PFAS-NÄTVERKSMÖTE 2024-10-22

PFAS in products and industries

Lisa Skedung (lisa.skedung@ri.se)

The POPFREE projects (started 2016)

Vision: A systemic shift where PFAS-free is obvious for both producers and consumers

- **POPFREE Industry – Towards a PFAS-free and Circular Industry (2021-2023)**
- **POPFREE - Promotion of PFAS-free Alternatives – UDI stage 3 (2020-2022)**
- **POPFREE Ski Goes Global – UDI Globalisation (2019)**
- POPFREE - Promotion of PFAS-free Alternatives – UDI stage 2 (2017-2020)
- POPFAS - UDI stage 1 (2016-2017)

All projects financed by Vinnova, Sweden's Innovation Agency, and partners.

There are PFAS-free solutions

in many products that traditionally have contained PFAS

But legislation is needed to remove non-essential uses

It is challenging for consumers to make educated choices due to limited awareness about hazardous chemicals, vague information about chemical content in products, and greenwashing attempts.

Top five major use sectors
Universal PFAS restriction proposal

- Applications of **fluorinated gases** (e.g. refrigeration, air conditioning, heat pumps, propellants)
- **TULAC** - Textile, upholstery, leather, apparel and carpets (e.g. home textiles, consumer apparel, professional apparel, technical textiles, leather)
- **Medical devices** (e.g. implantable devices, wound treatment, tubes, catheters, diagnostic laboratory testing, contact lenses and metered dose inhalers)
- **FCM** - Food contact materials and packaging (consumer cookware, food and feed production, food and feed packaging made of paper, board and plastic)
- **Transport** (e.g. construction, sealing applications, combustion engine systems, information technology, coating and finishings, hydraulic fluids, HVACR-systems)

Link to PFAS restriction proposal

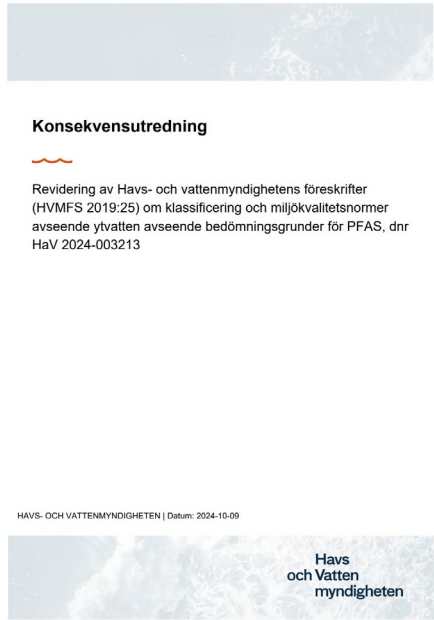
Other major use sectors
Universal PFAS restriction proposal

- **Construction products** (e.g. roofing, bridge bearings, sealings, adhesives, coatings and paints)
- **Electronics and semiconductors** (e.g. wires, cables, coatings, solvents, cleaning, electronic components, photolithography)
- **Lubricants** (e.g. low viscosity lubricants, dry-film lubricants, release agents and greases)
- **Petroleum and mining** (e.g. drilling fluids, well stimulation chemicals, anti-foaming agents and lining of piping, seals and cables)
- **Energy sector** (e.g. solar cells, wind energy, fuel cells, batteries)
- **Metal plating** and manufacture of metal products
- **Consumer mixtures, cosmetics and ski wax**

Link to PFAS restriction proposal

Industries with impact on the water environment

- Group 1: Industries assessed to potentially have significant impact on the water environment
- Group 2: Industries that are highly likely to have a potentially significant impact on the water environment
- Group 3: Industries where the spread is uncertain and that could potentially release PFAS into the water environment

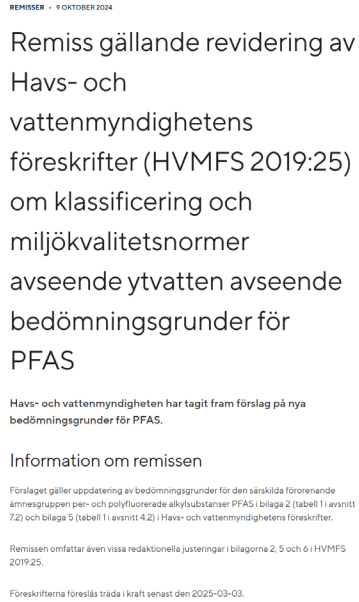


Konsekvensutredning

Revidering av Havs- och vattenmyndighetens föreskrifter (HVMFS 2019:25) om klassificering och miljökvalitetsnormer avseende ytvatten avseende bedömningsgrunder för PFAS, dnr HaV 2024-003213

HAVS- OCH VATTENMYNDIGHETEN | Datum: 2024-10-09

Havs och Vatten myndigheten



REMISSER • 9 OKTOBER 2024

Remiss gällande revidering av Havs- och vattenmyndighetens föreskrifter (HVMFS 2019:25) om klassificering och miljökvalitetsnormer avseende ytvatten avseende bedömningsgrunder för PFAS

Havs- och vattenmyndigheten har tagit fram förslag på nya bedömningsgrunder för PFAS.

