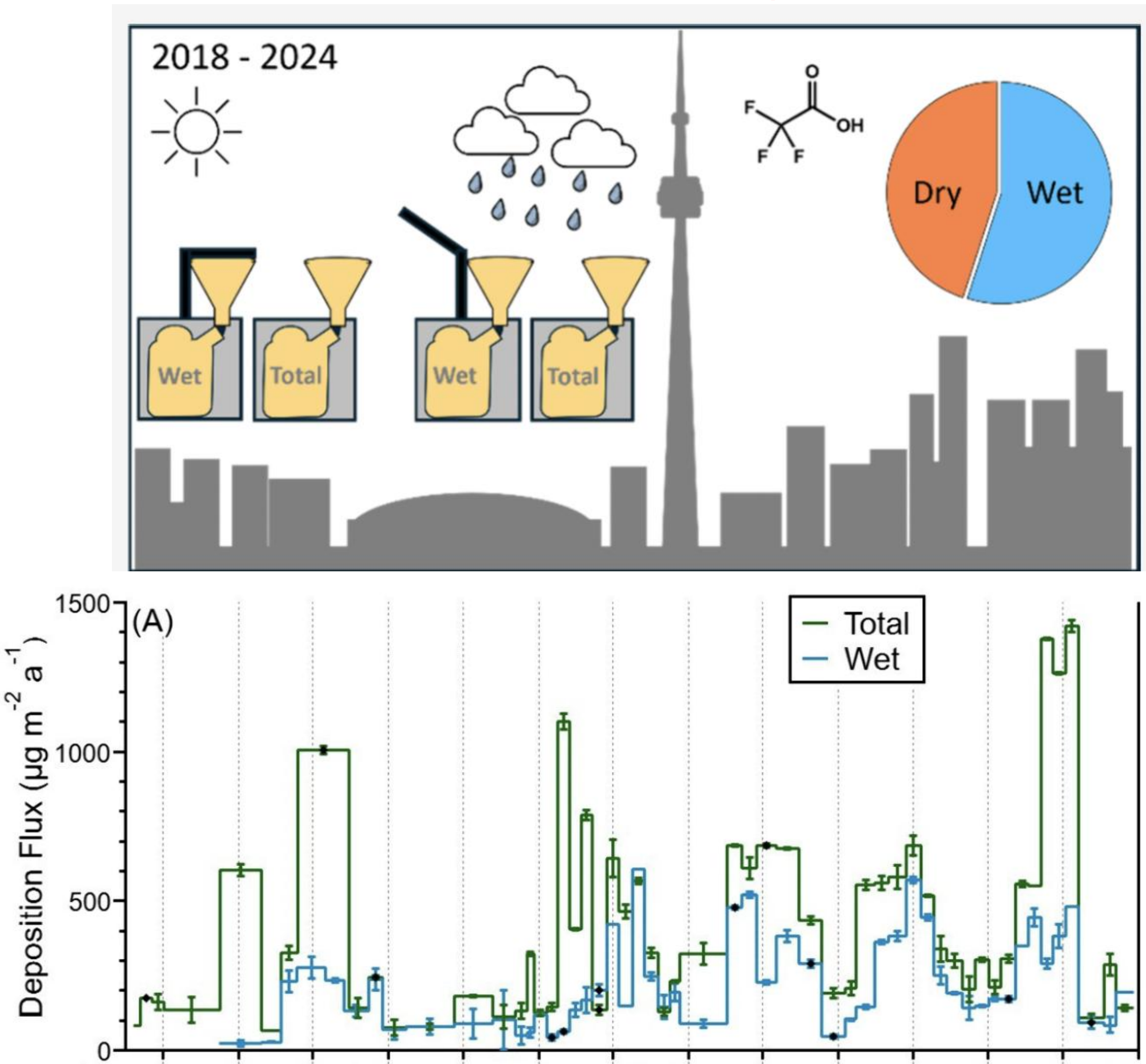
Emission and deposition



- Early emission from USA, Japan, Europe declined, but offset by China, India, Poland, Russia
- PFAS wet and dry atmospheric deposition Tibet
- Transport of PFAS and precursors by aerosols

