German Environment Agency

Umwelt Bundesamt

Why is PFAS getting so much attention now?

Ulrike Braun,
Ronny Wischer, Marcus Lukas

ulrike.braun@uba.de

Interreg Baltic Sea Region

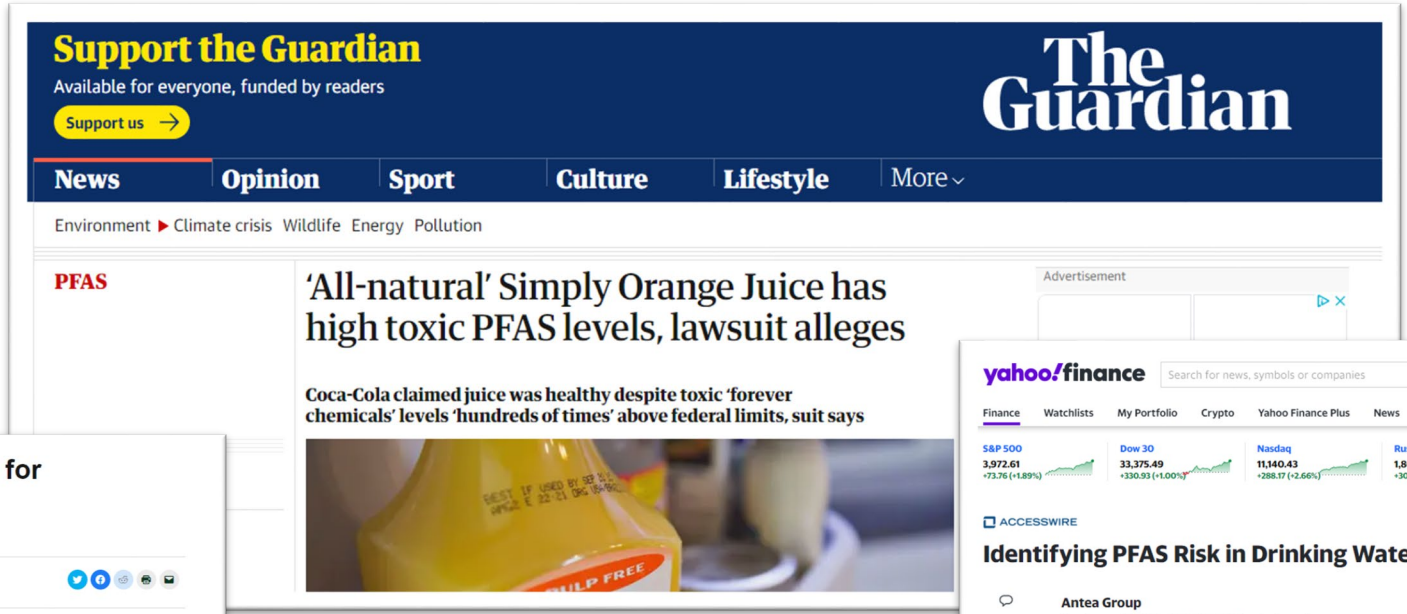
Co-funded by the European Union

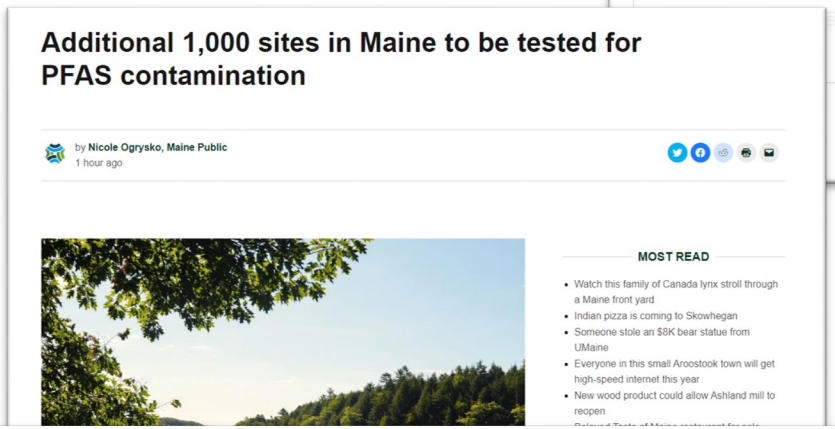
SUSTAINABLE WATERS
EMPEREST

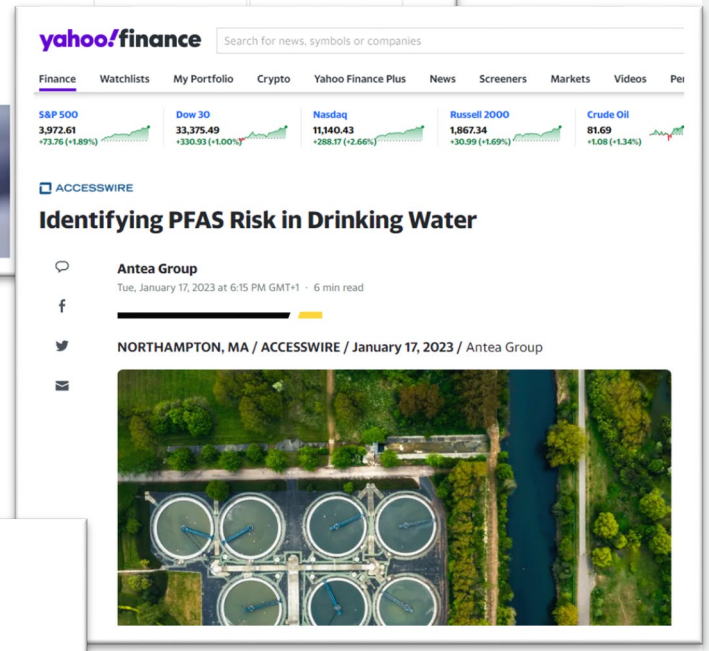
PFAS Public Media

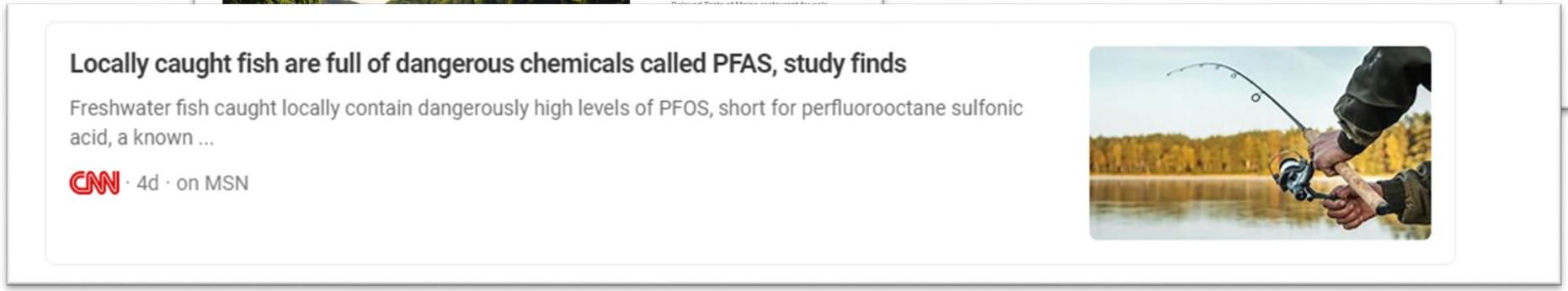
Google search (2023-01-21):