Information om remissen

Förslaget gäller uppdatering av bedömningsgrunder för den särskilda förorenande ämnesgruppen per- och polyfluorerade alkylsubstanser PFAS i bilaga 2 (tabell 1 i avsnitt 7.2) och bilaga 5 (tabell 1 i avsnitt 4.2) i Havs- och vattenmyndighetens föreskrifter.

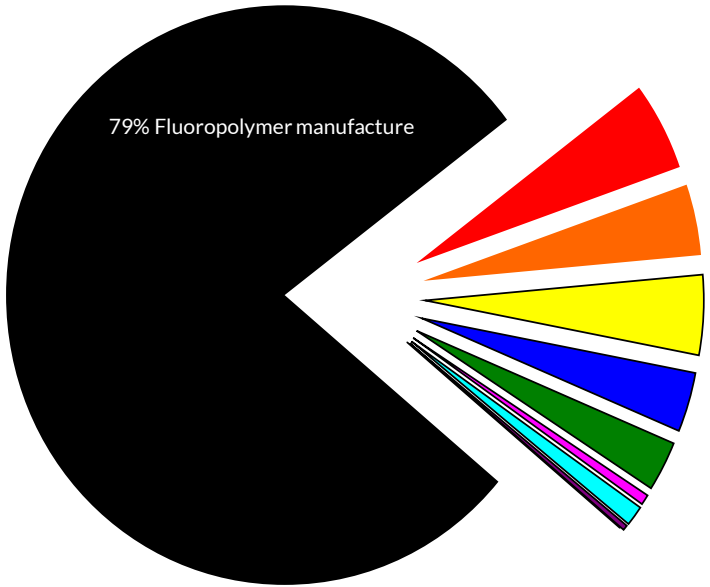
Remissen omfattar även vissa redaktionella justeringar i bilagorna 2, 5 och 6 i HVMFS 2019:25.

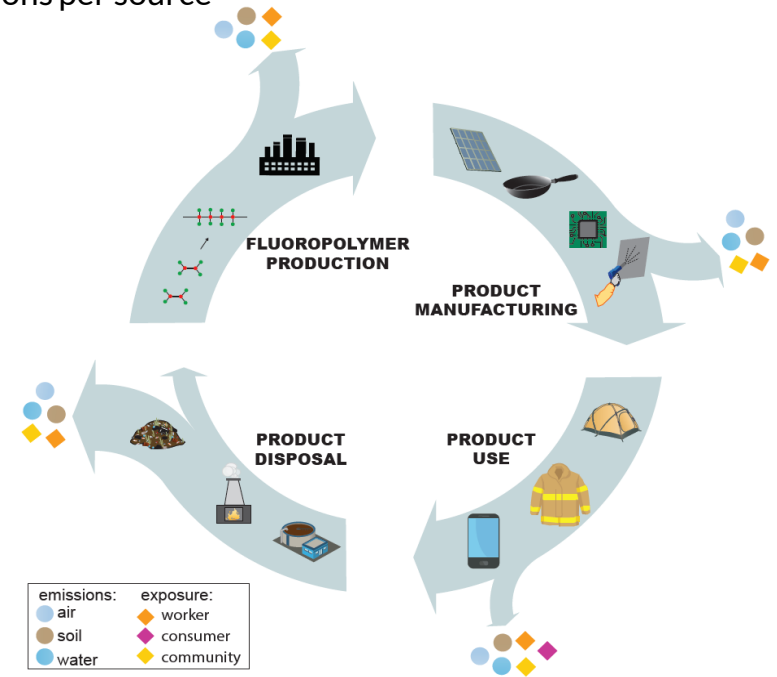
Föreskrifterna föreslås träda i kraft senast den 2025-03-03.

https://www.havochvatten.se/download/18.2abb1850192594111574ec30/1728487238990/remiss-pfas-2024-003213-bilaga-konsekvensutredning.pdf

Life-cycle perspective!!!

Percentage of total historical (1950-2004) global PFCA emissions per source





Prevedouros, Konstantinos, et al. "Sources, fate and transport of perfluorocarboxylates." Environmental science & technology 40.1 (2006): 32-44.
Lohmann, Rainer, et al. "Are fluoropolymers really of low concern for human and environmental health and separate from other PFAS?." Environmental Science & Technology 54.20 (2020): 12820-12828.

Where do we have PFAS?