Cui et al. 2026. Temporal Trends of Per- and Polyfluoroalkyl Substances (PFASs) in Tibetan Plateau Sediment Cores (1952−2020)- Tracking Global Emission History and Industrial Transformation in PFAS Production. ES&T.pdf

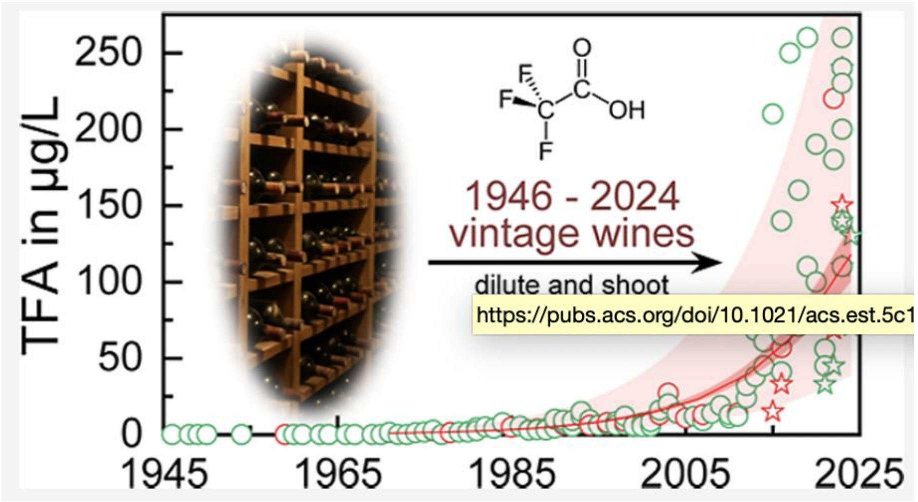
Urban deposition (Toronto: 2018−2024)

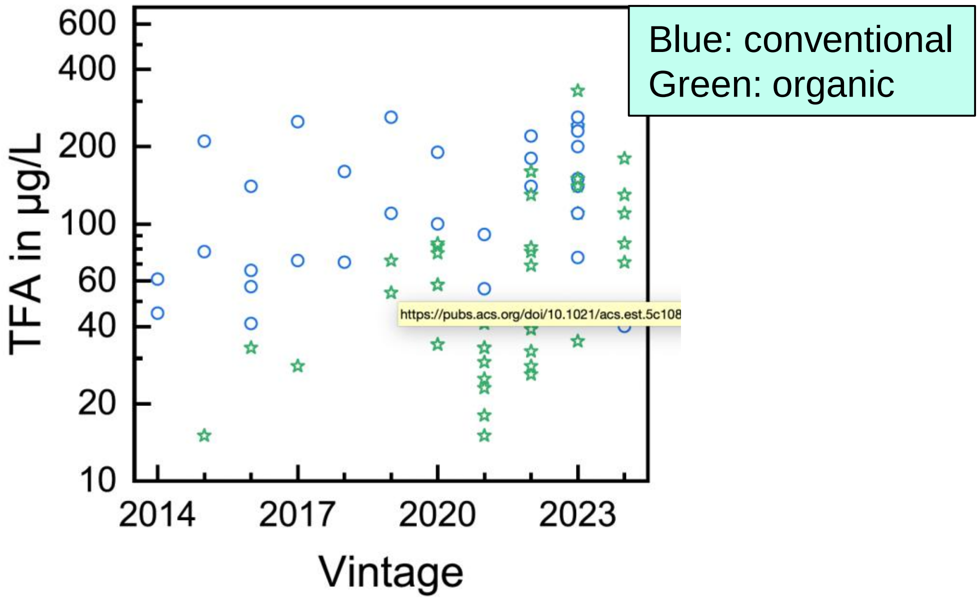


- All total and wet deposition samples contained TFA (0.1−4 µg L^{-1})
- Fluxes similar to Germany (193 µg m^{-2} a^{-1}) and Guangzhou (229 µg m^{-2} a^{-1}); lower than in Switzerland (555 µg m^{-2} a^{-1})
- Predicted future deposition (US: 500 µg m^{-2} a^{-1} ; EU: 540 µg m^{-2} a^{-1}) from HFO-1234yf alone