- Dioxin: 5.820.000
- Microplastic*: 5.160.000
- PFAS: 43.400.000

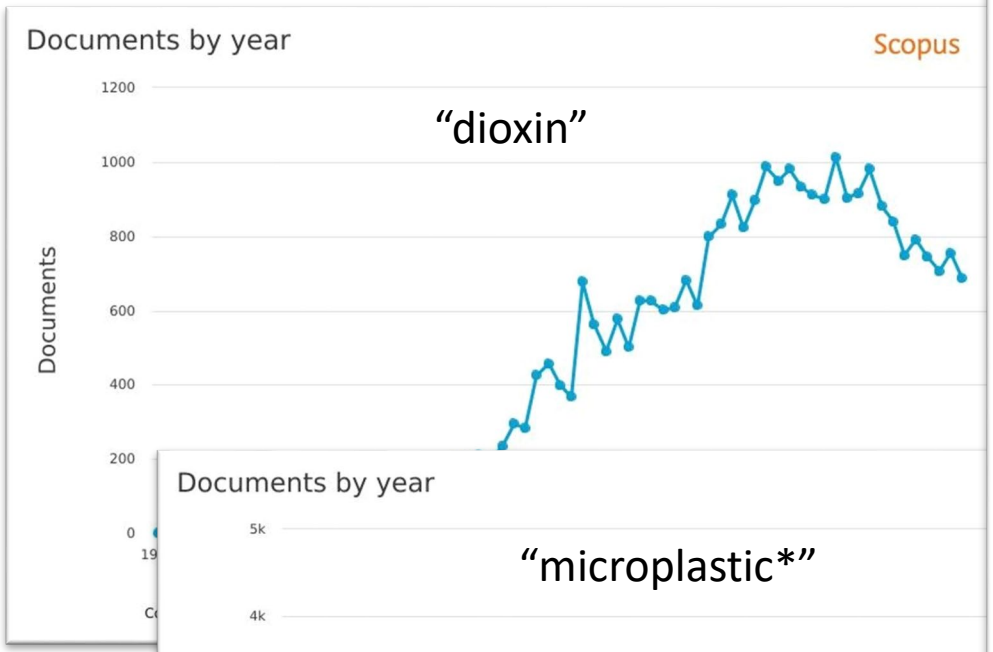


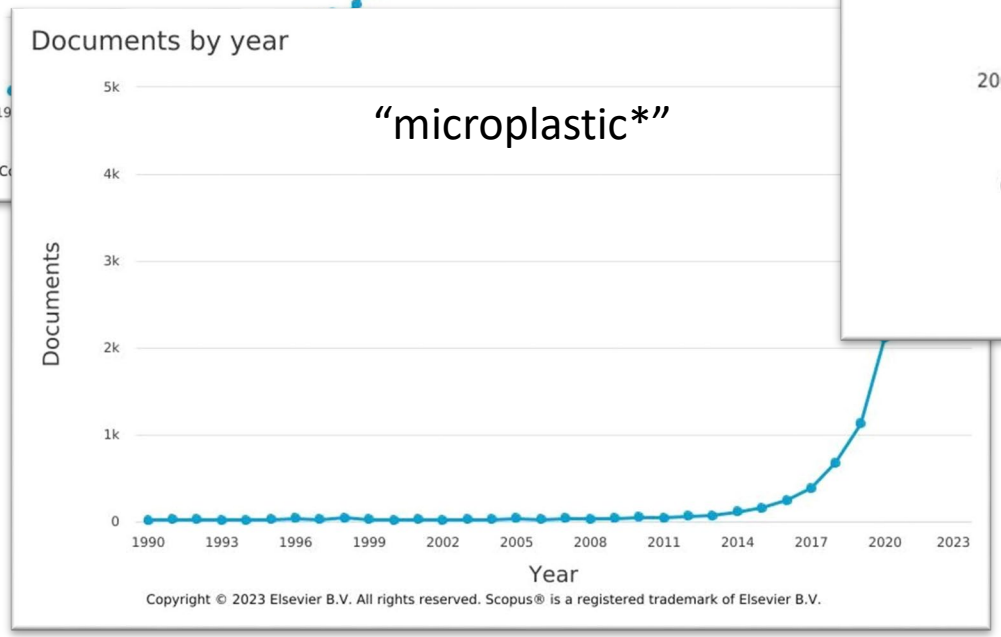


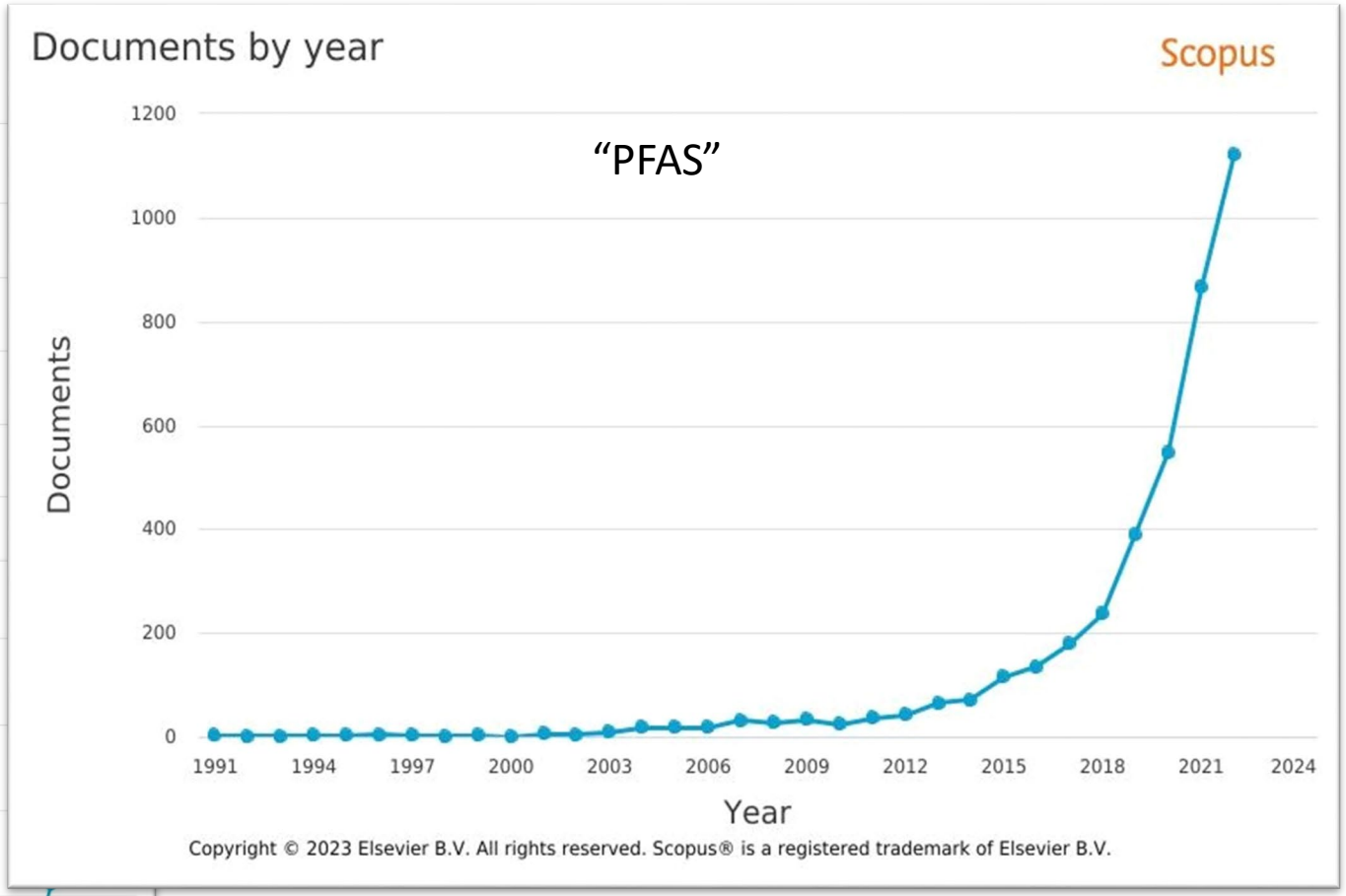




PFAS in Research







Definition: Per- and Polyfluoroalkyl Substances (PFAS)