Challenge for many companies right now

- Dialogue with suppliers
- Mapping potential use in articles, components and chemical products based on function
- PFAS-analysis

Good electric isolation properties
Electrochemical stability
Thermal stability
Flame retardancy – Melting properties
Chemical inertness
Weathering resistance
Hydrophobicity (water repellence)
Protection against corrosion
Oleophobicity (dirt/oil repellence)
Low friction and non-stick
Surfactant properties – Wetting – Smooth films

PFAS analysis

Targeted methods

- **Target-LC-MS/MS (e.g. $PFAS_4$, $PFAS_{21}$, $PFAS_{51}$)**
  - PFAS analysis of common substances such as perfluorocarboxylic acids (PFCAs) and sulfonic acids (PFSAs).
- **TOP** Assay (Total Oxidizable Precursor Assay)
  - PFAS analysis of common PFAS substances after oxidation that captures potential unmeasurable precursors to PFCAs och PFSAs. Method to capture for example PFOA-related substances.

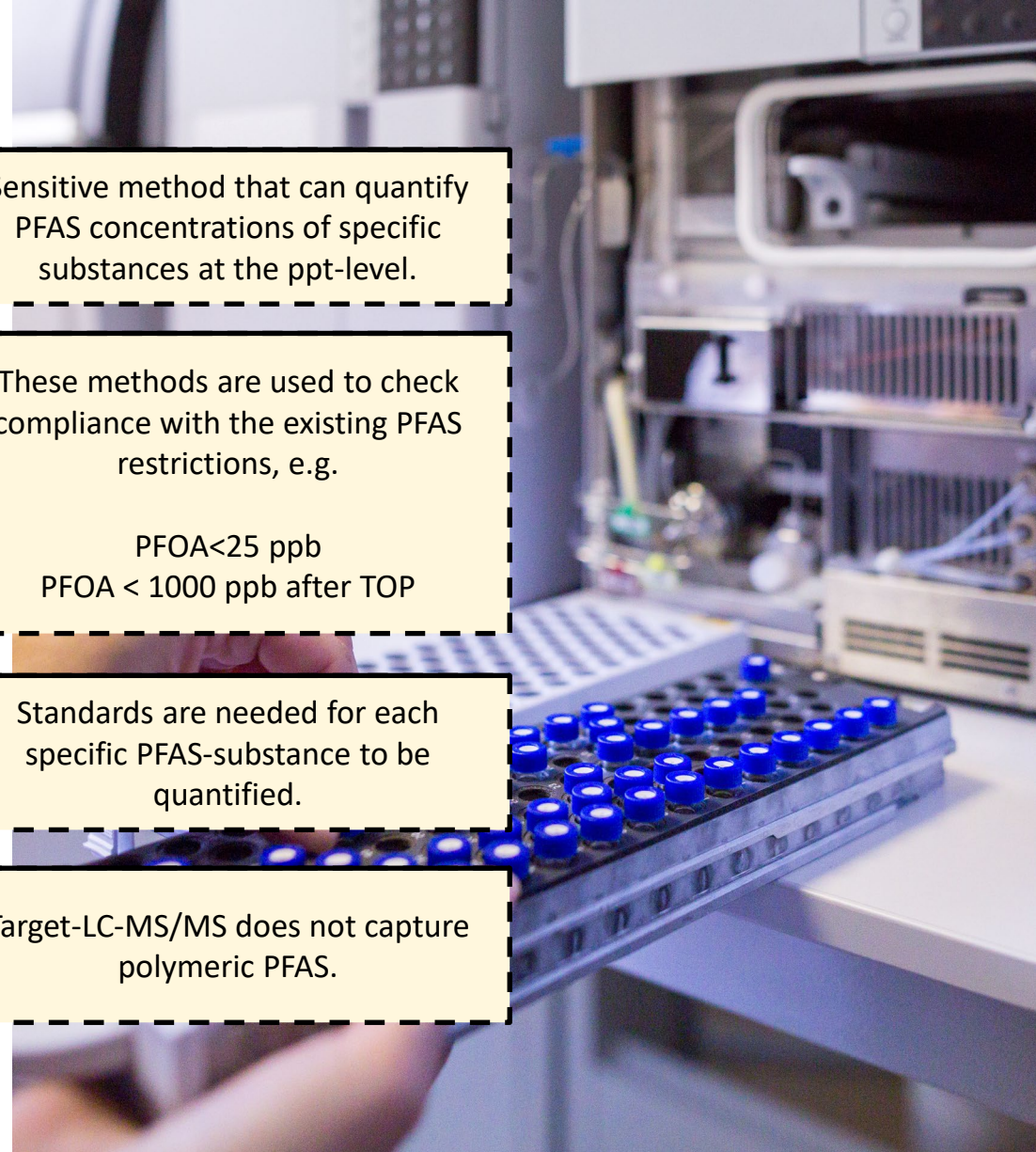
Sensitive method that can quantify PFAS concentrations of specific substances at the ppt-level.