Persaud et al., 2026. Atmospheric Removal of Trifluoroacetic Acid by Dry and Wet Deposition- A Multiyear Analysis in Toronto. ES&T L.pdf

Historical TFA record in wines

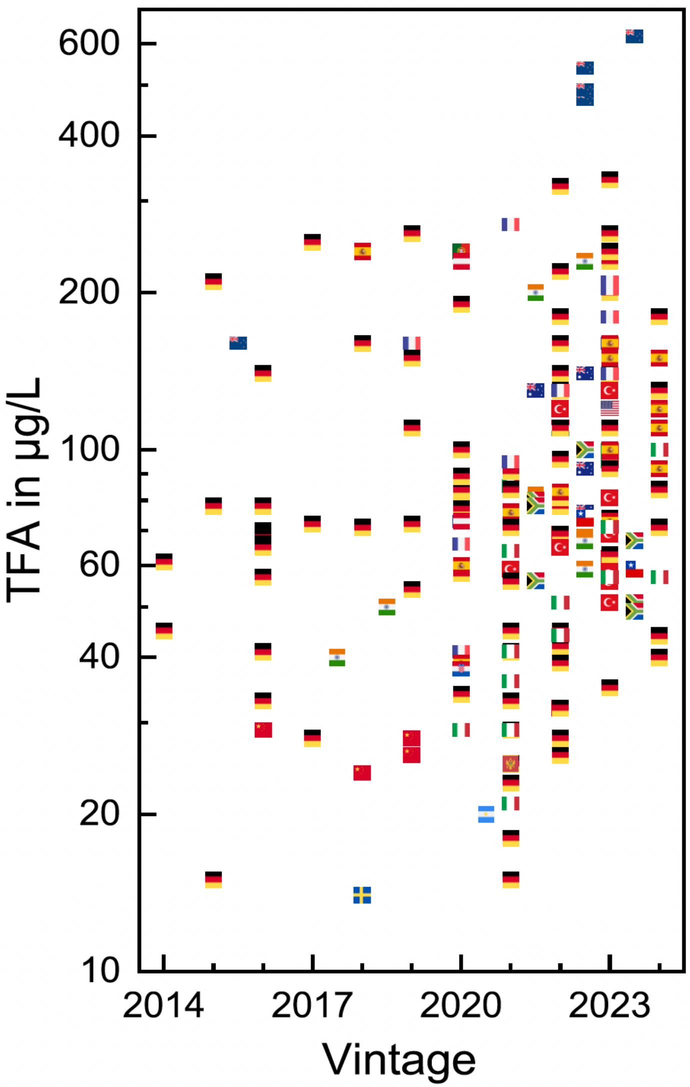




Freeling & Heidinger, 2025. Tracking Trifluoroacetate (TFA) through Time- A 78-Year Record from Archived Wines. ES&T

- 155 wine samples from wine archive (Staatliches Weinbauinstitut Freiburg)
- Atmospheric degradation of TFA-forming refrigerants and propellants used in the EU after 2015.
- Rising emissions in Europe from about 9000 tons in 2015 to 18,000 tons in 2022, with 40,000 tons projected for 2030…
- Role of pesticides?

