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Zentrum für Umweltforschung

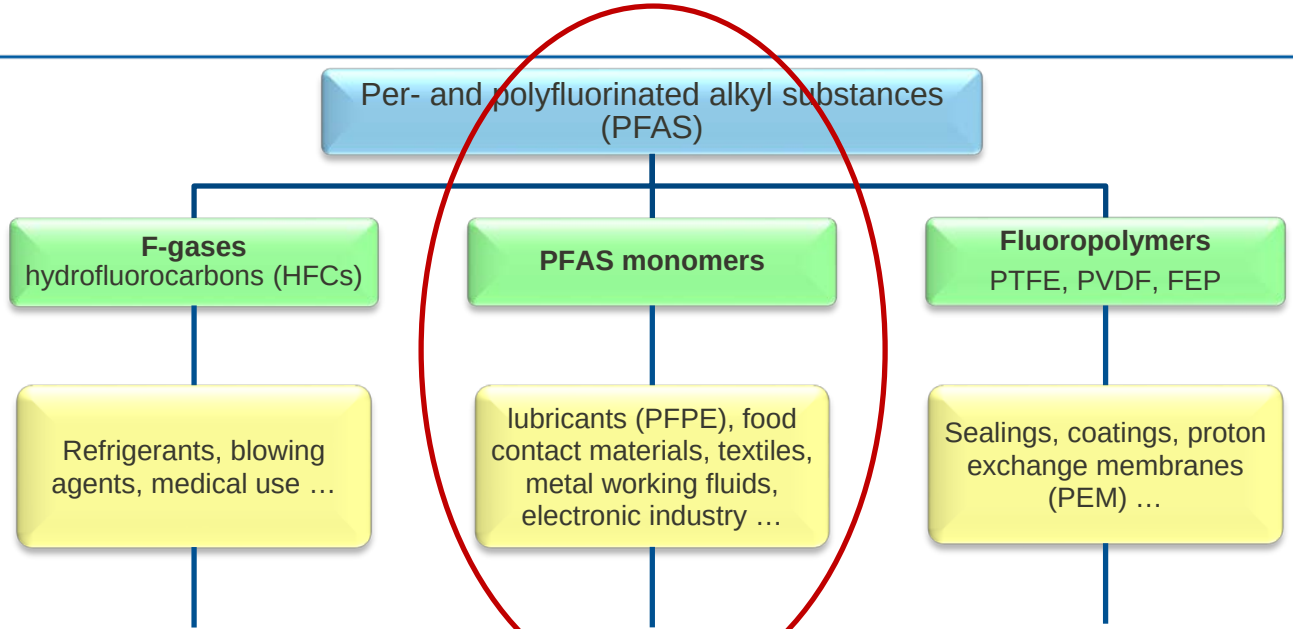
PFAS im Fokus

Was ist das Problem? Und was sind die Konsequenzen?

Thorsten Reemtsma

Department Environmental Analytical Chemistry
Helmholtz-Zentrum für Umweltforschung- UFZ

Drei Große Gruppen von PFAS



Enorme strukturelle Vielfalt an PFAS
Unzählige Anwendungen
(more than 200 use categories for more than 1400 individual PFAS*)

*) Glüge et al. (2020) Environ. Sci.: Processes Impacts, 22, 2345–2373

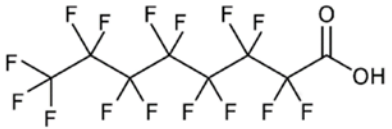
Stabilität von Perfluorierten Alkylsubstanzen

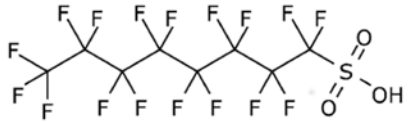
Allgemein

- C-F-Bindung sehr stabil
- F setzt Elektronendichte am Kohlenstoff herab
  - deaktiviert für oxidativen Angriff
    → Inerte Verbindungen
- Moleküle zugleich hydrophob und lipophob
  → ideal für Beschichtungen/Grenzflächen

Single bond strengths (kJ/mol)

C–H	413
C–C	347
C–N	305
C–O	358
C–F	**485**
C–Cl	339
C–Br	276
C–I	240
C–S	259





~~Persistenz~~ Stabilität von Perfluorierten Alkylsubstanzen

Allgemein

- C-F-Bindung sehr stabil
- F setzt Elektronendichte am Kohlenstoff herab
  - deaktiviert für oxidativen Angriff
    → Inerte Verbindungen

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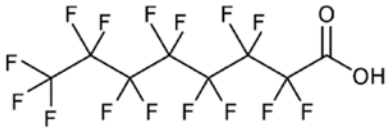
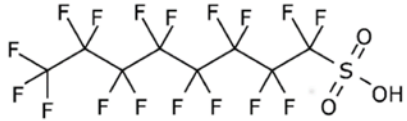
C–Br	276
C–I	240
C–S	259

Environmental half-lives of perfluorinated molecules

- Perfluorocarboxylic acids (PFCA):
  - PFOA: $t_{½}$ > 92 years (US EPA, 2014)



- Perfluorosulfonic acids (PFSA):
  - PFOS: $t_{½}$ > 41 years (US EPA, 2014)



Umgang mit PFAS nicht dementsprechend!