These methods are used to check compliance with the existing PFAS restrictions, e.g.

PFOA<25 ppb
PFOA < 1000 ppb after TOP

Standards are needed for each specific PFAS-substance to be quantified.

Target-LC-MS/MS does not capture polymeric PFAS.



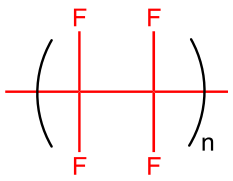
Polymeric PFAS

A macromolecule composed of many repeating subunits (monomers) for which one or more of the monomer units contains F, in the backbone and/or in the side chains

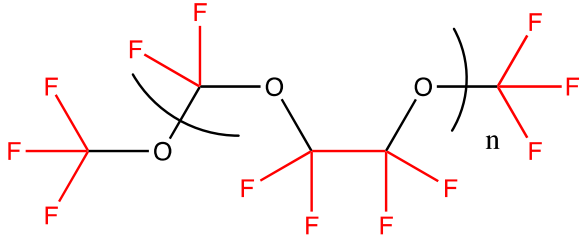
Many products contain polymeric PFAS when PFAS has been added to provide a function

Fluoropolymers

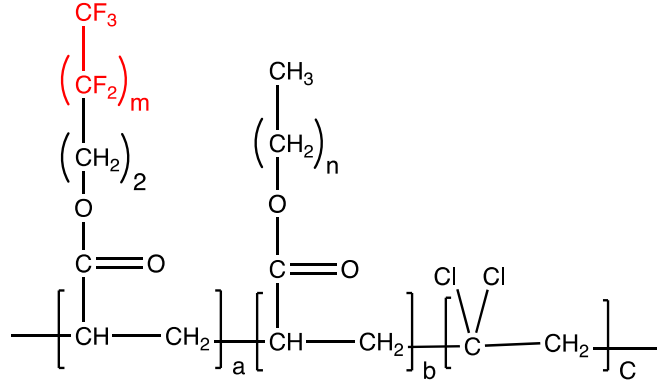
E.g. **PTFE**, ETFE, FEP, PFA, PVDF, FKM



Perfluoropolyethers

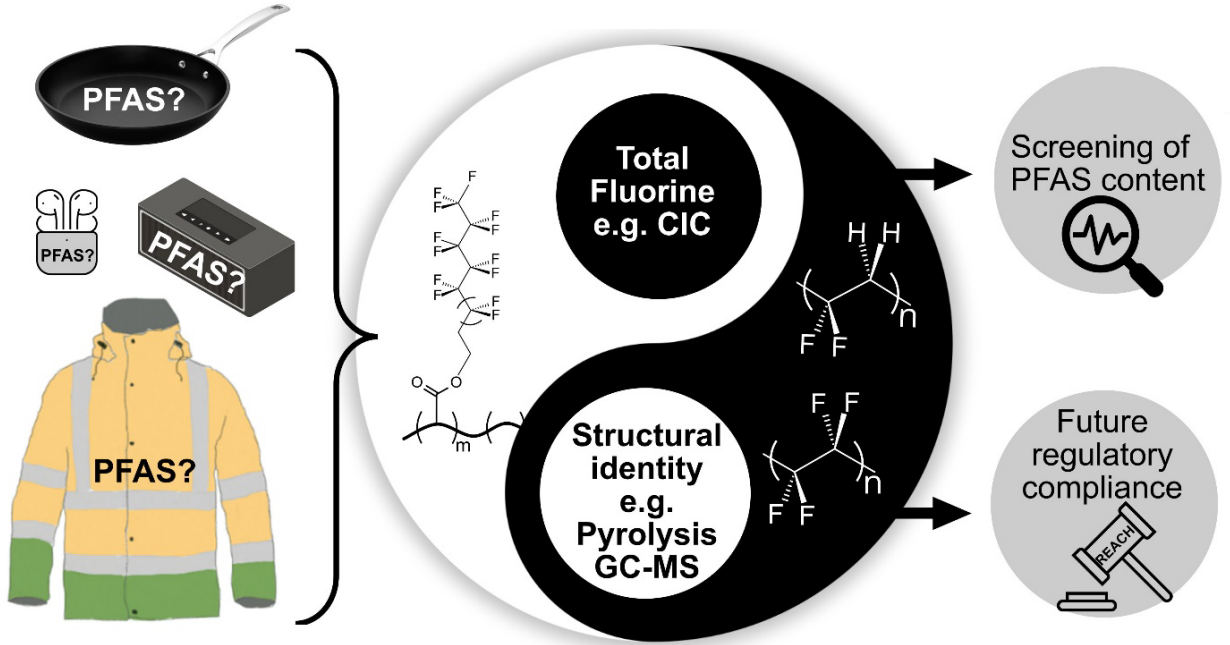


Side-chain fluorinated polymers



Analysis of PFAS in products

Combustion ion chromatography (CIC) and pyrolysis-GC/MS are two complimentary techniques