TFA - a worldwide problem

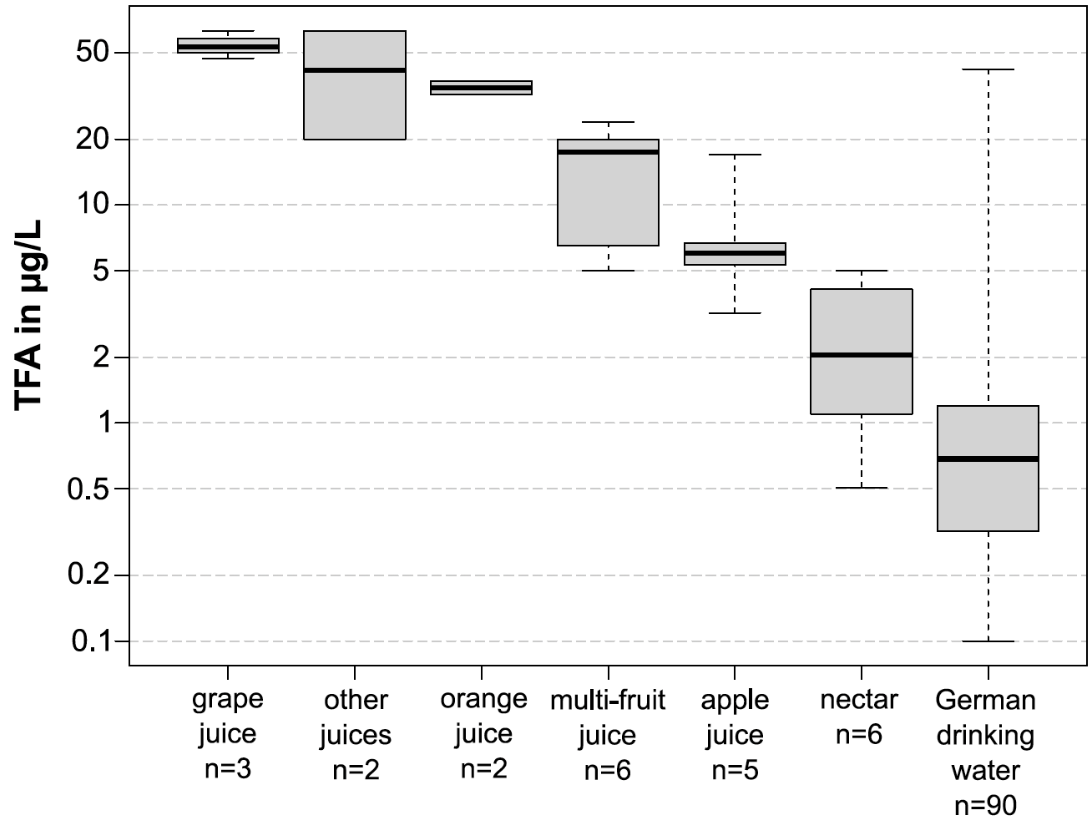


- 2020: 51% of samples with concentrations > 60 µg/L, (drinking water guidance value set by UBA in 2020).
  2022: 75%
  2023: 82%
  2024: 81%

- Still low: Ningxia, NW China (new), Mendoza, Argentinia (arid) and PIWI cultures in Sweden and Germany

Freeling & Heidinger, 2025. Tracking Trifluoroacetate (TFA) through Time-
A 78-Year Record from Archived Wines. ES&T

TFA - a worldwide problem, not just in vine



- Highest concentrations in grape juice, notably lower than in apple juice

Freeling & Heidinger, 2025. Tracking Trifluoroacetate (TFA) through Time- A 78-Year Record from Archived Wines. ES&T