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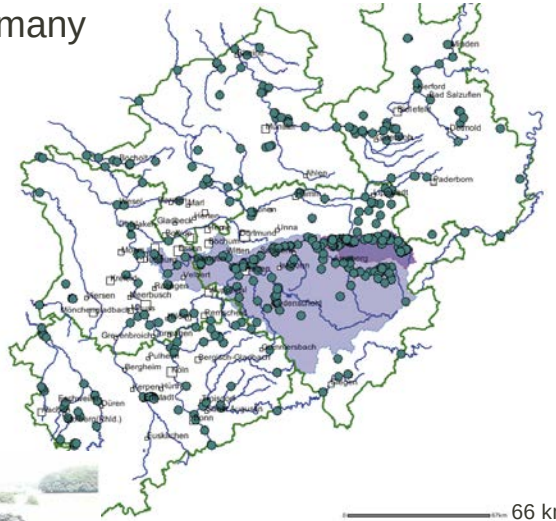
20 Years ago - Where it all began (in Germany)

Year 2006

- Elevated levels of PFOA found in Rivers Ruhr and Möhne
  - 0.1 – 0.5 µg/L
    - 50 times higher than downstream in River Rhine
    - Concentrations increase upstream in the catchment of River Moehne (drinking water reservoir!)
- Catchment is source of drinking water for > 4 million people (bank filtration)
- Origin: contaminated sludge from WWTPs mixed illegally with fertilizer and spread on agricultural land („TerraFarm“) (1000 ha)

- Contaminated catchment of North-Rhine Westphalia, Germany



LANUV-Fachbericht 34, 2011

Internal Human Exposure at Arnsberg, Germany

- PFOA in blood serum (ng/mL)

		N	N < LOD	Min	P50	
PFOA (µg/l)						
Children	Arnsberg 2006	20	0	9.6	22.4	(exposed)
	Arnsberg 2008	20	0	7.9	13.0	
	Siegen 2006	25	0	2.3	5.9	(Control)
	Siegen 2008	25	0	2.0	4.9	
Mothers	Arnsberg 2006	22	0	6.4	25.1	(exposed)
	Arnsberg 2008	22	0	3.5	14.4	
	Siegen 2006	24	0	0.8	3.8	(Control)
	Siegen 2008	24	0	0.8	2.8	
Men	Arnsberg 2006	23	0	15.1	32.8	(exposed)
	Arnsberg 2008	23	0	8.4	22.6	
	Brilon 2006	24	0	2.8	7.2	(Control)
	Brilon 2008	24	0	2.5	5.5	

Brede et al. (2010) Int. J. Hyg. Environ. Health 213, 217–223

Hotspots der PFAS-Kontamination gibt es überall

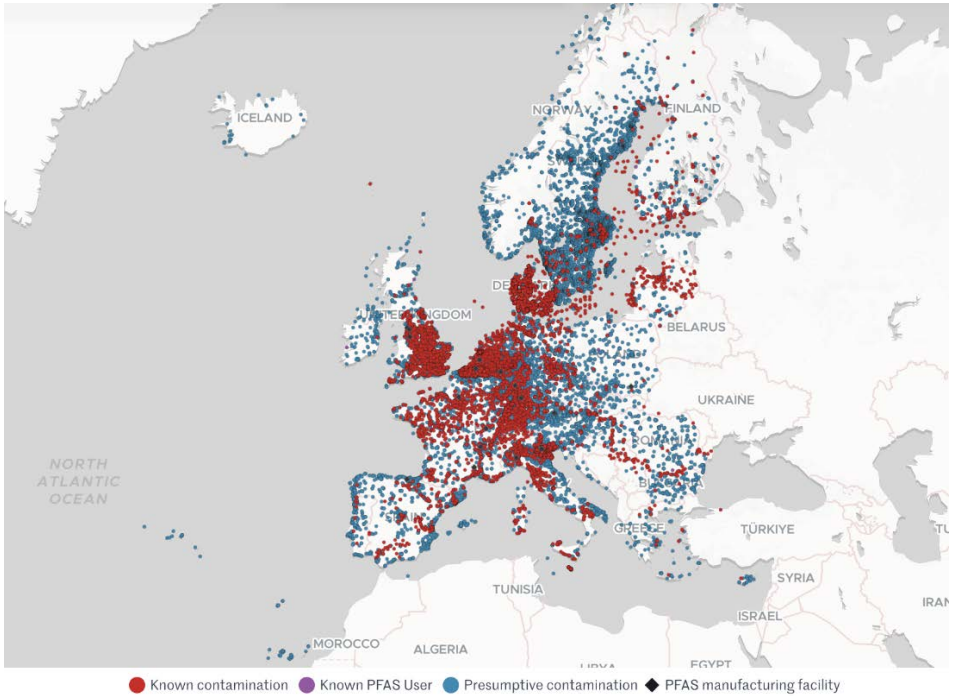
Besonders bekannte Fälle in Deutschland

- Möhne (sludge application on agricultural land)
- Gendorf (production)
- Rastatt (sluge application on agricultural land)

Commonalities

- Hotspot contamination due to
  - PFAS production and use
  - Fire fighting sites
  - Waste disposal
- Contamination of regional surface waters or groundwater bodies
- Distribution via drinking water to the thousands or hundred thousands of people

