IPCP Webinar Series: POPs in plastic and monitoring approaches

Part II: Sampling of plastics from major sectors to monitor POPs in plastics; 19.5.2023

Monitoring of PFAS in products & recycling including screening methods for fluorine in plastics, side-chain fluoropolymer coatings and other materials

Dr. Roland Weber
POPs Environmental Consulting, IPCP
73527 Schwäbisch Gmünd, Germany
https://www.researchgate.net/profile/Roland-Weber-2
https://scholar.google.com/citations?user=-Cexto4AAAAJ&hl=en

IPCP International Panel on Chemical Pollution

UN environment programme

gef

34 POPs listed in the Stockholm Convention (05/2023)

Chemical	Pesticides	Industrial chemicals	Unintentional production	Annex
DDT	+			B
Aldrin, Dieldrin, Endrin, Chlordane, Chlordecone, Toxaphene	+			A
Alpha-, Beta-, Gamma-HCH	+			A
Endosulfan, Heptachlor, Mirex	+		By-product of lindane	A
Pentachlorophenol (PCP), *Dicofol*	+			A
	+	+		A
Commercial PentaBDE		+		A
Commercial OctaBDE (Hexa/HeptaBDE)		+		A
Commercial DecaBDE		+		A
Hexabromobiphenyl (HBB)		+		A
Hexabromocyclododecane (HBCD)		+		A
PFOS, its salts and PFOSF	+	+		B
PFOA and related compounds		+		A
PFHxS and related compounds		+		A
Short chain chlorinated paraffins		+		A
PCB, PeCBz, HCB, PCN, *HCBD*	+	+	+	A/C
PCDD, PCDF			+	C

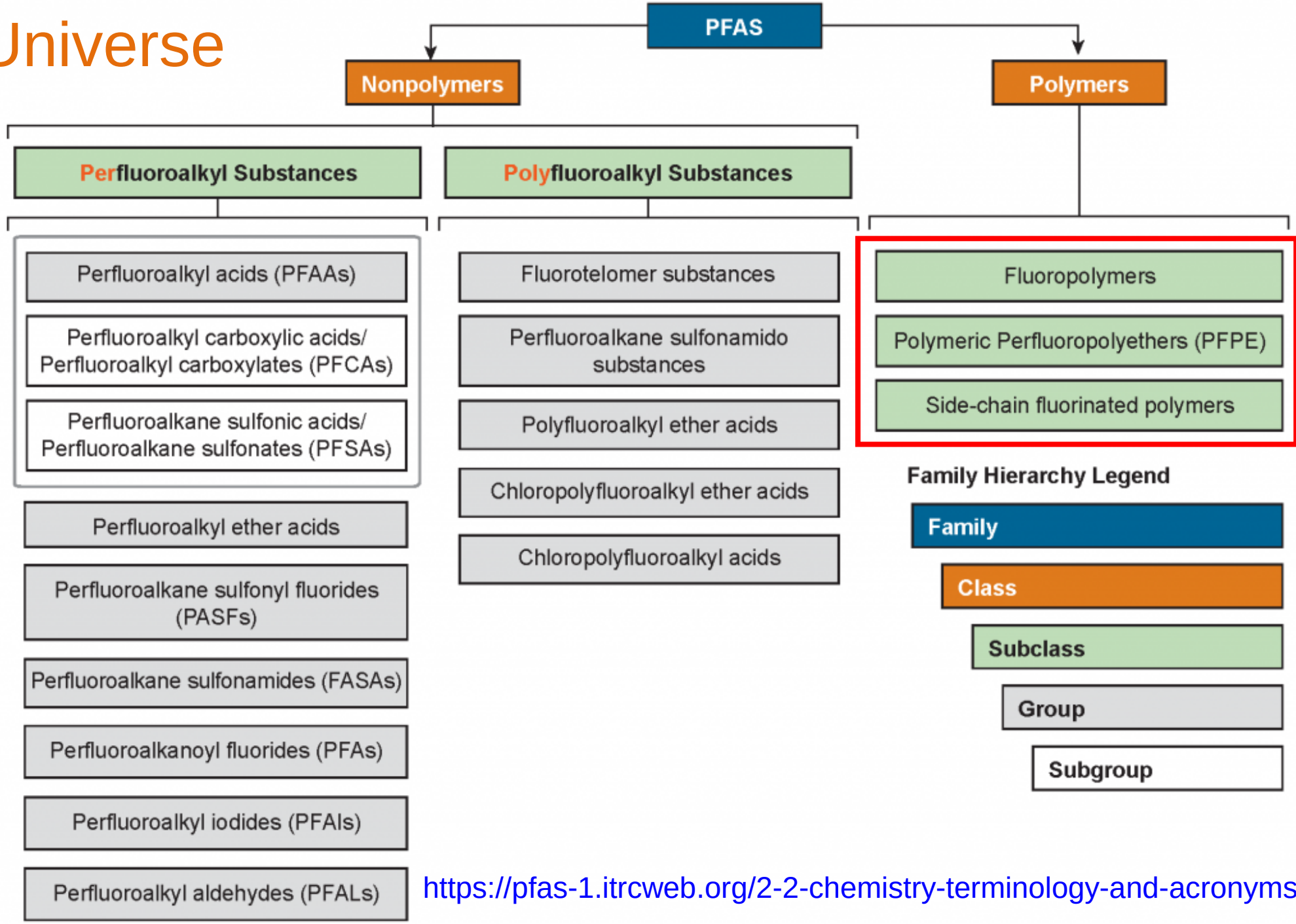
Three groups of perfluoroalkyl and polyfluoroalkyl substances (PFASs) have been listed in the Stockholm Convention with hundreds of „related compounds“ which mean precursor chemicals.