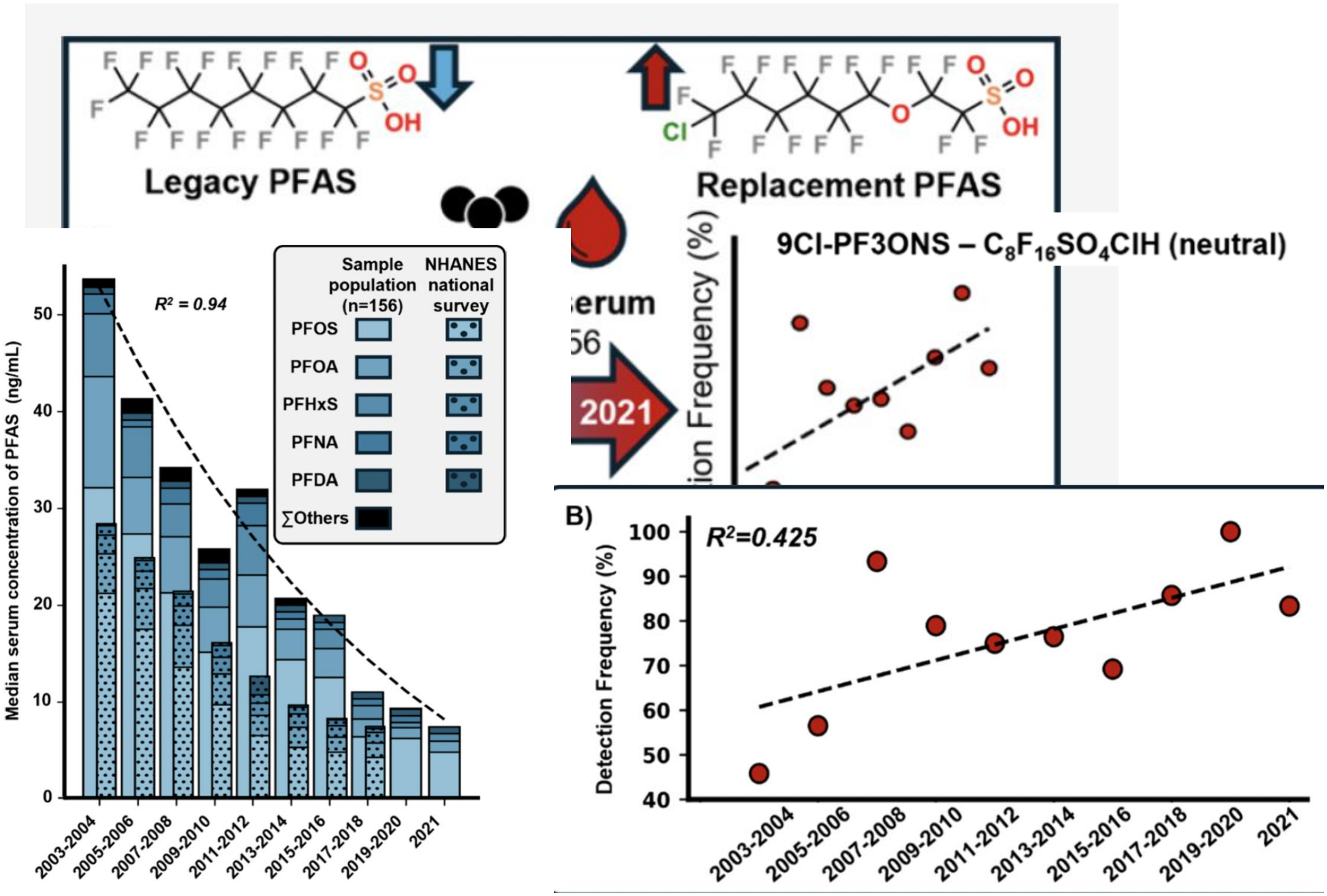
Regulation is possible

Dasom Han of the Republic of Korea competed at the 2026 Winter Olympics on Feb. 18. FTIR tests found organic fluorine—an indicator for banned fluoro waxes—on the base of her skis. | Credit: Maja Hitij/Getty Images