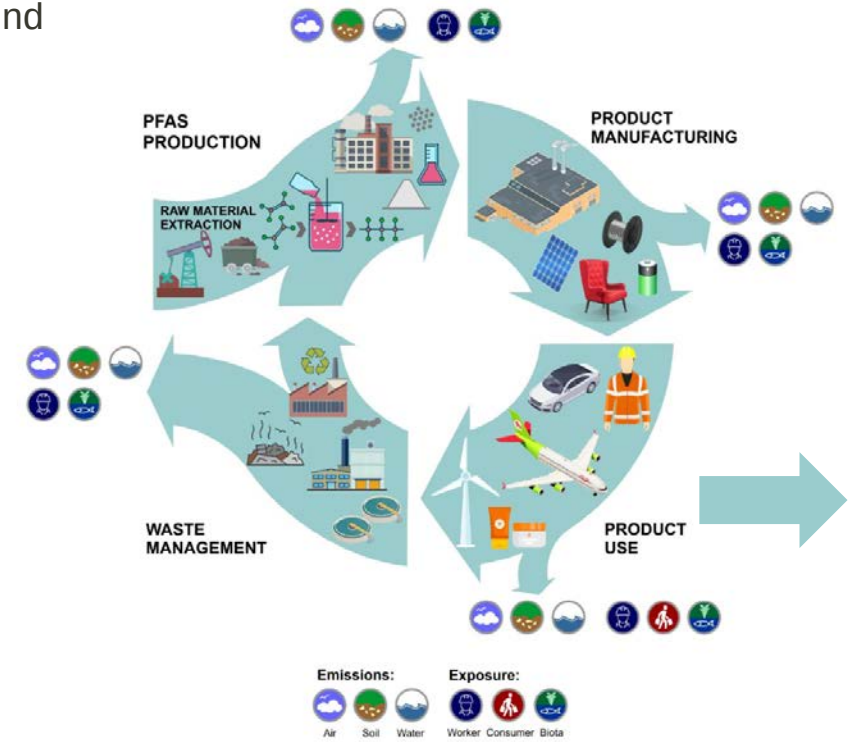
And more unknown ones?



Credit: Forever Pollution Project / Le Monde

PFAS Emissionen über ihren „Life Cycle“

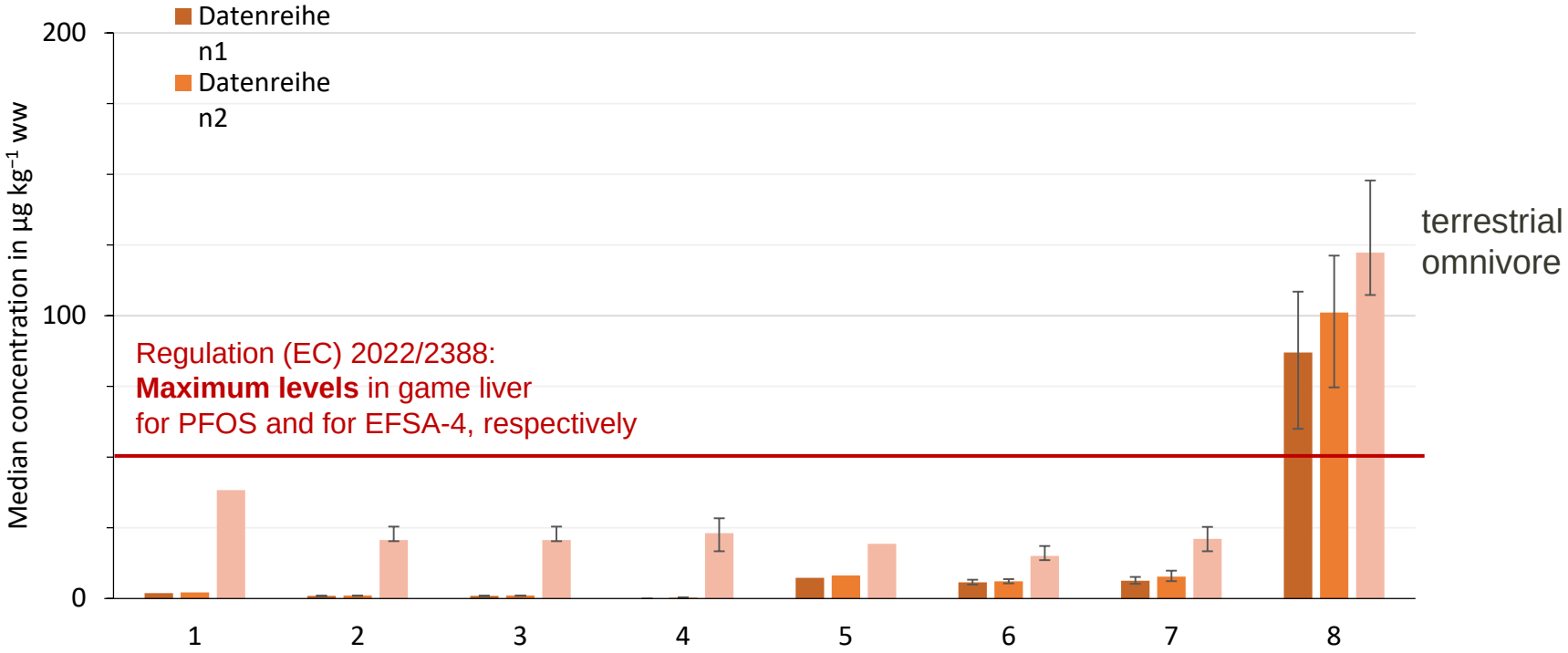
- Lokale hohe Emissionen und diffuse Emissionen überall