A large volume of these precursor chemicals are side-chain fluorinated polymers.

The detailed link between listed PFAS and polymers & plastic has been described by Prof. Ian Cousins in the webinar 24 April where you can watch recordings on the IPCP website.

POP Review Committee: Chlorpyrífos, MCCP, LC-PFAA **COP11 listed:** Methoxychlor; **UV328, Dechlorane Plus**

The PFAS Universe



Prof. Ian Cousins,
IPCP Webinar 24. April

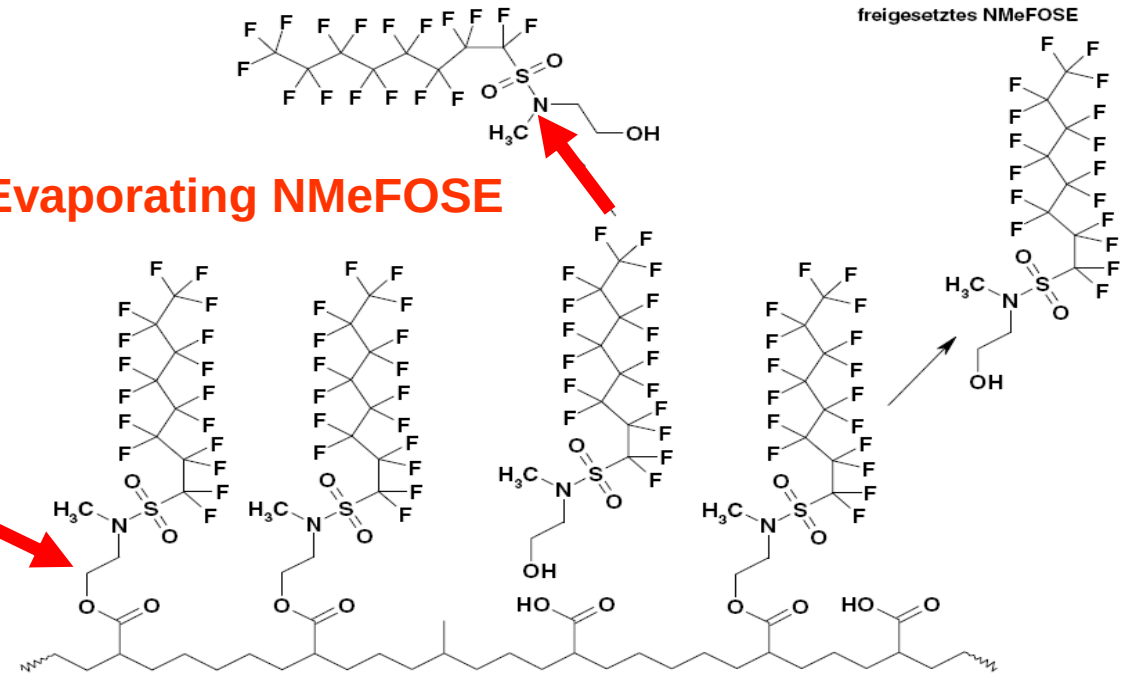
https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms

Polymeric PFAS

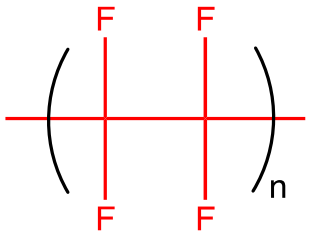
side-chain fluorinated (SCF) polymers

- Polymers
  - Fluoropolymers
  - Perfluoropolyethers (PFPE)
  - Side-chain fluorinated polymers

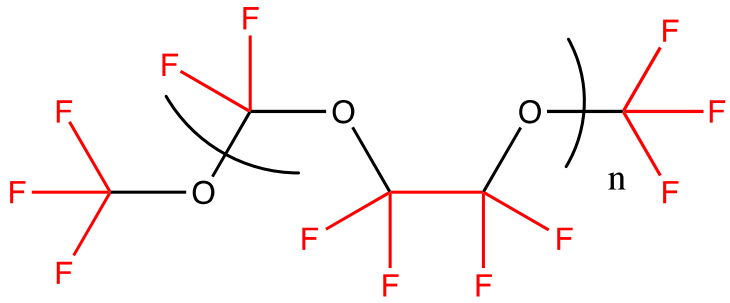
Fluorinated polymers = all polymers for which one or more of the monomer unit contains F, in the backbone and/or in sid chains (Buck et al., 2011), including