Carbon (chain) with perfluoroalkyl moiety structure :

CF_3-$(CF_2)_n$ -R

-R = acids: i.e. –COOH, -SO_3H

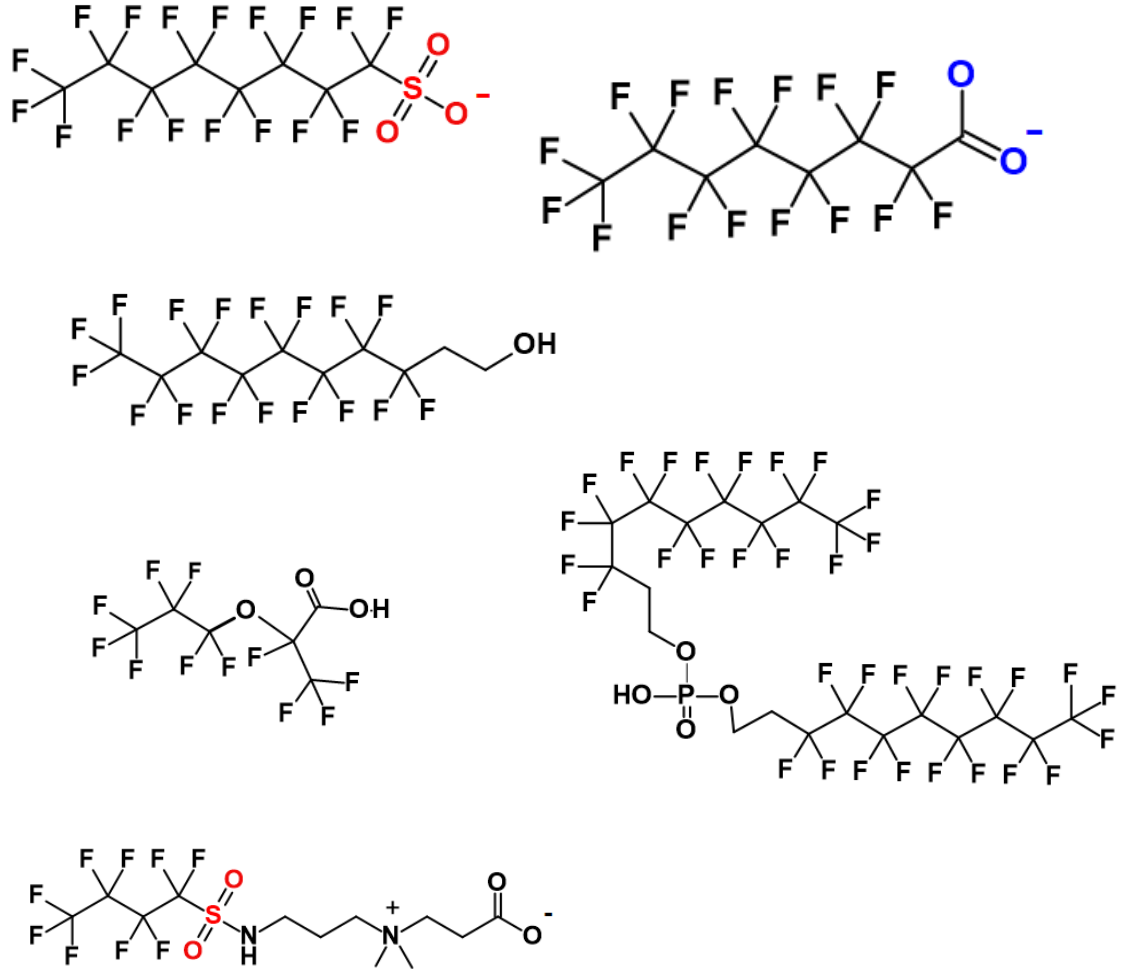
-R = telomere: i.e. -C_nH_{2n}-OH, -C_nH_{2n}-SO_3H

-R = ether (-O-), phosphate ether (-P(=O)O_2OH)

-R = crosslinked fluoroalkyl carboxyl acids

-R = implemented nitrogen containing functionalities:

i.e. –(O=)C-NH-, -$CH_2N(CH_3)_2^+CH_2$-



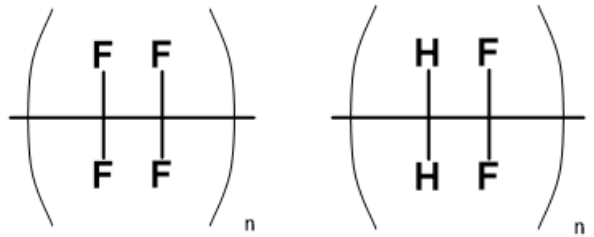
Further Per- and Polyfluoroalkyl Substances

- **Fluoropolymers with repeating structural units,**

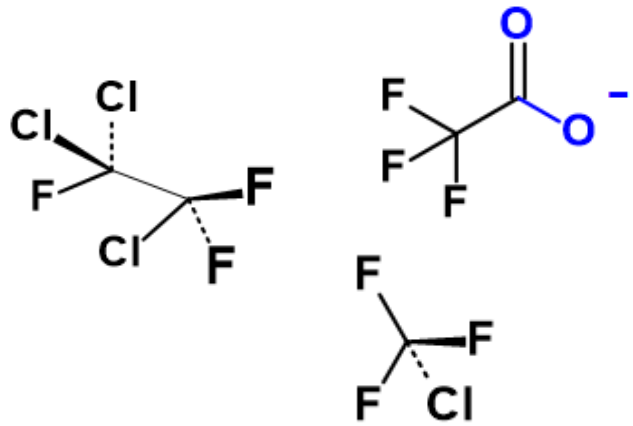
  minimum of 10.000 Da (100 – 150 x Monomer units)

  Polytetrafluorethylene (Teflon), PTFE: $-(CF_2)_n-$

  Polyvinylendifluorid, PVDV: $-(CF_2-CH_2)_n-$



- **Fluor compounds of less than three fluorinated carbons**
- Trifluoroacetic acid (TFA): CF_3CO_2H
- Fluoro-(chloro)-carbons: CCl_nF_{4-n} (n =1-2), CCl_mF_{3-m}-CCl_mF_{3-m} (m= 1-2)



Large Scale Processing of PFAS

Source: Per- and Polyfluoroalkyl Substances (PFAS) Team Contacts Robert Mueller; Bob Mueller, New Jersey Department of Environmental Protection, Virginia Yingling, Minnesota Department of Health; April 2020