- „background contamination“ of the environment
- emissionen in households
- exposure of the general population

https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:52020SC0249

PFAS in Livers of Wildlife in Germany



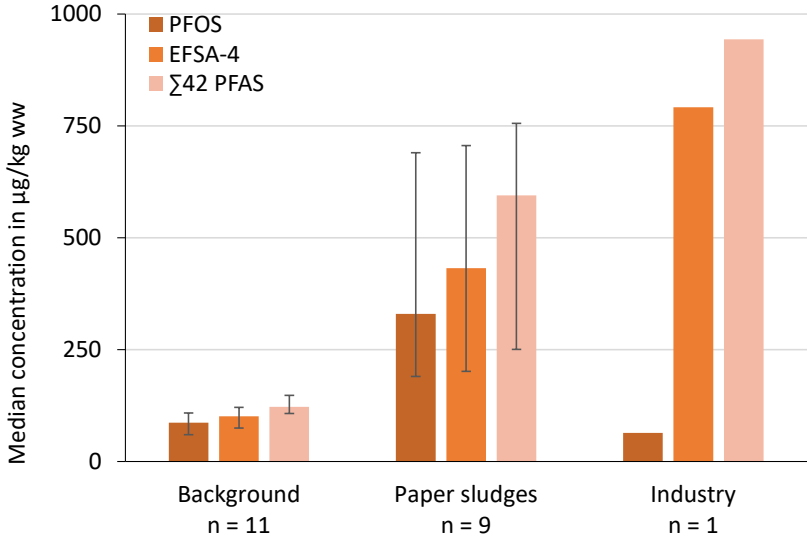
Guckert, M. et al. (2023) Sci. Total Environ. 875, 162361.

PFAS in Livers of Wild Boars

- Can PFAS screening in wild boar liver help identify hotspots of contamination in the terrestrial environment?

https://www.breakinglatest.news/technology/wild-boar-as-a-pfas-trap-hot-online/

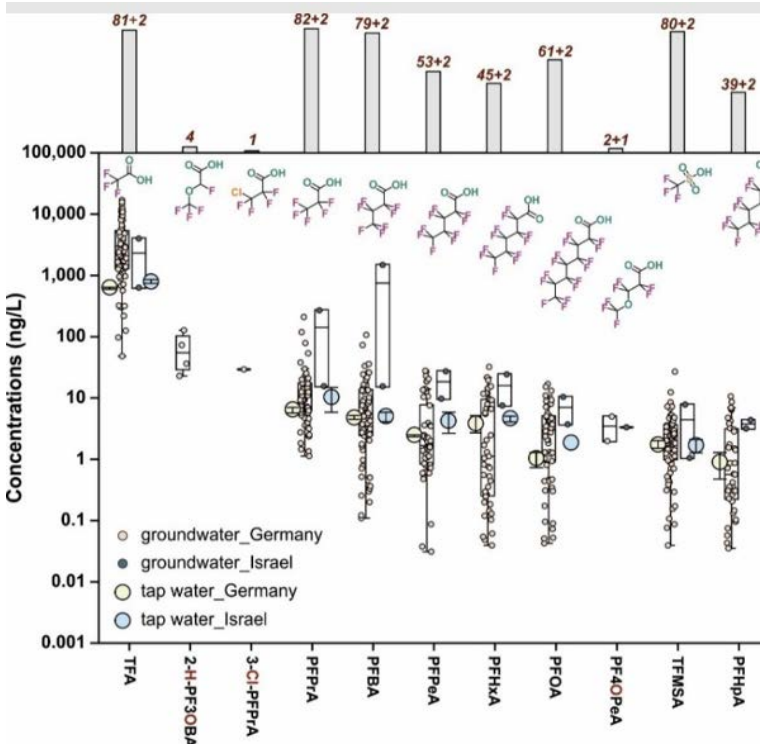
- PFAS in wild boar liver
  - from hotspots and background contamination



Rupp et al. (2023) Sci. Tot. Environ. 871, 162028

PFAS in Groundwater in Saxony

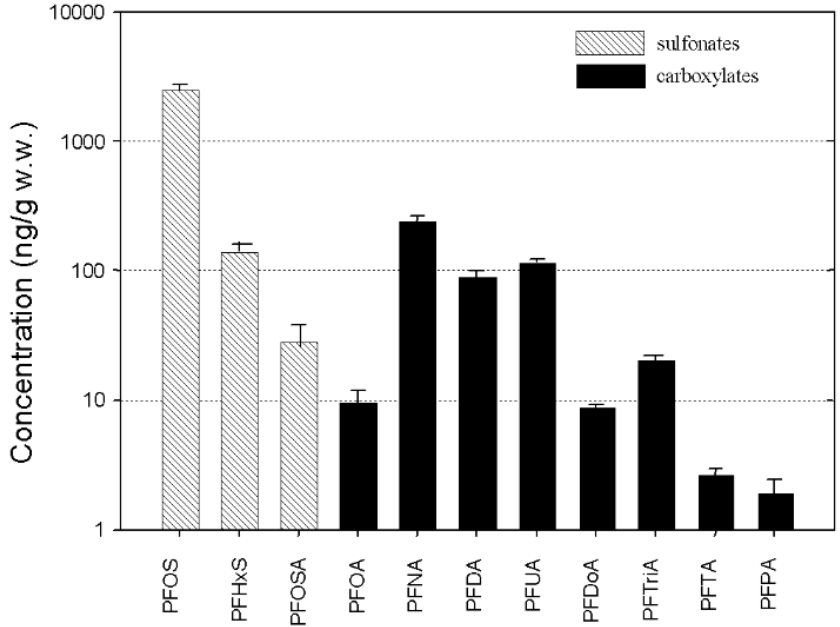
- Monitoring of approx 100 groundwater wells



Zhu, X. et al. (2024) UFZ, in prep.