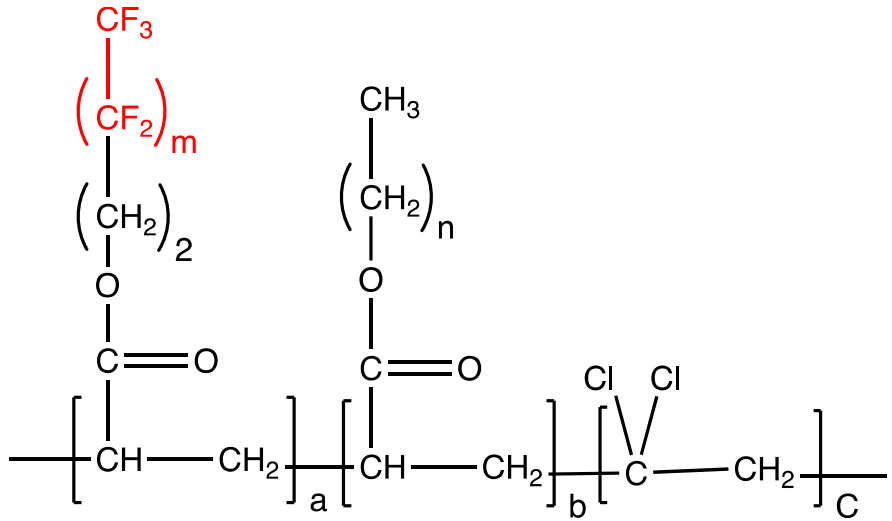


fluoropolymers



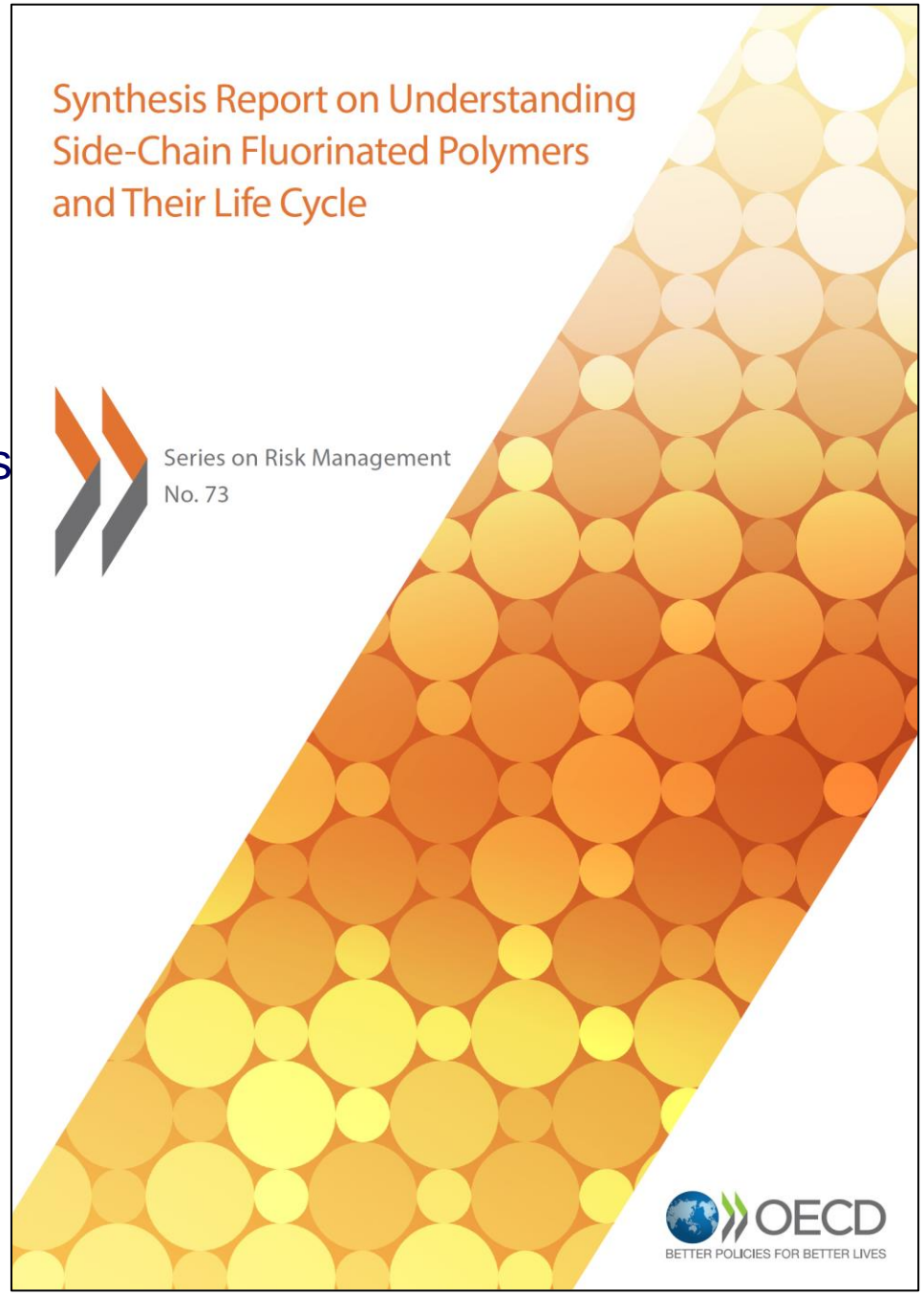
perfluoropolyethers





POPs PFAS used in high volumes in side-chain fluorinated polymers

- Side-chain fluorinated (SCP) polymers are defined as polymers with a non fluorinated polymer backbone and with PFAS moieties on the side chain(s).
- A non-exhaustive list of 103 SCF polymers 42 PFAS monomers in an OECD report (2022) with different polymer backbone
    - acrylates, urethanes, oxetanes, ethoxylates, etc.
    - Often exact structures cannot be identified



OECD (2022), Synthesis Report on Understanding Side-Chain Fluorinated Polymers and Their Life Cycle, OECD Series on Risk Management, No. 73,Environment, Health and Safety, Environment Directorate, OECD

Former PFOS Consumption in the European Union

Historically, many **SCF polymer containing *long-chain* PFAS** on the side chains were produced in high amounts on the scale of thousands of tonnes or more per annum which were at least one order of magnitude higher than the production of many non-polymeric PFASs like firefighting foams (OECD 2022)

Many long-chain SCFPs have been replaced by short-chain ones, while some long-chain ones may still be used (details are unknown due to confidentiality) (OECD 2022)