	1930	1940	1950	1960	1970	1980	1990	2000s
Teflon	Invented	Non-stick coatings			Waterproof fabrics			
PFOS		Invented	Water resistant products	Firefighting foam				Starting reduction / regulation
PFOA		Invented	Protective coatings					
Fluoro-telomers					Invented	Firefighting foams		

Electrochemical Fluorination (ECF) (since 1940)

$H_3C\text{-}(CH_2)_n\text{–}COOH + xHF \rightarrow F_3C\text{-}(CF_2)_n\text{–}COOF + xH_2$

$F_3C\text{-}(CF_2)_n\text{–}COOF + aq \rightarrow F_3C\text{-}(CF_2)_n\text{–}COOH + F^- + aq$

original, synthesis method:
low yields, large proportion of branched by-products

Telomerisation / Polymerisation (since 1990)

$F(CF_2\text{-}CF_2)I + nCF_2\text{-}CF_2 \rightarrow F(CF_2\text{-}CF_2)_{n+1}I$

$F(CF_2\text{-}CF_2)_{n+1}I + CH_2{=}CHOH + aq \rightarrow F(CF_2\text{-}CF_2)_{n+1}\text{-}(CH_2)_2\text{-}OH + I^- + aq$

„new“ catalytic, synthesis method:
more selective for specific compounds

Production of PFAS

Source	Mass / time frame	Sort of PFAS	Country
Multi-Industry Per- and Polyfluoroalkyl Substances (PFAS) Study – 2021 Preliminary Report, United States Environmental Protection Agency Office of Water, EPA-821-R-21-004	85.000 tons / a	Non-polymer PFAS & Fluoropolymers	US
An overview of the uses of per- and polyfluoroalkyl substances (PFAS), J. Glüge, M. Scheringer, I. T. Cousins, J. C. DeWitt, G. Goldenman, D. Herzke, et al., Environmental Science: Processes & Impacts 2020 Vol. 22 Issue 12 Pages 2345-2373	11.340 tons / a	Reported as “Flour containing compounds” in chemical registration	US
	~ 6.300 tons / 2000-2017	Non-polymer PFAS	SW, N, DK, FN (SPIN Database)
	~ 11.700 t / 2000-2017	Fluoropolymers	
Report summary PFAS and PFAS polymer production July 2021, BauA, www.prokunststoff.de	75.610 tons / a	Fluoropolymers	EU
	85.977 tons / a	Other PFAS	

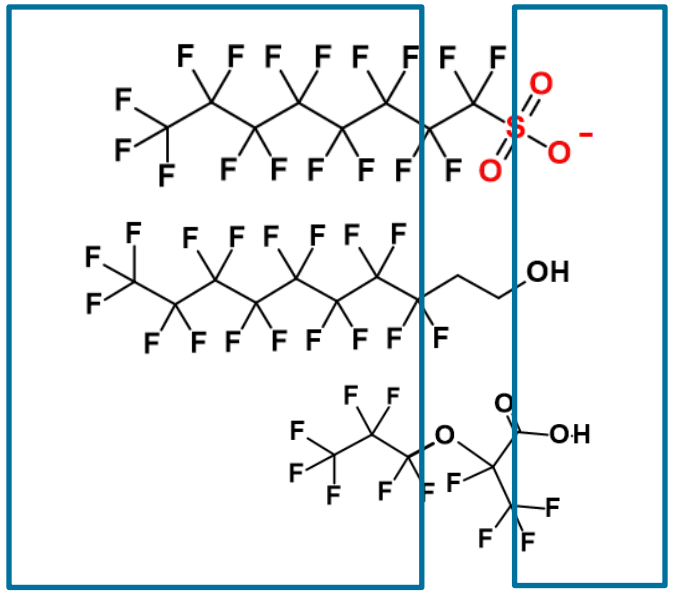
- OECD: 4.730 compounds; US EPA: 14.735 compounds; PubChem: 6 Mio compounds
- More than 200 applications

Fluor-Carbon Chemistry

	$^{\delta+}$C-F$^{\delta-}$	C-C	$^{\delta-}$C-H$^{\delta+}$
Bond dissociation energy	460 - 530 kJ/mol	350 - 380 kJ/mol	370 - 440 kJ/mol
Mean bond length	132 – 138 pm	137 – 154 pm	108 – 110 pm

C-F bonds are very stabile

Hydrophobic,
inert,
temperature stabile,
non-oxidative,
variable length

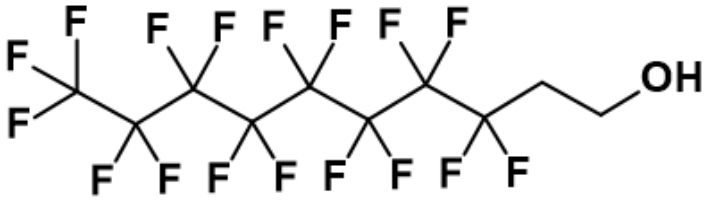


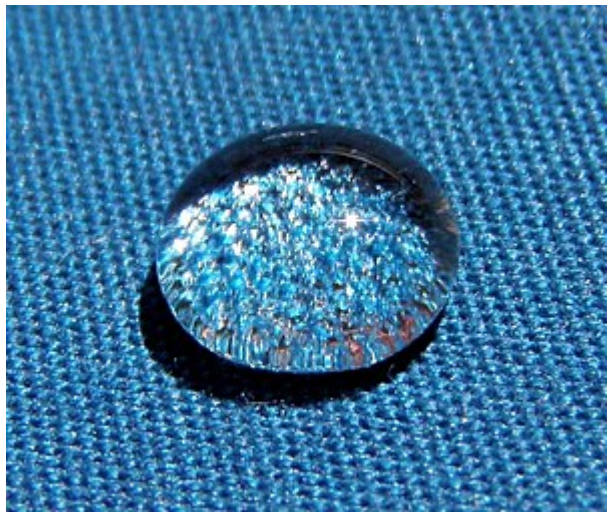
Variable chemistry:
polarity,
reactivity
(also dependent on the connection to fluorocarbon chain)

PFAS in Applications (1)

Water-, dirt-, fat-repellent properties of textiles & fibres:

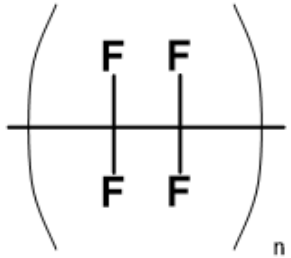
Impregnation of surface by reactive connection to fibres

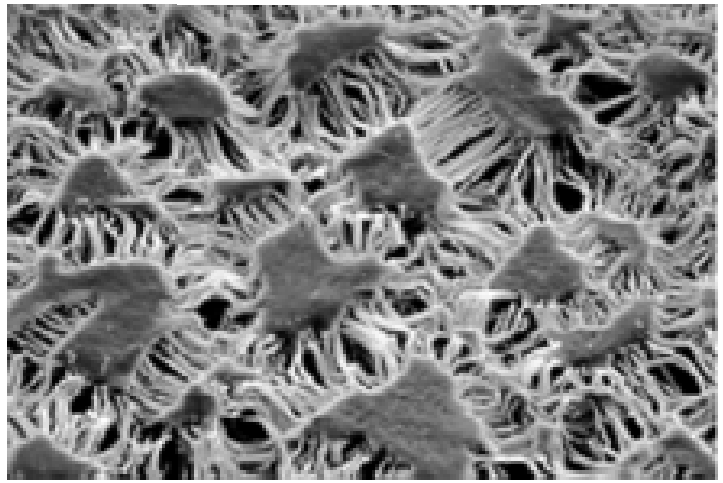




Breathable properties of textiles:

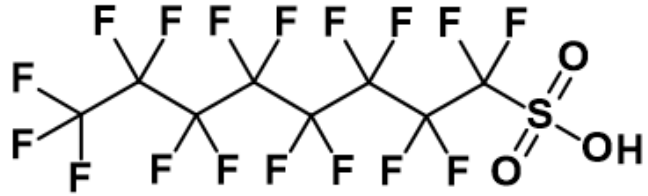
by sticking / lamination of synthetic fibres to textile materials with small pore sizes



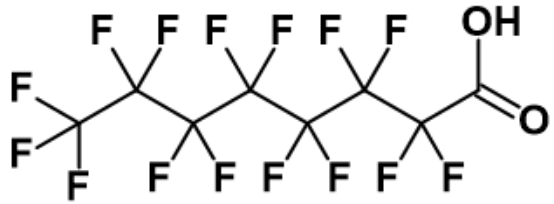


PFAS in Applications (2)

surfactant properties in galvanic industry:
compatibilizer under hard pH conditions



surfactant properties for fire protection:
aqueous film forming foam
between surfaces / liquids and fire zone



PFAS in Applications (3)

Inert / durable properties:
lubricants / oils for mechanical processes
(Fluor-Carbon waxes)

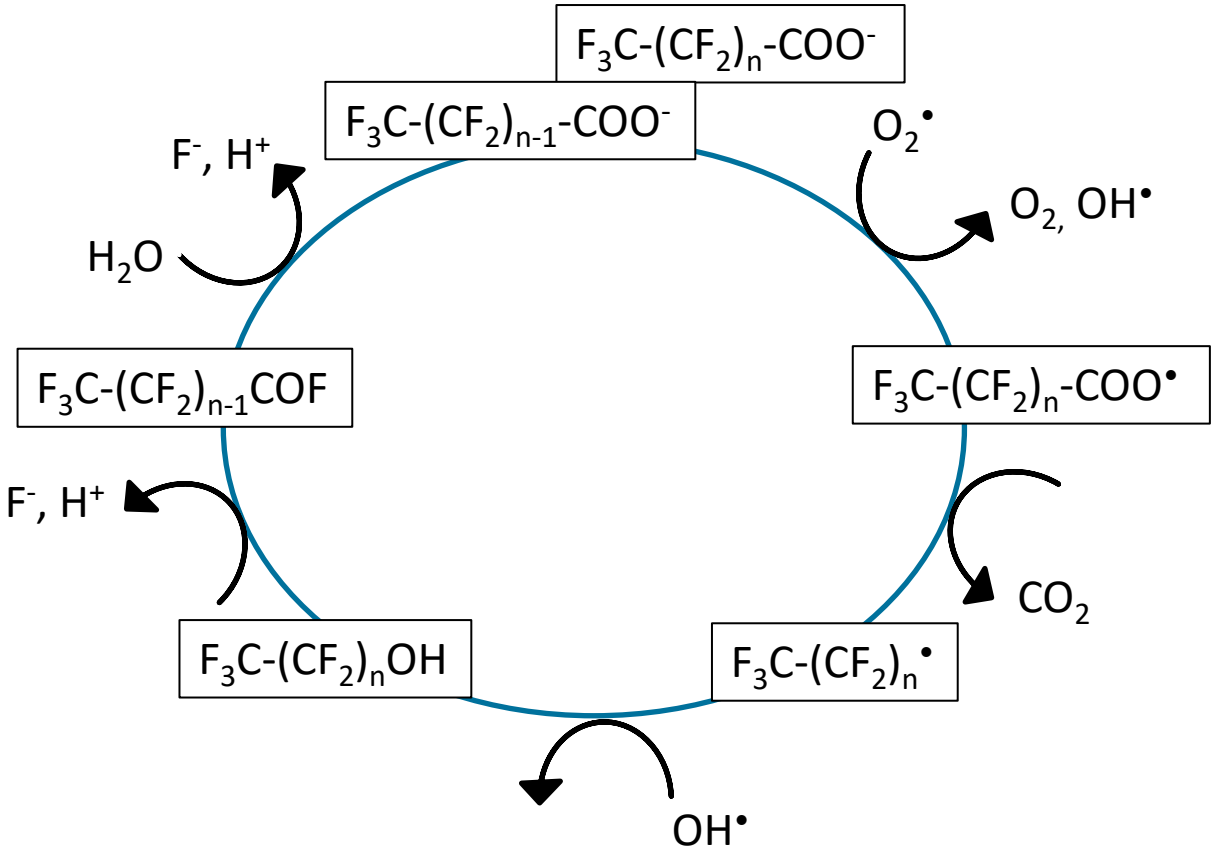
High temperature properties:
Surface layer at high temperature applications
(Teflon coating)

Heat capacity properties:
(also: non-flammable, non-toxic)
Refrigerant
(Fluor-Carbon gases)

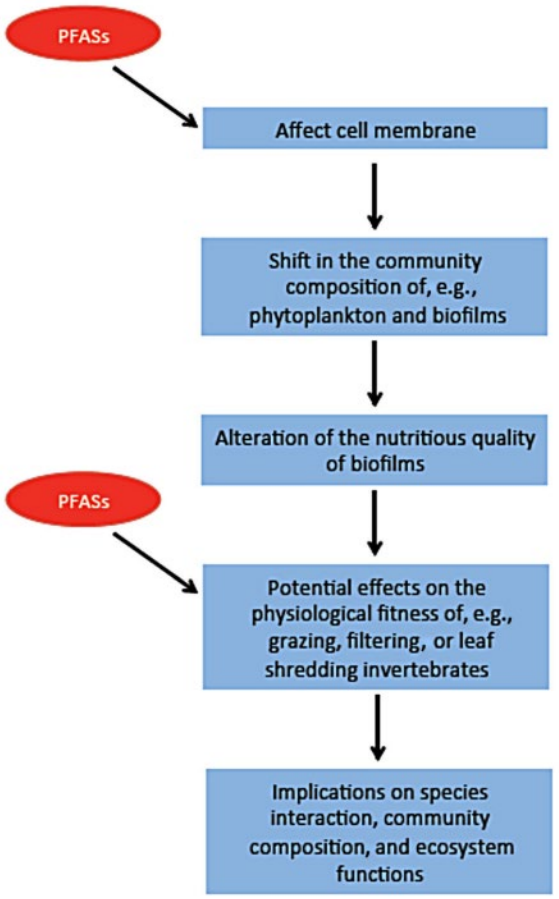
Degradation of PFAS

- No thermal, hydrolytic and biological degradation under environmental conditions
- "Incomplete" degradation:
  $F_3C\text{-}(CF_2)_n\text{-}(CH_2)_2\text{-}OH \Rightarrow F_3C\text{-}(CF_2)_n\text{-}COOH$
  $F_3C\text{-}CH_2F \Rightarrow F_3C\text{-}COOH$
- Photo-oxidative degradation possible:
  presence of $O_2^{\bullet}$ radicals:
  back zipping of carbon chain
- Low mechanic performance of Teflon:

	E-Modul	Shore Hardness
Teflon	420 MPa	D55
Polypropylen	1450 MPa	D70
Polystyrene	3200 MPa	D80



Ecotoxicology of PFAS



(Ahrens & Bundschuh, 2014; Ding and Peijnenburg, 2013)