PFAS – „Background Contamination“

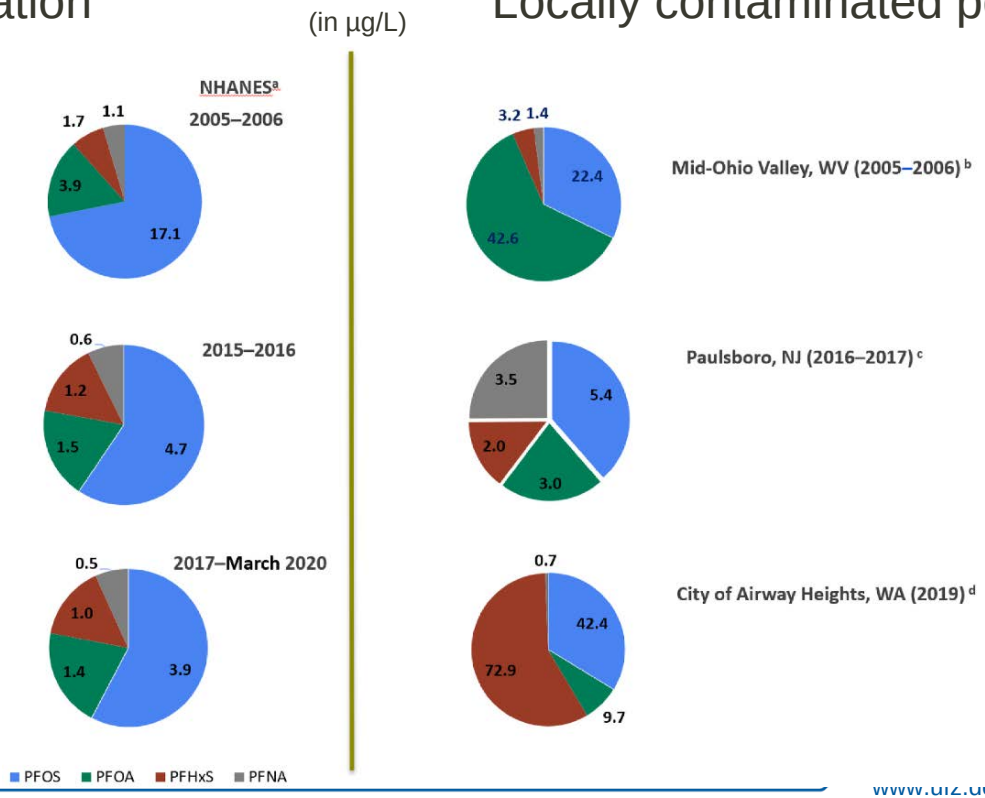
- PFSA and PFCA concentrations (ng/g wet wt) in liver tissue from East Greenland polar bears (*Ursus maritimus*) sampled in 1999 to 2001.



- “More than 12% were attributed to perfluorinated organics other than PFOS.”
- “Significant correlations between concentrations of contaminant groups indicated a common anthropogenic source.”
- **“Fluorotelomer alcohols** have sufficiently long atmospheric half-lives to allow for **long-range transport** and their atmospheric oxidation yields perfluorinated acids and telomer acid precursors.“

Smithwyck et al. (2005) Environ. Toxicol. Chem. 24, 981-986

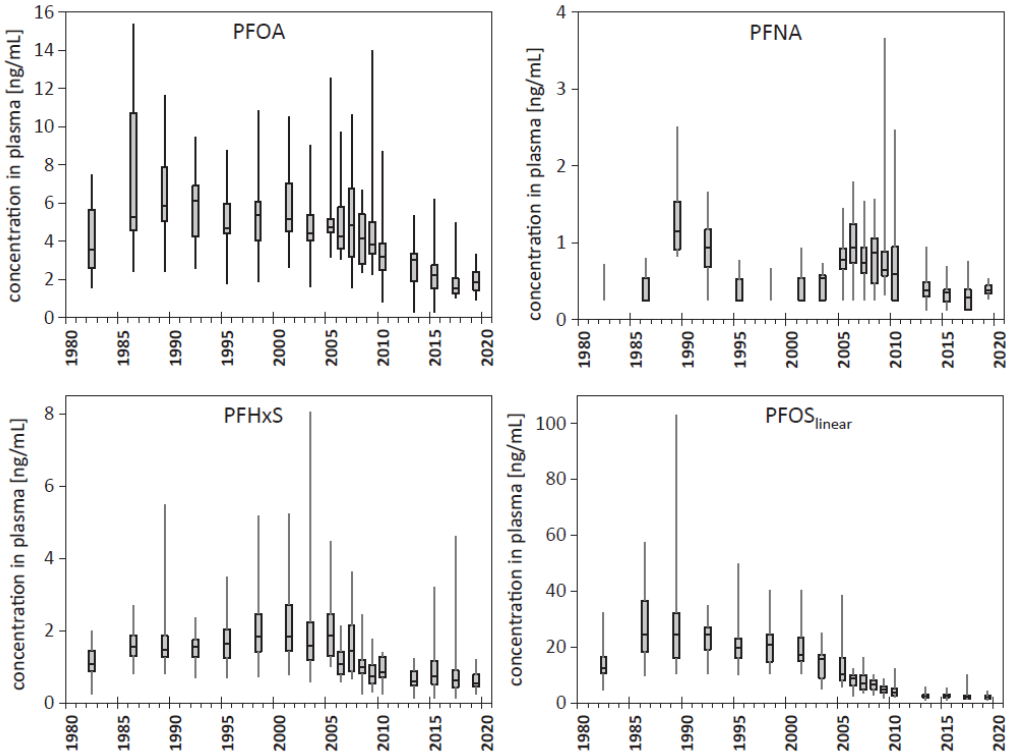
Exposition der Bevölkerung in den USA (1999 – 2020)