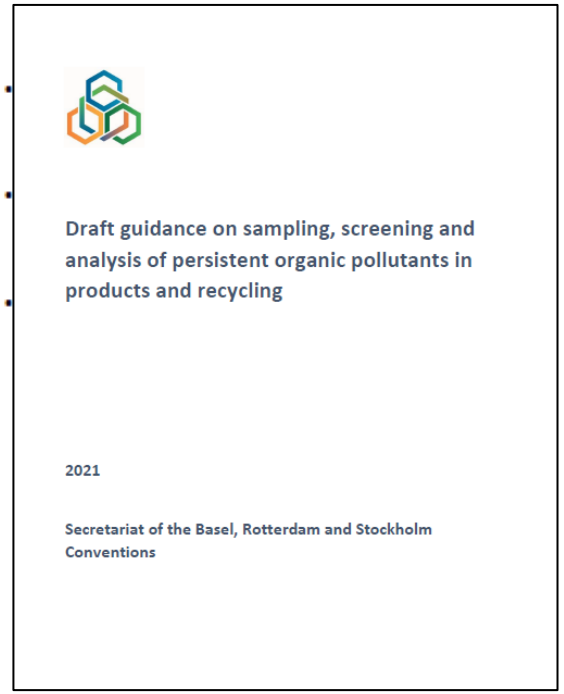
Estimated yearly use sectors of PFOS in the EU (2000)

Industrial application	EU consumption (Tonnes/year)	PFOS & PFOS-related chemical
Verchromung **Plating**	10	PFOS, FOSE
Fotolithografie	0,47	
Fotografie	0,85	FOSAAcOH
Photographic use	0,75	Polymer
Luftfahrt **Aviation**	0,73	Perfluorsulfonate
Feuerlöschmittel **AFFF**	0,57	FOSA
Faserveredelung **Fiber coating**	240	FOSE-Polymere
Papierveredelung **Paper**	160	FOSE-Polymere
Beschichtung **Polymersurface**	90	

Source: Risk and Policy Analysts (2004); Fricke & Lahl, UWSF 17, 36 – 49 (2005)

Step by step approach for monitoring (POPs-) PFASs in products and recycling

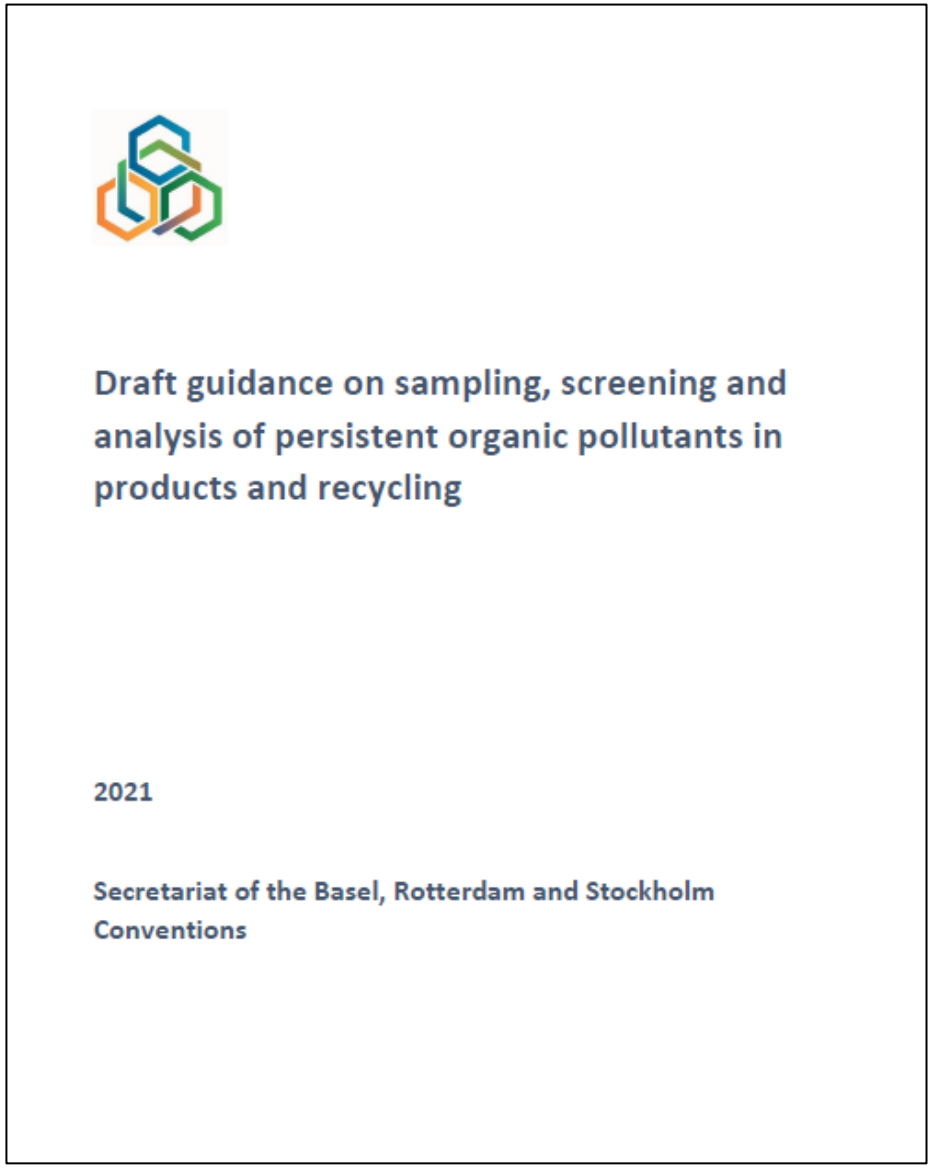
The monitoring guidance has a step by step approach to monitor POPs in articles and products and these steps are elaborated for the major POPs groups.