Both methods use direct thermal breakdown (no prior extraction step) and **capture polymeric PFAS.**

Skedung, L., Savvidou, E., Schellenberger, S., Reimann, A., Cousins, I. T., & Benskin, J. P. (2024). Identification and quantification of fluorinated polymers in consumer products by combustion ion chromatography and pyrolysis-gas chromatography-mass spectrometry. *Environmental Science: Processes & Impacts*, 26(1), 82-93.

A systematic workflow for PFAS-testing

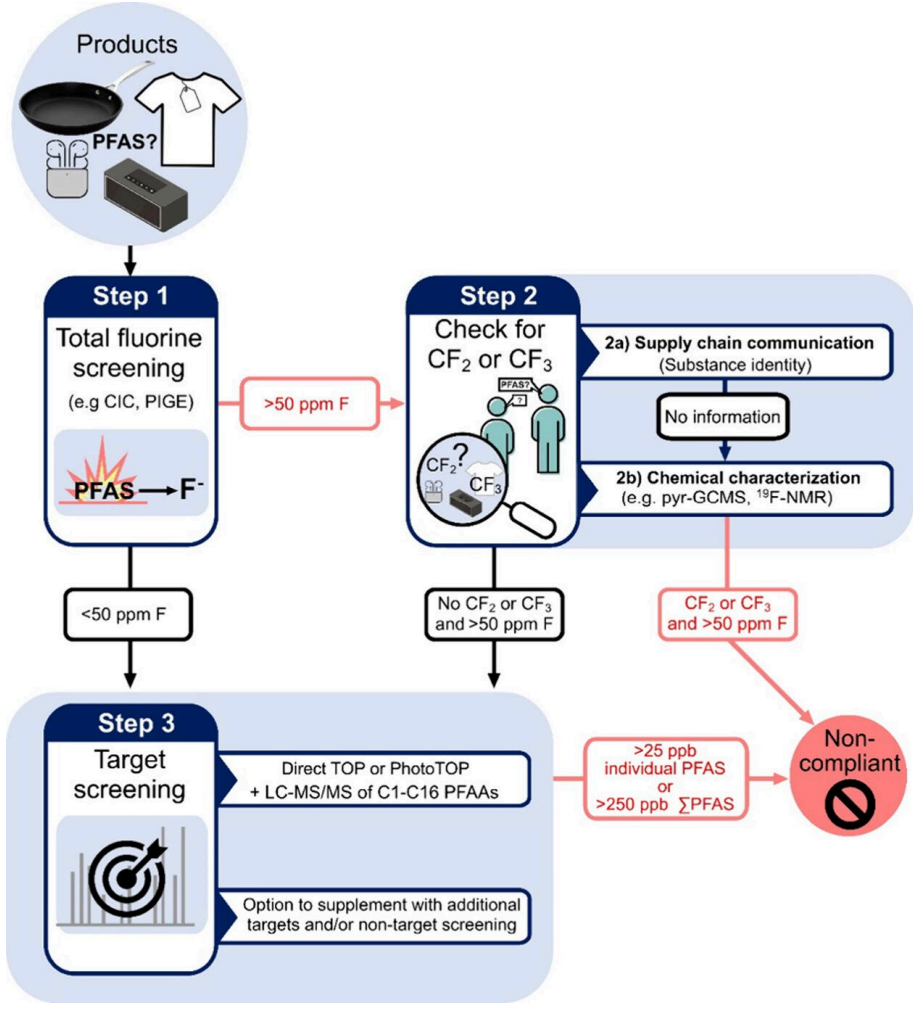
Environmental Science & Technology >
ASAP > Article

Open Access

VIEWPOINT | August 14, 2024

A Systematic Workflow for Compliance Testing of Emerging International Classwide Restrictions on PFAS

Robin Vestergren*, Anders Appelblom, Simona A. Bălan, Sicco H. Brandsma, Thomas A. Bruton, Ian T. Cousins, Jeremy R. Gauthier, Audun Heggelund, Jenny Ivarsson, Anna Kärrman, Lisa Melymuk, Chijioke Olisah, Amanda Rosen, Eleni K. Savvidou, Steffen Schellenberger, Lisa Skedung, Petteri Talasniemi, Tonie Wickman, Jonathan Zweigle, Christian Zwiener, and Jonathan P. Benskin*



Vestergren, R., Appelblom, A., Bălan, S. A., Brandsma, S. H., Bruton, T. A., Cousins, I. T., ... & Benskin, J. P. (2024). A Systematic Workflow for Compliance Testing of Emerging International Classwide Restrictions on PFAS. *Environmental Science & Technology*, *58*(34), 14968-14972.