CEN, 06/26: The science behind the fluoro wax tests at the Olympics

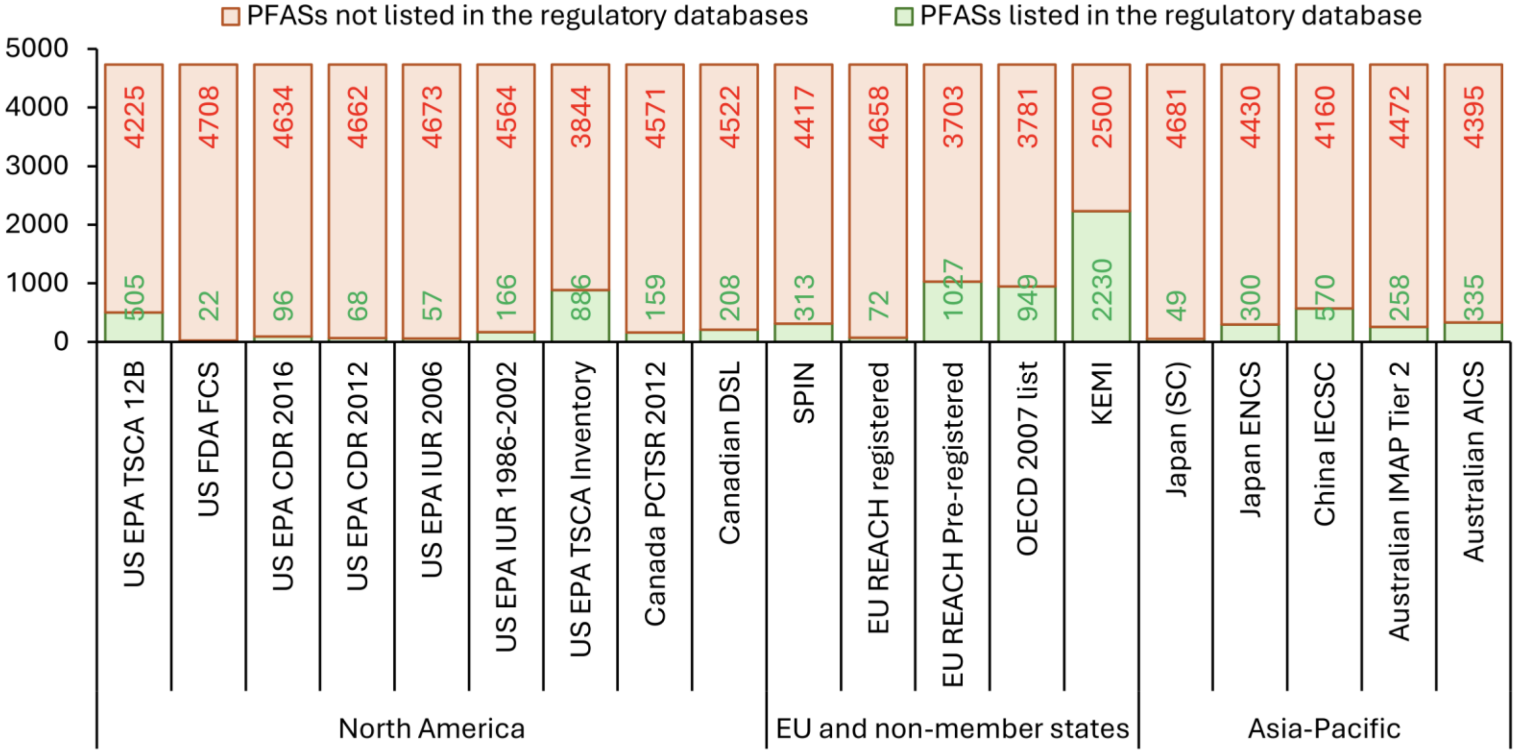
Fluorine-containing waxes were banned from ski competitions in 2023