Step by step approach for monitoring (POPs-)PFAS in products and recycling

Step 1: Survey of products and articles possibly containing POPs-PFASs

- Before collecting samples, a survey would be conducted to preliminarily determine target presence of consumer products **in use, and in re-use that might contain POPs-PFAS.**
- Also material flows known to possibly contain POPs-PFAS and further used **in recycling** should be evaluated. For this the main former use of PFOS, PFOA, PFHxS and related substances need to be considered.
- Within this assessment also evaluation how much is in plastics/polymer related uses, in particular in SCF-polymers and has been formerly used.



Former PFOS Consumption in the European Union

Historically, many SCFPs containing *long-chain* PFAS on the side chains were produced in high amounts on the scale of thousands of tonnes or more per annum (OECD 2022)

Synthetic carpets (nylon) had the largest PFOS reservoir in German PFOS inventory. Synthetic carpets can have long service life and carpets are reused and recycled!

Estimated yearly use sectors of PFOS in the EU (2000)

Industrial application	EU consumption (Tonnes/year)	PFOS & PFOS-related chemical
Verchromung **Plating**	10	PFOS, FOSE
Fotolithografie	0,47	
Fotografie	0,85	FOSAAcOH
Photographic use	0,75	Polymer
Luftfahrt **Aviation**	0,73	Perfluorsulfonate
Feuerlöschmittel **AFFF**	0,57	FOSA
Faserveredelung **Fiber coating**	240	FOSE-Polymere
Papierveredelung **Paper**	160	FOSE-Polymere
Beschichtung **Polymersurface**	90	

Source: Risk and Policy Analysts (2004); Fricke & Lahl, UWSF 17, 36 – 49 (2005)

End of life management of carpets – exposure risk with reuse/repurpose

By recycling of carpets containing PFAS or flame retardants exposure can continue & increase.

Suggestions to consumers to repurpose/recycle carpets on internet platforms:

- **Reuse of carpet in garden or allotment** "*Carpet can be used to reduce weeds in your garden or allotment*". **PFAS** can be **released** to the **garden** and **accumulate** in **fruits** and **vegetables**.
- **Upcycled Carpet Compost Insulation** "*Old carpet is perfect for keeping your compost insulated. Carpet over the top of your compost bin will keep it plenty warm in the winter time*." Risk: PFAS can be released to the compost/garden and accumulate in fruits and vegetables.
- "***Upholstered headboard*** *of* ***bed*** *or* ***pillow*** *cover*". Increased exposure to chemicals in carpets.

https://www.diyncrafts.com/28151/repurpose/20-brilliant-carpet-repurposing-ideas-will-astound

High exposure risk! Study supported by California EPA stressed the risk of such carpet recycling and reuse

Investigating PFAS Removal Strategies During Carpet Recycling: A Greener Solutions Approach

DTSC Department of Toxic Substances Control

School of Public Health

Textiles of tents – hazardous chemicals, recycling and increased risk

- **Tents** can be treated with **PFASs** to repel water **and with hazardous flame retardants** to reduce fires risk. Hence care is needed in the end-of-life management of tent fabrics.

However suggestion to consumers to repurpose/recycle tent fabric on internet platforms:

https://cleaning-hacks.sharkclean.co.uk/15-ways-to-recycle-your-old-festival-tent/

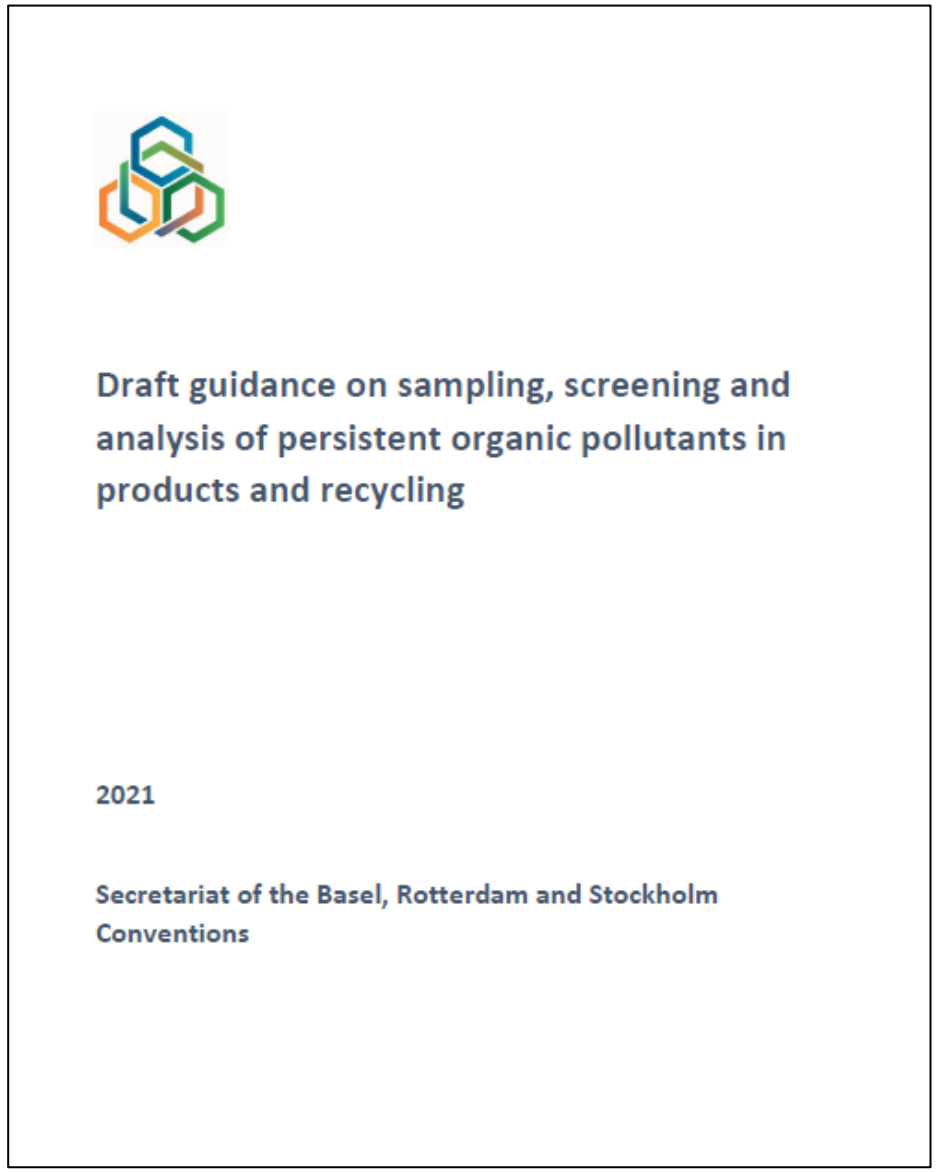
- ***"Line your child's school bag"***
- ***"Arts and crafts:*** *Cut old tent up for arts and crafts.* ***Let children express their artistic flair."***
- ***"As groundsheets.*** *Rather than restricting your child's access to carpeted areas, use tent as a groundsheet. Tent fabric is a perfect barrier between kids and carpeting."*
- ***"Make a table protector****: If you're draping a table cloth, tent fabric is a good waterproof barrier underneath is. is and great at protecting wooden tables from spillages."*
- ***"Mattress protector****: Nothing degrades a mattress more quickly than moisture. Fit your old festival tent fabric to your mattress before you fit the first sheet."*
- ***Storage sacks****: for long-term storage or packed lunches.*