PFAS restriction proposal

PFAS shall not be manufactured, used or placed on the market as substances on their own; nor not be placed on the market in another substance, as a constituent; in a mixture, or in an article in a concentration of or above:

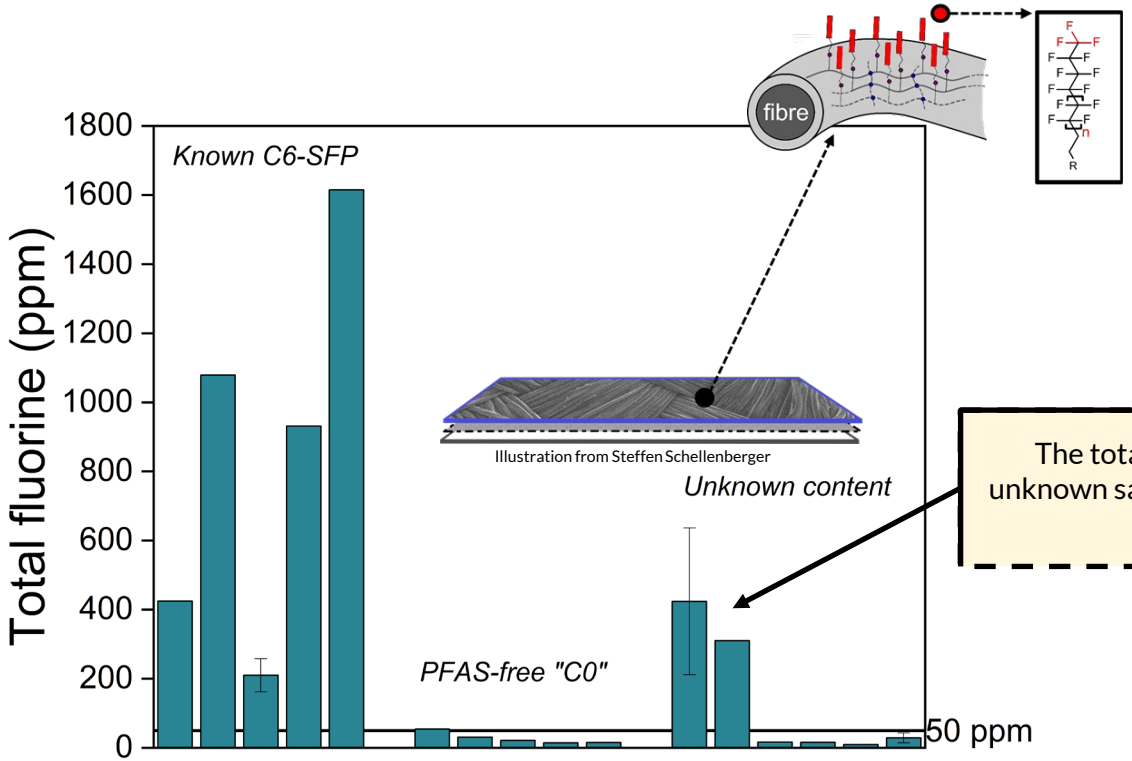
- 25 ppb for any PFAS
- 250 ppb for the sum of PFASs
- **50 ppm for PFASs (polymeric PFASs included)**
  If total fluorine exceeds 50 mg F/kg the manufacturer, importer or downstream user shall upon request provide to the enforcement authorities a proof for the fluorine measured as content of either PFASs or non-PFASs.

Also applies to imported goods and recycled materials!

Link to PFAS restriction proposal

Total fluorine in textile samples

The 50 ppm level in the restriction proposal makes sense



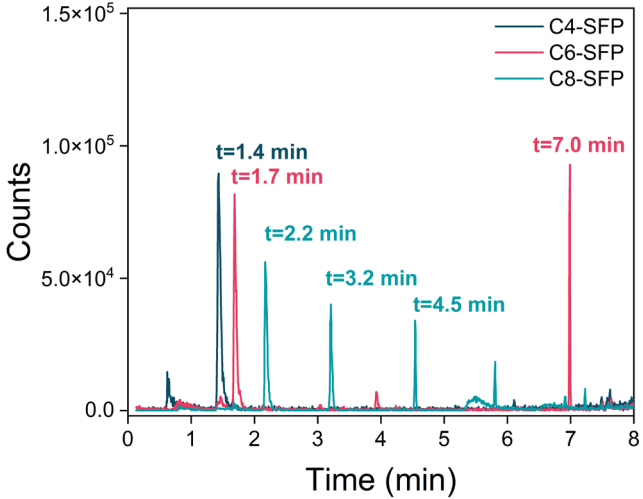
PFAS-containing textile impregnation consist of **side-chain fluorinated polymers (SFPs)** where the side-chains with 4, 6 or 8 fluorinated carbons provide water and dirt repellence.