Botelho et al. (2025) Environ. Res. 270, 120916

Biomonitoring Studies on PFAS Exposure of the General Population

- USA
  - NHANES
- DE
  - GerES



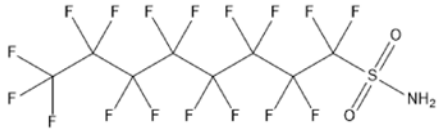
- Temporal trends for PFOA, PFNA, PFHxS, and $PFOS_{linear}$ in human blood plasma in Germany
  - Students from Univ. of Münster (10 f/10m)
  - 1983 – 2019

Göckener et al. (2020) Environ. Int. 145, 106123

Polyfluorierte Alkylsubstanzen

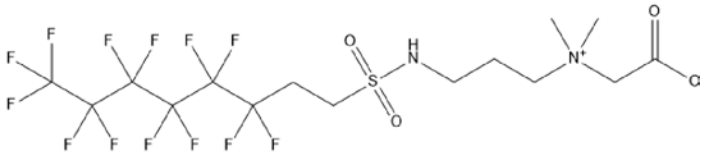
Vorläufersubstanzen (precursors)

- PFAS, welche durch Transformation die bekannten Perfluoralkyl-Sulfonsäuren (PFSA) oder –Carbonsäuren (PFCA) bilden
- insb. zu PFOS und PFOA
- Z.B. FOSA



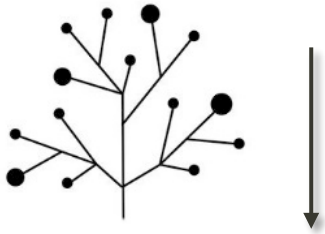
Ersatzstoffe (substitutes)

- Polyfluorierte Alkylsubstanzen, die nicht bereits PFSA oder PFCA sind
- Z.B. Capstone B



- Diese Substitute enthalten immer eine perfluorierte Molekülstruktur
  - sind immer auch (potentielle) Vorläufersubstanzen

Vorläufer / Substitute

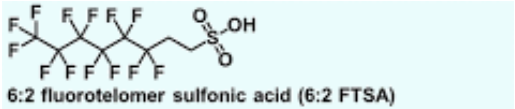


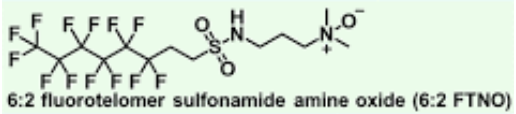
Persistente Transformationsprodukte
(PFCA und PFSA)

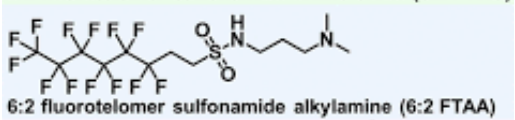
Polyfluorierte Alkylsubstanzen

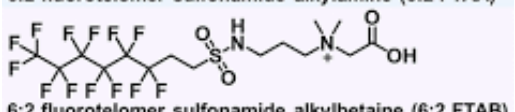
Polyfluorinated molecules

- Have non-fluorinated reactive moieties that can be attacked by enzymes
- -CH2, -O-, sulfonamide
- → less stable, shorter half-lifes