Regulation helps, but new compounds come up



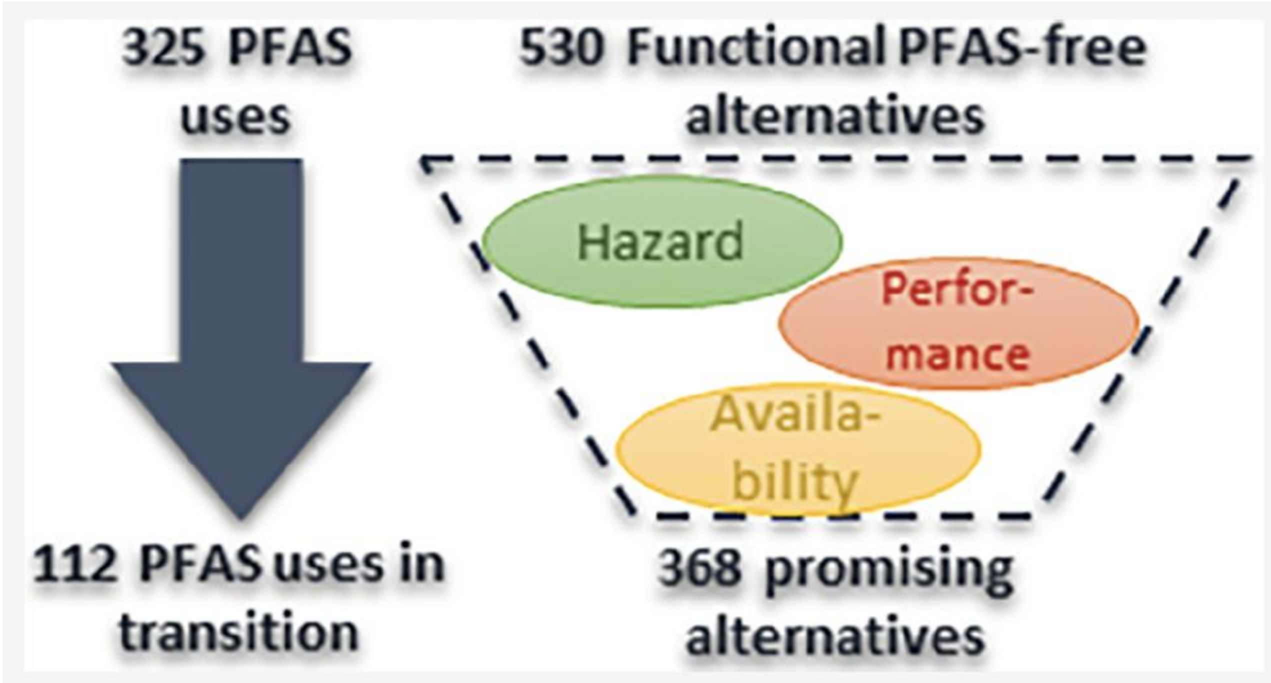
Kudzinb et al. 2026. Evaluating Legacy and Emerging PFAS in Human Blood Collected from 2003 to 2021. ES&T

Numbers of PFAS regulated worldwide



Sharma et al. 2026. Global Disparities in the Regulation of PFASs- The Risk of Shifting the PFAS Pollution Burden to Developing Countries. ES&T, DOI: 10.1021/acs.est.5c14777

What now? Replacement is possible



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Article

An Overview of Potential Alternatives for the Multiple Uses of Per- and Polyfluoroalkyl Substances

Romain Figuière,* Luc T. Miaz, Eleni Savvidou, and Ian T. Cousins

Cite This: *Environ. Sci. Technol.* 2025, 59, 2031−2042

Read Online

ZEROF

https://www.zerof.eu/

ZeroPM Zero pollution of Persistent, Mobile substances
Part of EU Open Research Repository

https://zenodo.org/records/10852739

Summary and Conclusions

- Persistent compounds do not vanish from the environment – disposal does not end exposure (don't let them out!)
- New compounds come up and cause similar or worse problems than the old ones
- PFAS cleanup almost impossible and extremely expensive (several 100 M€ per site)
- Regulation under international frameworks needed
- Replacements needed: Abolish nice to have uses, keep remaining uses in closed systems
- Strengthen accountability: More producer responsibility, polluter-pays principle, product labeling, transparency….