The total fluorine concentrations in the unknown samples indicate intentionally added PFAS in two articles.

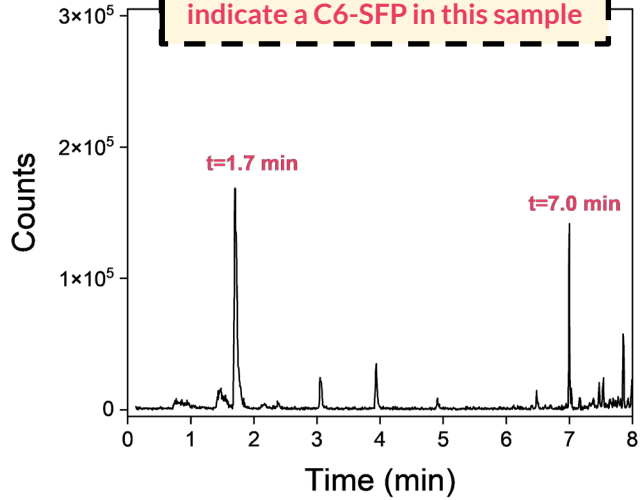
Pyrolysis-GC/MS for verification

The fluorinated side-chain is kept intact during pyrolysis, providing structural information

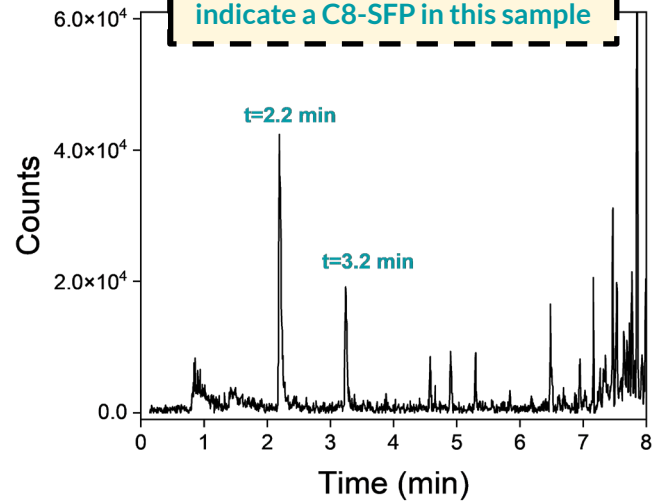
Reference textiles



The retention times of PFAS-fragments in the ion chromatogram and corresponding mass spectra indicate a C6-SFP in this sample



The retention times of PFAS-fragments in the ion chromatogram and and corresponding mass spectra indicate a C8-SFP in this sample



PFAS in 57% of the PPE articles

Total fluorine (TF) concentrations in 13/23 articles in the range 65 ppm - 1450 ppm