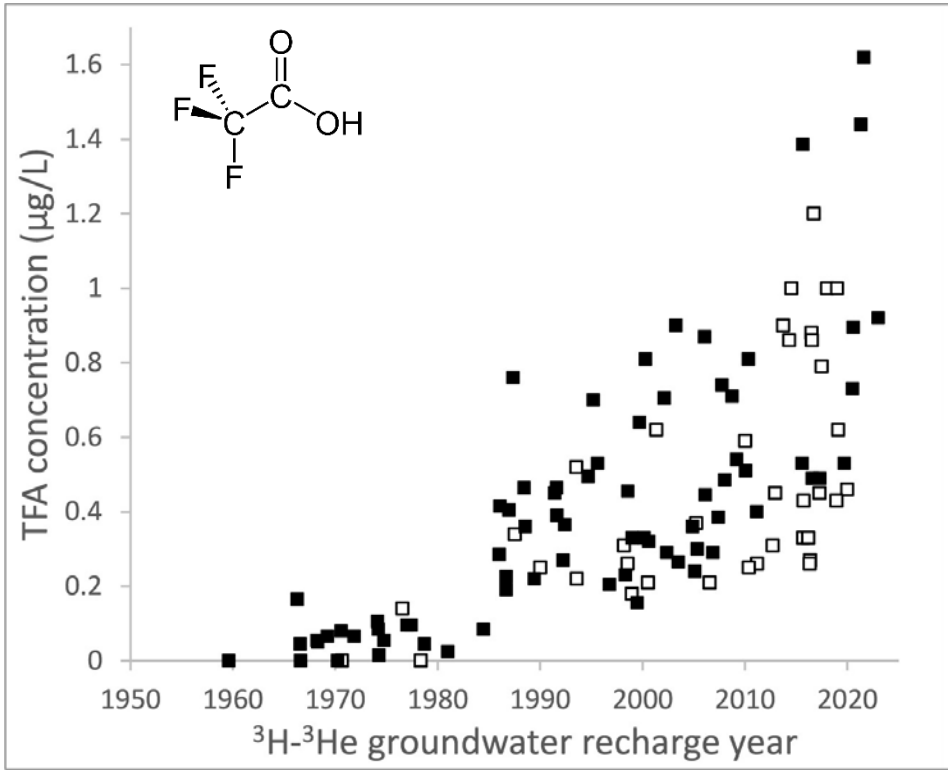


- But transform into perfluorinated subunits

PFAS	conditions	Half-life (d)	Ref.
6:2 FTNO	activated sluge	1.2	1
6:2 FTAB	activated sluge	n.d.	1
6:2 FTSA	activated sluge	30	1
6:2 FTAA	activated sluge	11.5	1
6:2 FTSA	wetland, glycole	20	2

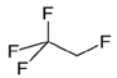
1) Fang et al. (2024) Environ. Sci. Technol. 58, 2446; 2) Fang et al. (2024) J. Hazard Mater. 477, 135261

Trifluoroacetic Acid in Groundwaters 1960 - 2022

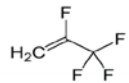


- Concentration of trifluoroacetic acid (TFA) on groundwater versus it‘s (recharge) age for 113 Danish groundwaters

- Possibly over 2000 chemicals as precursors*
  - Most contribution from hydrofluoroolefins (HFOs) in the atmosphere



R 134a



R 1234yf

  - Other compounds with C-CF3 moiety as precursor
    - in many pesticides, pharmaceuticals
  - Thermolysis of fluoropolymers

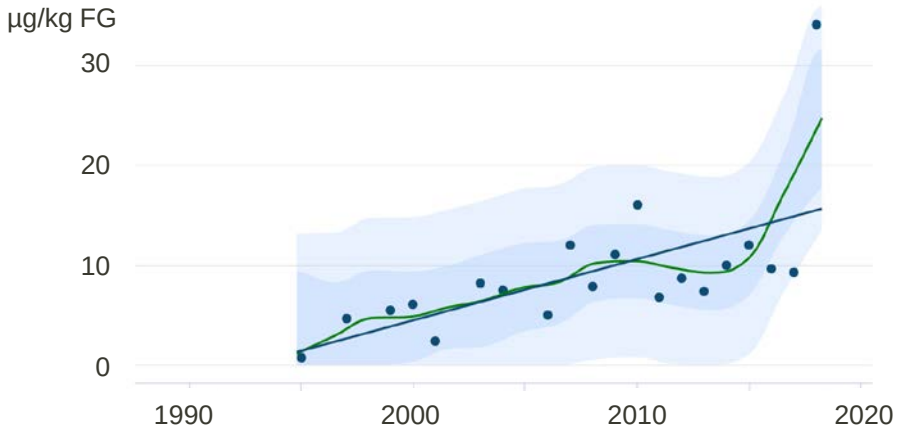
Adlunger et al. (2021) Fed. Environ. Agency, UBA

Alberts and Sültenfuss (2024) ES&T Letters; on-line since 4 Sept. 2024

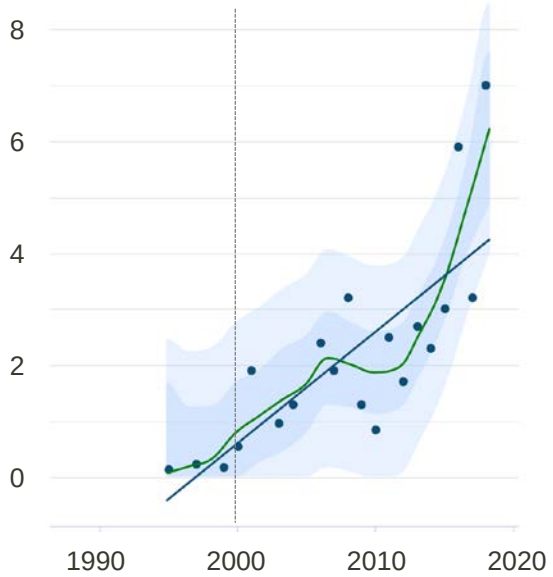
Biomonitoring in Zebra Mussel (Elbe, Germany)

- *Dreissena polymorpha* from Blankenese/Elbe, 1995–2018

Trifluoroacetic acid (TFA)



6:2 FTSA-PrB (Capstone B)



Rupp et al. (2025) UFZ, subm.