Effects in aquatic ecosystems

- Effects* of single PFAS on all trophic levels and whole aquatic communities

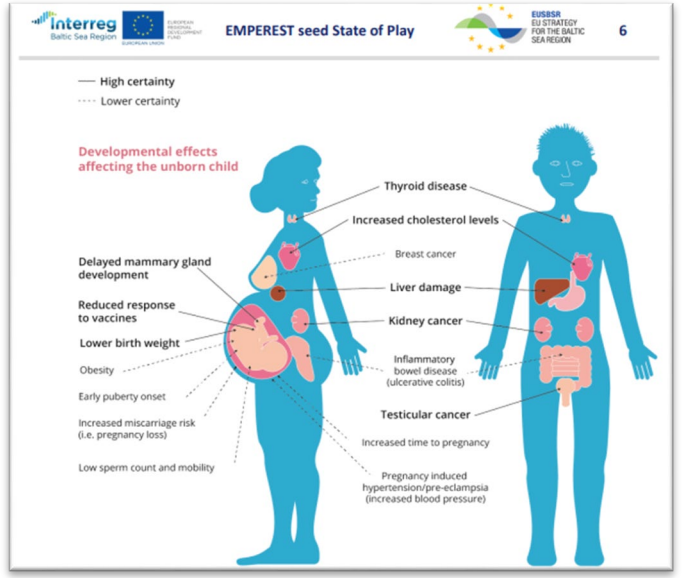
Impact of multiple stressors

- PFAS may interact with other chemical substances/pollutants

Complexity in species interaction and ecosystem function of PFAS effects:

- E.g. direct and indirect effects on invertebrates via affected algae

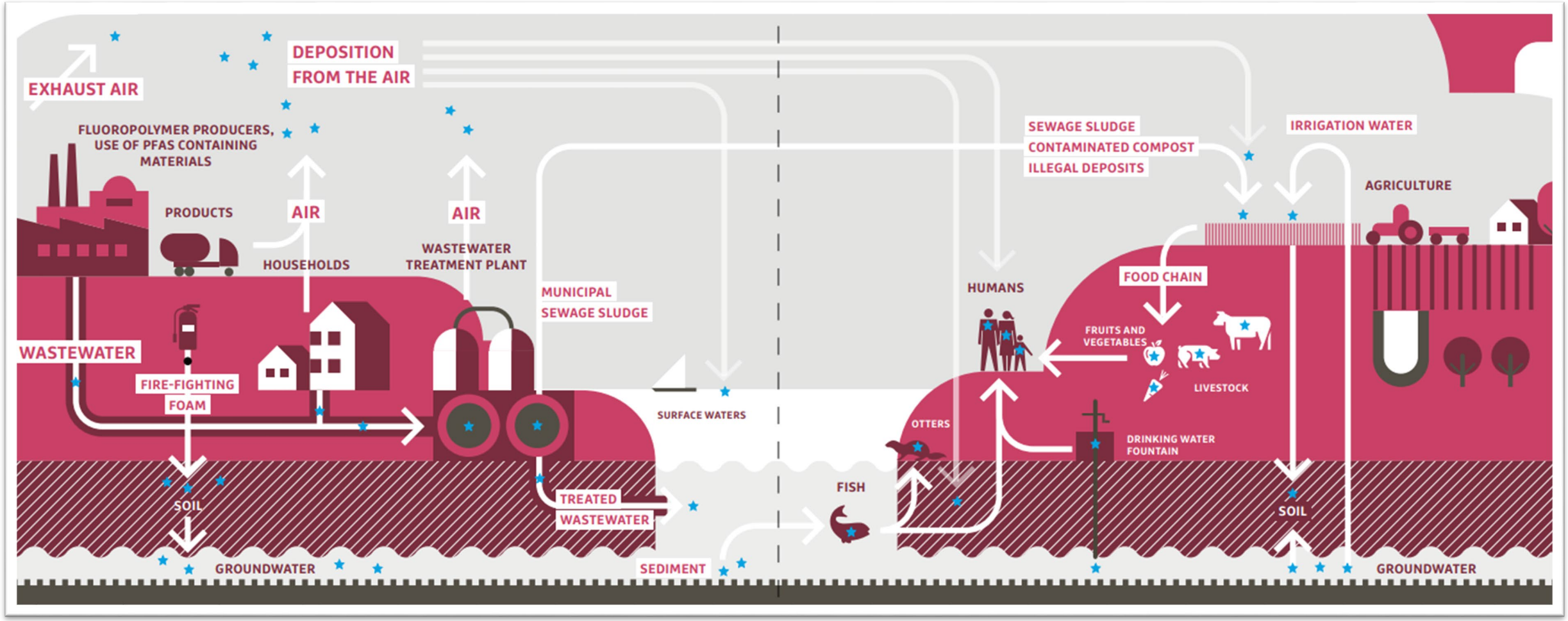
(*in µg L^{-1} to mg L^{-1} range)



Potential PFAS effects:

- Bioaccumulation
- Oxidative stress
- Endocrine disruption
- Liver damage
- Growth inhibition
- Lower reproduction

Dissemination via water, soil and air



- Emission pathways known – but emission quantities are not quantified

Regulation

- Restriction efforts since 15 - 20 a
- PFOS and PFOA are included in Stockholm Convention list of persistent organic pollutants.
- PFOS and PFOA are also included in the HELCOM recommendation 31E/1 (List of Priority Hazardous Substances).
- PFAS are considered contaminants of emerging concern in the updated Baltic Sea Action Plan 2021-2030.
- In 2021 C_9-C_{14} PFCA were added to REACH. A group restriction for about 200 PFAS.
- Broader PFAS regulations are currently in the works in the EU. Also meant to go under REACH. First drafts are expected late 2022 …

Water Sort	Limiting values
Surface Water (Priority Substance list of Water Framework Directive)	6.5 10–4 µg/L and 1.3 × 10–4 µg/L (averaged) 36 µg/L for inland and 7.2 µg/L (maximum)
Drinking water (Drinking water directive)	0,1 µg/l (PFOS, PFOA)
Sewage sludge	100 µg/kg (PFOA & PFOA)
Biota / Fish (Priority Substance list of Water Framework Directive)	9,1 µg / kg wet weight (PFOS)
Human blood	2 ng/ml (PFOA), 5 ng/ml (PFOS)

- 7.2.23: Dossier of ECHA - Proposal: “use of all PFAS compounds only there, where no alternatives exist, i.e. social-economic advantages for human and environed predominate”