16 commercial workwear garments

TF>50 ppm

10 garments

7 work shoes/boots

TF>50 ppm

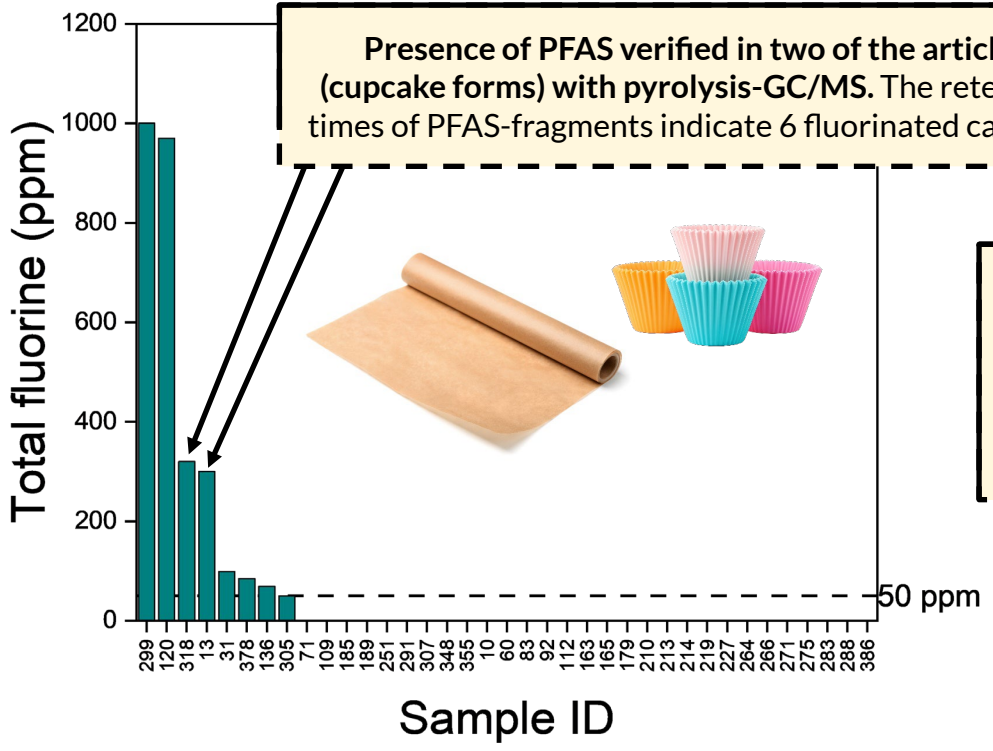
3 shoes

Presence of PFAS was verified in the 13 articles with pyrolysis-GC/MS.

C6-SFP was found in 10 of the articles and C8-SFP was found in 3 of the articles.

PFAS in 5% of the analysed articles

Total fluorine (TF) concentrations of 8/37 articles in the range 50 ppm - 1000 ppm



Presence of PFAS verified in two of the articles (cupcake forms) with pyrolysis-GC/MS. The retention times of PFAS-fragments indicate 6 fluorinated carbons.

Presence of PFAS could not be verified with pyrolysis-GC/MS in the other samples with a TF-concentration > 50 ppm indicating inorganic source of fluorine (e.g. mica).

Comparison different methods

Possible underestimation of PFAS with target analysis

All units in ppb (parts per billion)

Method	Sample A	Sample B	Proposed regulatory threshold
∑PFAS22 (LC-MS/MS)	15	150	250
∑PFAS22 (LC-MS/MS) after oxidation (TOP)	28 400	500	250
Total fluorine (CIC)	1 450 000	275 000	50 000 (50 ppm)

Method	299	120	318	13	31	378	136	305	71	109	185	189	251	291	307	348	355
∑PFAS22 (LC-MS/MS)	1.3	1.0	49	5.0	2.4	1.7	28	0.79	34	1.5	0.7	0.05	0.11	54	2.1	1.6	0.43
∑PFAS22 (LC-MS/MS) after oxidation (TOP)			17 000	20 700					5.5					210			
Total fluorine (CIC)	1 000 000	970 000	320 000	300 000	100 000	85 000	70 000	50 000									

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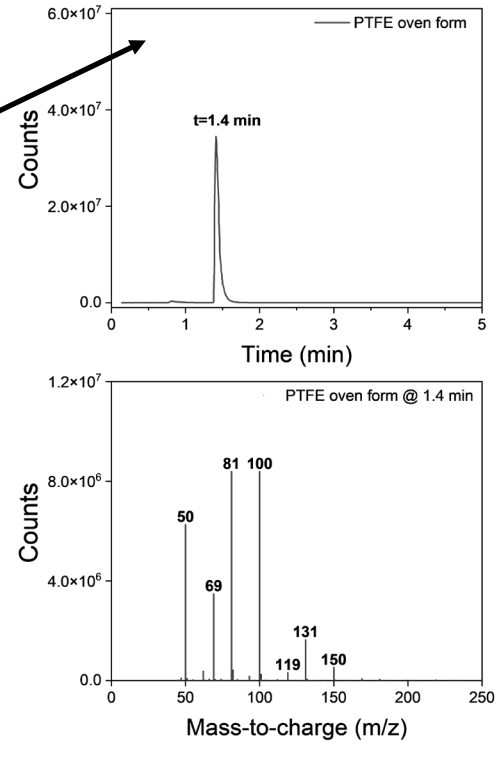
These were the two samples where PFAS-chemistry was verified with pyrolysis-GC/MS.

Detection of flouropolymers

Total fluorine quantification and verification with pyrolysis-GC/MS

Sample	Total fluorine (ppm)	Verification with pyrolysis-GC/MS
Dental floss	600 000	PTFE
Non-stick bake form	550 000	PTFE
Air fryer	23 000	Alternative main coating but we also found PTFE
Ceramic frying pans		Have found both with and without PFAS-chemistry
Bike lube	4000	PTFE
Electronic plastic and battery cases	1500	PTFE
Paint	400	PTFE
Paint	166 000	PVDF
Black mass from battery	700	PVDF
Cable		ETFE



Concluding remarks

- Many products now have PFAS-free solutions, but legislation is needed to eliminate PFAS in non-essential uses and to further boost innovation.
- Direct thermal breakdown is crucial for detecting polymeric PFAS. Traditional target analysis often underestimates PFAS content in articles and chemical products.
- The proposed PFAS-testing workflow is effective across various products.
- Pyrolysis-GC/MS complements total fluorine quantification, confirming the organic nature of fluorine (PFAS) and distinguishing different polymeric PFAS.
- Analysis should be conducted at the component level in complex products.

Thank you!

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