High exposure risk which should be assessed and avoided! No monitoring study published!!

Step by step approach for monitoring (POPs-)PFAS in products and recycling

Step 1: Survey of products and articles possibly containing POPs-PFAS

- The **large amount of PFOS and PFOA in SCF-polymers result in the need to monitor in particular carpets, textiles, paper and related recycling as well as reuse of carpets & other PFAS-treated textiles.**
- Stakeholders for the different use groups might be contacted for support and input and possibly for providing samples. Relevant stakeholders to be contacted for the different use categories are listed in the Stockholm Convention PFOA/PFOS inventory guidance.



Step-approach for monitoring POP-PFAS in products & recycling

Step 2: Sample collection

- Sampling campaigns might be conducted by research institutions possibly in collaboration with the ministry or other competent authorities or directly with the industry or waste management facilities.
- Samples can also be collected e.g. by the customs at the import or by competent authorities such as factory control or consumer protection authorities and related institutions.

ANNEX 1 compiles selected products and recycling streams which can contain industrial POPs

- Annex 1-A contain information on PFOS, PFOA, PFHxS and related compounds in products and recycling

Step-approach to monitor POP-PFAS in products and recycling

Step 2: Survey of products and recycling possibly containing PFOS/PFOA and related compounds

Following criteria and information may be used:

a) The product contains PFOS, PFOA or related compounds identifiable by the chemical names, CAS numbers or if their structural formulas contain more than three fluorine atoms; or

b) The product contains fluorinated chemicals identifiable by their trade names; or

c) Products potentially containing PFOS/PFOA or related compounds compiled in Annex 1-A; or

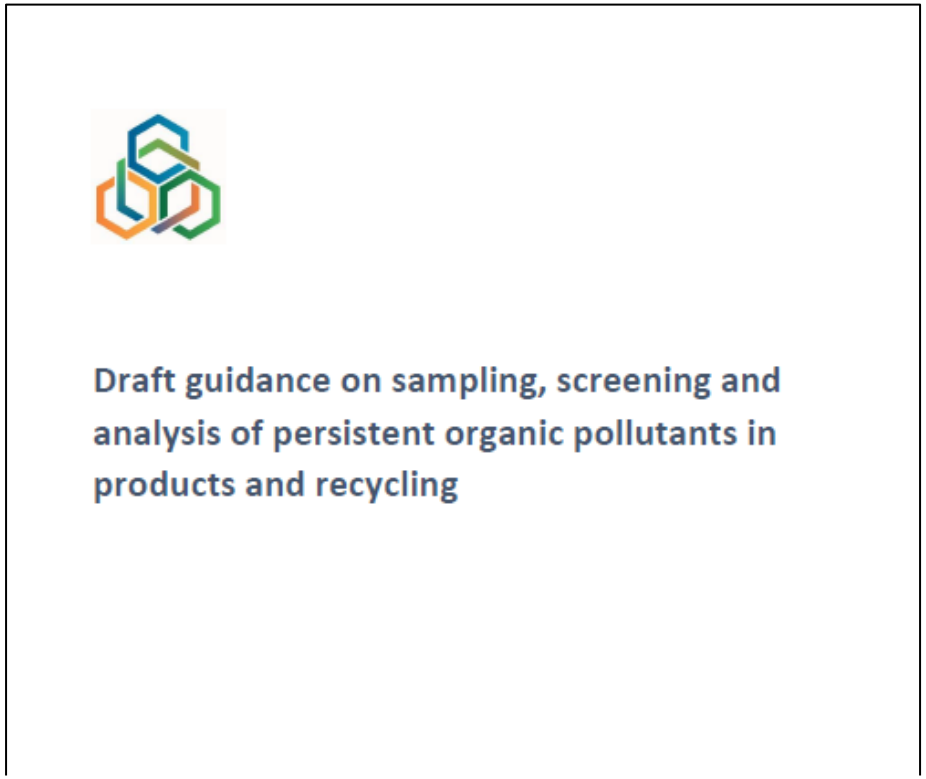
d) The product was identified as having certain properties that are common for products treated with PFOS, PFOA and its related compounds (e.g., stain resistant, water repellent and anti-grease), as can be identified with e.g., the droplet test (Section 3.4.2).