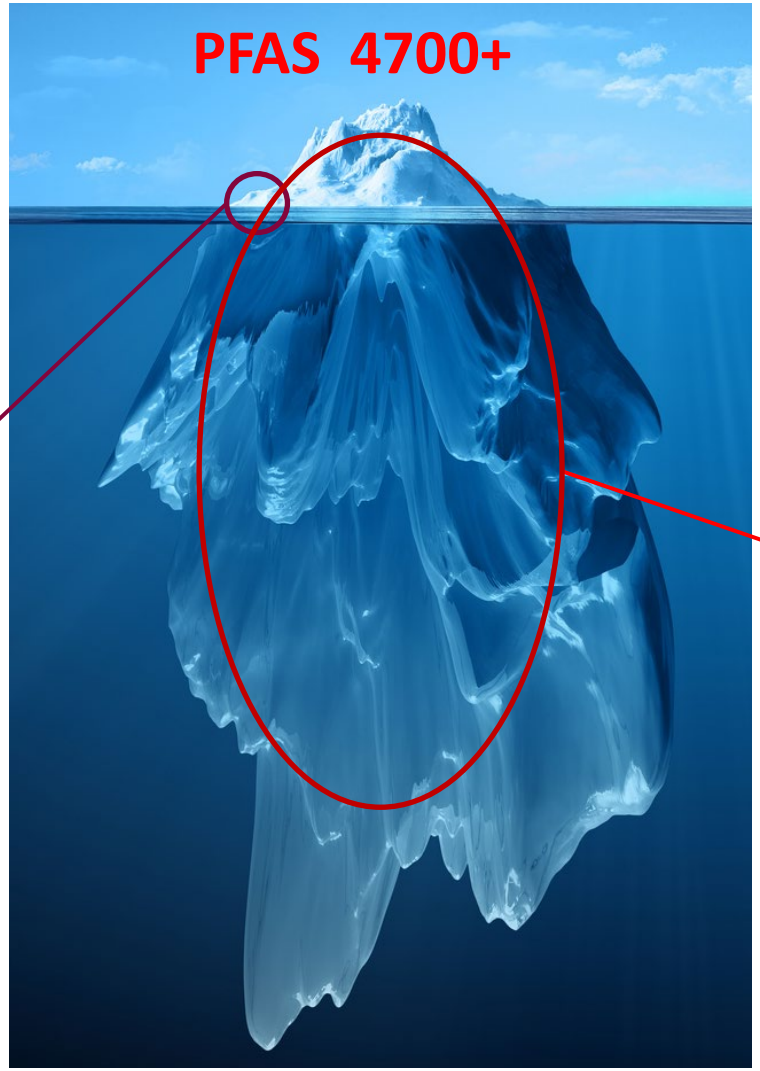
=> When accepted - restriction from 2025

Principles of PFAS Detection

Single substance analysis

- ☺ Identification of specific substances possible, including entry pathways
- ☺ Low detection limit
- ☹ No detection of non-targed compounds, including PFAS degradation products

=> HPLC-MS



adimas, Fotolia

Sum parameter

- ☺ Determination of all known, new, replaced or unexpected compounds as a sum value
- ☹ No separation between different substances possible
- ☹ False positive results from other flour containing compounds (AOF only)

=> TOP Assay
=> AOF

Chromatography – Mass spectroscopy

- Measure principle by chromatographic separation and subsequent identification my mass spectroscopy
- In general, solid phase extraction (SPE) is needed
- Focus on target substances: Standardized or Lab methods

Standard	Method	Number of PFAS
DIN 38407-42 (water, wastewater, sludge)	SPE-LC-MS/MS	10 Compounds
DIN 38414-14 (sludge, compost, soil)	HPLC-MS/MS	10 Compounds
ISO 21675:2019 (water)	SPE -LC-MS/MS	30 Compounds
ASTM D7979-19 (water, sludge, influent, effluent, wastewater)	LC/MS/MS	21 Compounds
ASTM D 7968-17a (soil)	LC/MS/MS	21 Compounds

Total Oxidisable Precursor Assay (TOP Assay)

Principle:

- Thermolysis of persulfate ($K_2S_2O_8$) under basic pH conditions (NaOH) results in formation of hydroxy radicals (ΔT ~ 80-90 °C, ~ 6 h)

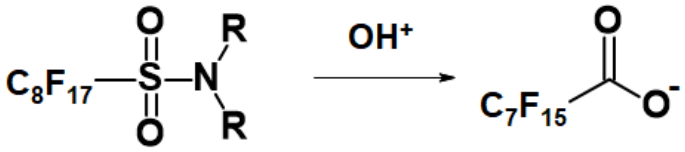
⇒ "All" perfluoroalkyl compounds are transformed to perfluoro-carboxyl acids of related chain length

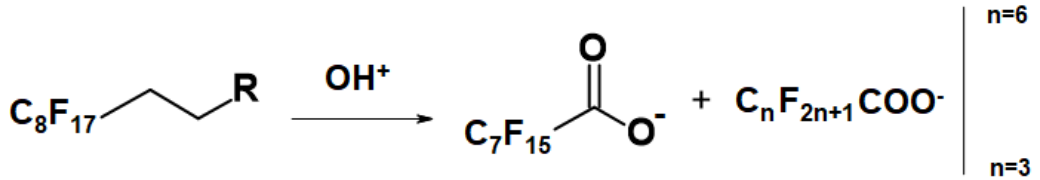
- Cooling down, neutralisation
- Solid Phase Extraction (SPE)
- Detection by LC-MS

Limits of quantification ~ 10-500 ng/L

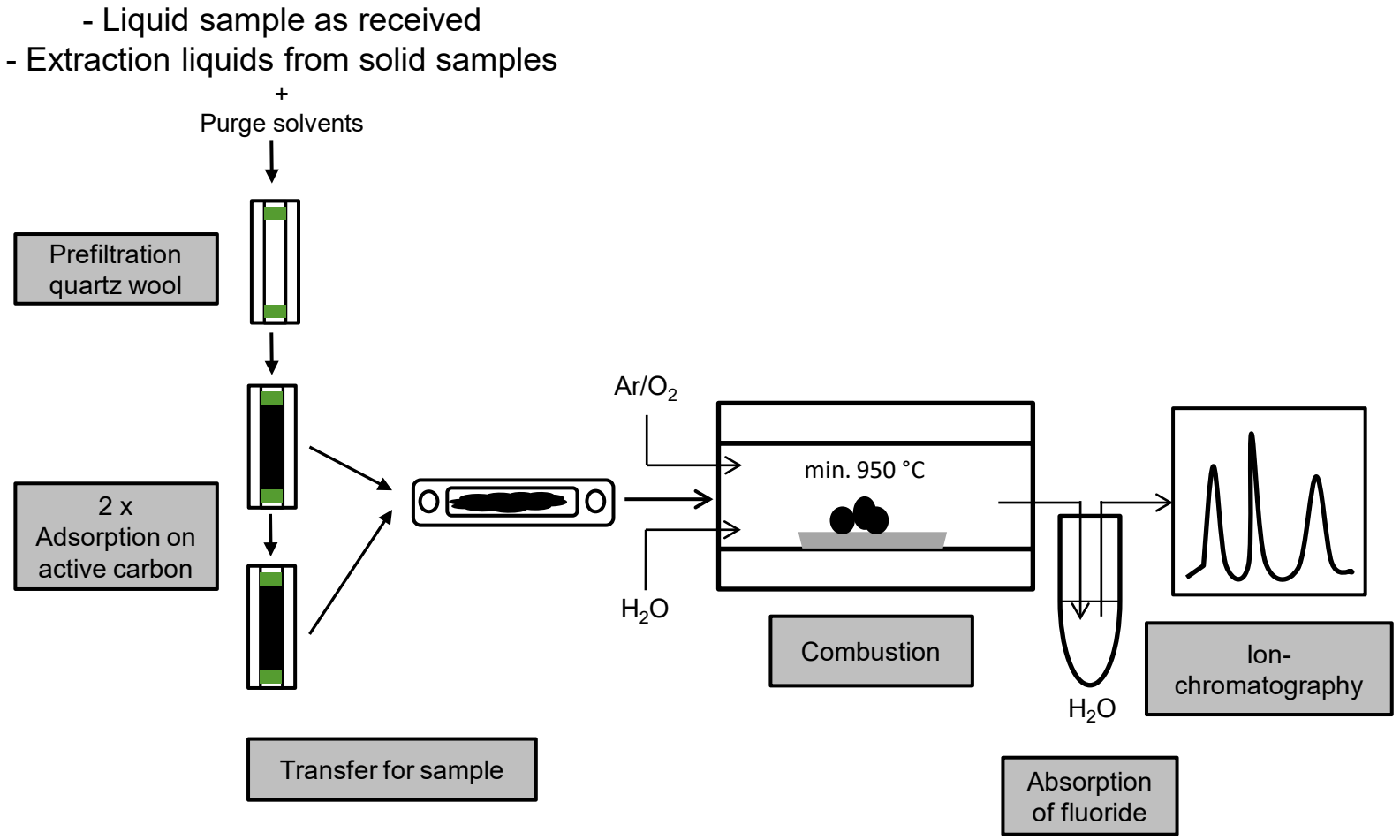
☺ Applicable for all water matrices

☹ Additional sample preparation is needed or solid phase extraction (SPE)