Humanexposition und Wirkung

Exposition

- Exposition der Allgemeinbevölkerung auf verschiedenen Wegen
  → kontinuierliche Aufnahme von PFAS
- Hohe Halbwertzeiten im menschlichen Körper
  →Anreicherung

PFAS Chemical	Half-Lives from Referenced Literature [years]						
	Fu et al., 2016	Zhang et al., 2013 [1]	Zhang et al., 2013 [2]	Li et al., 2018	Li et al., 2022	Xu et al., 2020	Olsen 2007
PFOS	1.9	5.8	18	3.4	–	2.9	4.8
PFOA	1.7	1.5	1.2	2.7	2.5	1.8	3.5
PFHxS	3.6	–	–	5.3	4.5	2.9	7.3
PFHpS	–	–	–	–	4.6	1.5	–

Zhang et al. (2013) [1] & [2] are different groups reported in the same study. [1] is data from women under tl
50 as well as men of any age.
Li et al. (2018) and Li et al. (2022) are two different studies based on study populations exposed to the same c
(2018) used blood samples collected from 2014 to 2016 from 106 participants, and Li (2022) used blood san

- Akute Toxizität niedrig, aber chronische Exposition
  → Langzeiteffekte

Wirkung

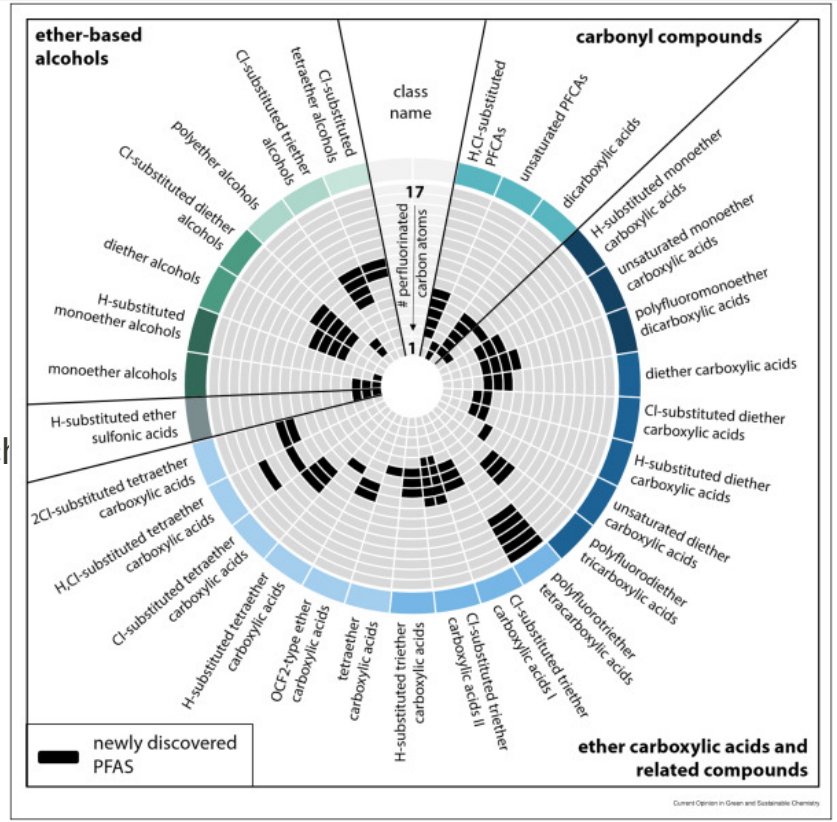
- **2008:** Tolerable Daily Intake (TDI)
  - PFOA: 1.500 ng/kg bw/d = 10.5 µg/kg bw/week
  - PFOS: 150 ng/kg bw/d = 1.5 µg/kg bw/week
- **2018 :** Tolerable Weekly Intake (TWI)
  - PFOA: 6 ng/kg bw/week
  - PFOS: 12 ng/kg bw/week
- **2020:** Tolerable Weekly Intake (TWI)
  - Sum of PFOA, PFNA, PFHxS, PFOS: 4,4 ng/kg bw/week

Decrease by **3** orders of magnitude!

Rosenfeld et al. (2023) Environ. Res. 220, 115164

Diversity of PFAS

- There is more around than
  - alkylsulfonic acids (PFSA)
  - carboxylic acids (PFCA)
- Many different end groups
- variable chain lengths
- Linear and branched alkyl ch
- Neutral, acidic …



Joerss and Menger (2023)
COGSC 40:100775

- More than 5000 PFAS known…
- but
- Human exposure known for only a few of them

- → PERFORCE 3 project

Schlussfolgerungen

- PFAS haben sehr attraktive Eigenschaften, die zu einer großen Vielfalt an Einsatzstoffen und einer extremen Breite an Anwendungen geführt haben.
- Stabilität bedeutet extreme Langlebigkeit in der Umwelt.

Der Umgang mit diesen ungewöhnlichen Stoffen war sehr gewöhnlich:

- Fragwürdige Produktionsprozesse
- Oftmals skandalöse „Entsorgung“
- Sorgloser Einsatz in offenen Systemen
  - Brandbekämpfung etc
- Einsatz in verbrauchernahen (!) Produkten ohne Chance auf „Rückholung“

- **Weltweite PFAS-Belastung** von Umwelt und Menschen
  - Hot-spots
  - „Hintergrundbelastung“
- Polyfluorierte („abbaubare“) Verbindungen werden zu kleineren stabilen perfluorierten Verbindungen umgewandelt.
  - Sie sind KEINE Lösung
- Effekte chronischer Exposition führen zu sehr niedriger zulässiger Humanexposition.
- Ein nennenswerter **Teil der Exposition** der Umwelt und des Menschen mit PFAS **noch unklar.**
- PFAS in Produkten sind ein Problem für die Kreislaufwirtschaft

Danksagung

- Funding

Umwelt Bundesamt

SPONSORED BY THE
Federal Ministry of Education and Research

Deutsch-Israelische Zusammenarbeit
שיתוף פעולה גרמני-ישראלי
German-Israeli Cooperation

Project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodovska-Curie Action Grant agreement No 860665

- Project partners of

re: PM

FLUORBANK

PERFORCE

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Vielen Dank für Ihre Aufmerksamkeit!