Adsorbed Organic Fluorine - Combustion Ion Chromatography (AOF-CIC)



Application range ≥ 2 µg/L fluorine absolute

Limits of quantification ~ 0.5 - 5 µg/L

☺ Applicable for fluorine, chlorine, bromine, iodine compounds

☺ Applicable for all water matrices without pretreatment

☹ High fluoride contents can interfere - >1 mg/L in the analysis sample

AOF-CIC Validation and Optimisation

Acceptable (> 80 %)
Still in range (50 – 80 %)
Non Acceptable (< 50 %)

- Optimisation by change of purge water for adsorption process from acid to neutral conditions
- Reference experiments with water: No influence of anorganic flouride on AOF result below 1mg/L
- Real waste water samples: No influence of anorganic flourid on AOF result below 10mg/L
- Optimal results for PFAS with C_5 - C_{11}
- PFAS OH-Telomers – some are critical ???

Compound	Formular	Recovery rates under acid conditions / %	Recovery rates under neutral conditions / %
PFBA	$C_4HF_7O_2$	95 – 97	83 – 85
PFPeA	$C_5HF_9O_2$	95 – 99	91 – 93
PFHxA	$C_6HF_{11}O_2$	99 – 100	99 – 100
PFHpA	$C_7HF_{13}O_2$	94 – 98	91 – 94
PFOA	$C_8HF_{15}O_2$	90 – 92	92 – 94
PFNA	$C_9HF_{17}O_2$	71 – 76	97 – 100
PFDA	$C_{10}HF_{19}O_2$	71 – 74	86 – 97
PFUnDA	$C_{11}HF_{21}O_2$	68 – 81	85 – 91
PFDoDA	$C_{12}HF_{23}O_2$	40 – 50	78 – 90
PFTrDA	$C_{13}HF_{25}O_2$	32 – 38	51 – 61
K-PFBS	$C_4HF_9O_3S$	95 – 100	96 – 100
K-PFHxS	$C_6HF_{13}O_3S$	97 – 99	91 – 96
K-PFOS	$C_8HF_{17}O_3S$	72 – 82	87 – 91
4-FBA	C_6H_5FO	95 – 97	92 – 98
HFPO-DA (GenX)	$C_6HF_{11}O_3$	92 – 96	89 – 98
6:2 FTOH	$C_8H_5F_{13}O$	34 – 46	50 – 59
8:2 FTOH	$C_{10}H_5F_{17}O$	16 – 25	38 – 47
10:2 FTOH	$C_{12}H_5F_{21}O$	73 – 78	70 – 81

Research Project: PFAS-Detection in different waste water

	Metal /Semi-conductor	Chemical industry	Solid waste / Landfill	Textiles / Leather	Paper / Printing	Municipal
Number of sampling sides	10 x 4-6 Samples	5 x 5-6 samples	9 x 2-6 samples	3 x 5-6 samples	7 x 5-6 samples	7 x 5-6 samples
Backgound anorganic flouride	up to 35 mg/l	up to 50 mg/l	up to 23 mg/l	below 0,5 mg/l	below 0,3 mg/l	below 0,4 mg/l
Single substance analysis (HPLC)	Neraly in all samples: 6:2 FTS, PFOS, PFBS	Mainly processed PFAS compounds	Nearly in all samples different PFAS compounds	Nearly in all samples: 6:2 FTS, PFBA	Nearly in all samples different PFAS compounds	Nearly in all samples different PFAS compounds
Sum parameter (AOF-CIC)	up to 600 µg/l, Strong variation	up to 300 µg/l, Strong variation	up 200 µg/l, Strong variation	up to 10 µg/l, Moderate variation	up to 300 µg/l, Moderate variation	up to 10 µg/l, Moderate variation

- Strong variations / variation of HPLC and AOF-CIC results in all samples even at high sampling and measurement repetitions (continuous discontinuous discharge of waste water, processing conditions)

Conclusion of Research Project:

Advantage of sum parameter (AOF-CIC):

- Changing raw materials (especially recycling) or source materials (e.g. waste)
- Changing production / processes / products (incl. degradation products)
- Use of unspecific PFAS compounds, including degradation products
- Unknown substitutes

Advantage single compound analysis (HPLC):

- Specific use of known PFAS compounds
- Constant and known production
- Known/expected substitutes

⇒ Critical: Homogeneity control (surfactant applications)

⇒ Influence of anorganic fluoride on AOF signal is observable – needs i.e. removal before measurement (solid phase extraction)

Forschungskennzahl 3718263200

Orientierende Untersuchungen zur Belastung von Abwässern mit fluororganischen Verbindungen durch die Bestimmung des adsorbierbaren organisch gebundenen Fluors (AOF)

Abschlussbericht

von

Maria Redeker, Emily Fischer, Manoj Schulz, Christian Dietrich, Arne Wick
Bundesanstalt für Gewässerkunde, Koblenz

Im Auftrag des Umweltbundesamtes

Standardisation

- **AOF-CIC** – Draft for an ISO standard **ISO 18127** (working draft, not published), Water quality - Determination of adsorbable organically bound fluorine, chlorine, bromine and iodine (AOF, AOCl, AOBr, AOI) - Method using combustion and subsequent ion chromatographic measurement
  AOF-CIC – Validation document for german standard **DIN 38409-59** → https://www.wasserchemische-gesellschaft.de/dev/validierungsdokumente

- **LC/MS** – Water quality - Determination of the sum of perfluorinated substances (Sum of PFAS) in drinking water - Method using liquid chromatography/mass spectrometry (LC/MS);
  German and English version **prEN 17892:2022**

- **Total Fluorine-CIC** – Environmental matrices - Halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography detection and complementary determination methods;
  German and English version
  prEN 17813:2022

- **TOP ASSAY** – National standardisation project for solids, **DIN 3608** - Determination of perfluoroalcanoic acids by LC-MS/MS after oxidative digestion (not published)

Thank You! Questions ?

Interreg Baltic Sea Region

Co-funded by the European Union

SUSTAINABLE WATERS EMPEREST

Thanks to J. Bartz (UBA) for support in graphical design!

Principles of Environmental Analysis

Analysis: Sampling – Sample Preparation – Detection

Target group	Basic Research	Applied research / Authorities	Politics
Goal	Scientific and academic visualisation	Comprehensive monitoring / screening	Transfer to society / legislative
Requirements on the procedures / methods	New and improved procedures	Established, high-trough-put procedures with defined limits	Standardised procedures, Guarantee of legal certainty
Requirements on the analytical depth / result	High interest of detailed information	As needed for praxis	Simplification
Requirements on the time for analysis	High	Moderate - Low	Low