Step-approach for monitoring POP-PFAS in products & recycling

Step 2: Sample collection

ANNEX 2 best practice case studies for screening POPs in products and recycling

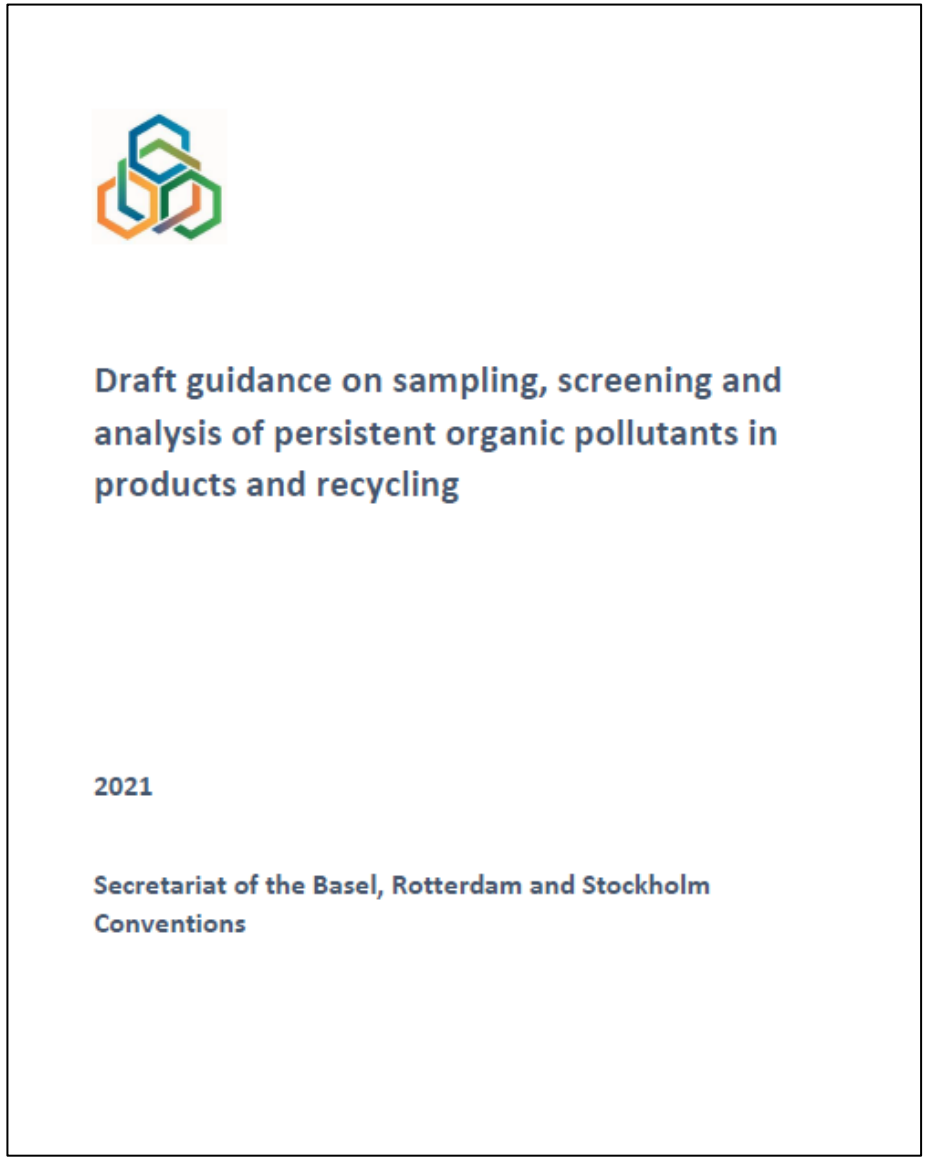
- Annex 2-A compiles best practice case studies forscreening PFOS, PFOA, and related compounds in products and in recycling.



Step-approach for monitoring POP-PFAS in products & recycling

Step 3: Screening in the field or laboratory:

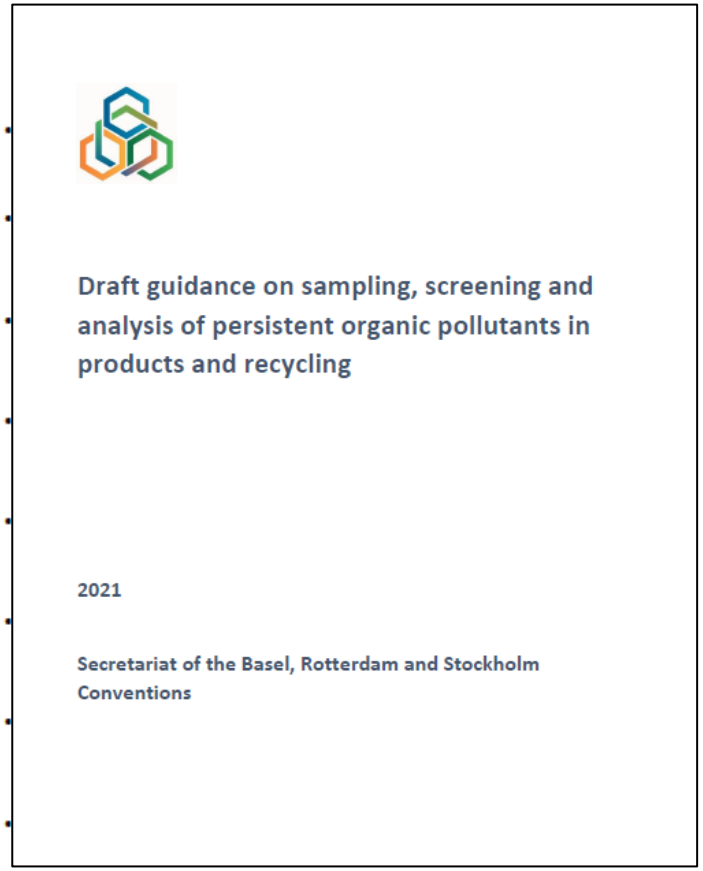
- The guidance gives an introduction to screening approaches. **This includes screening technologies for fluorine** (and bromine and chlorine).
- Screening helps to minimise the time and expenses (by pre-selection of samples) for confirmation analysis, which requires laborious extraction and appropriate clean-up steps.
- **Such screening enables relatively cheap and simple pre-selection of products with regards to their possible (POP-)PFAS content (e.g. carpets, textiles, paper) with fluorine as indication for PFAS including SCF polymers potentially containing PFOS in older products produced before 2013 or PFOA and PFHxS and related compounds used until recently or still used in these applications).**



Screening of fluorine as indicator for PFAS in products

Step 3: Screening of fluorine in the field or laboratory – available technologies

A range of screening technologies for fluorine/organofluorine have been compiled in the Stockholm Convention monitoring guidance.



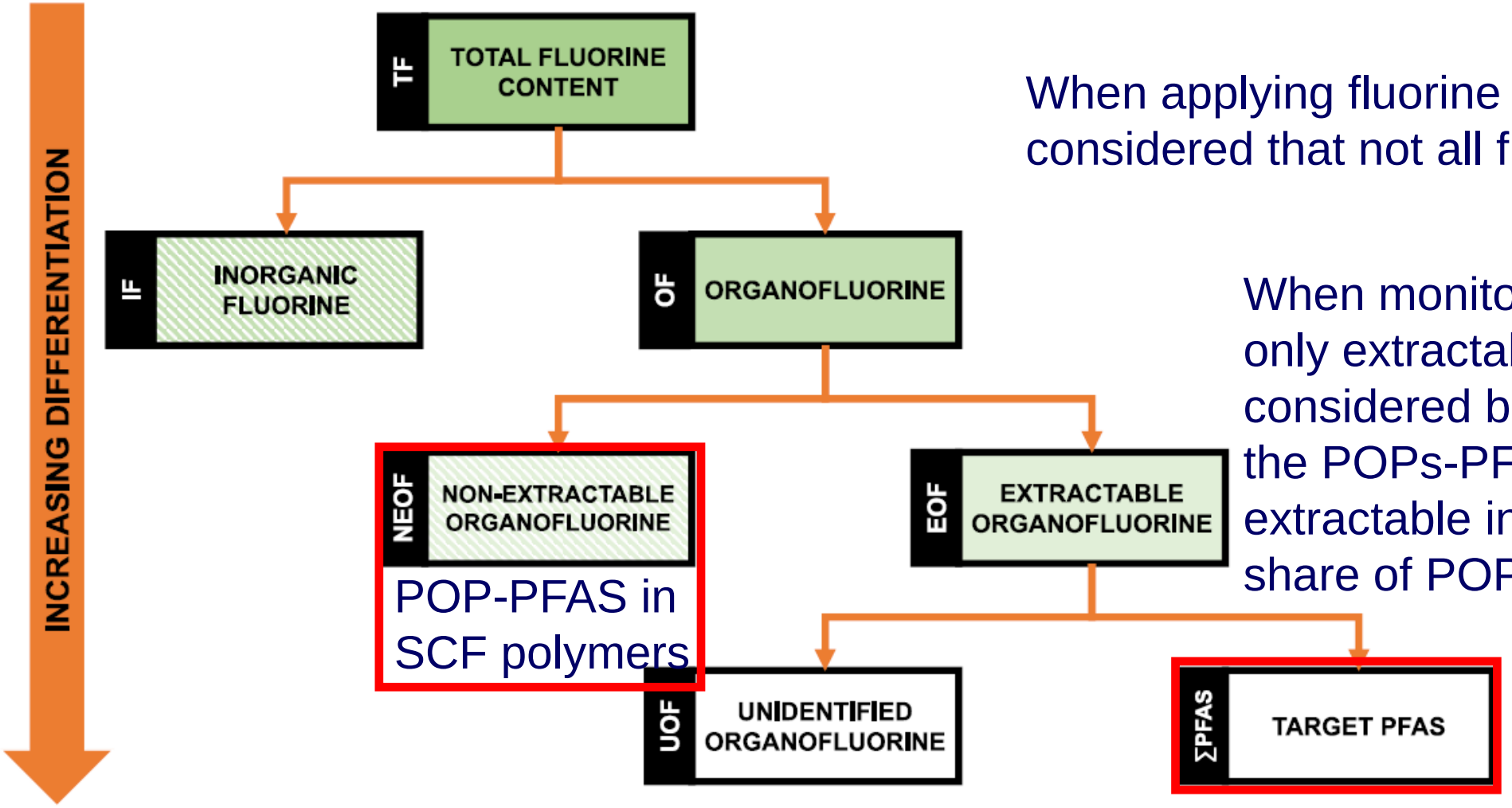
Draft guidance on sampling, screening and analysis of persistent organic pollutants in products and recycling

2021

Secretariat of the Basel, Rotterdam and Stockholm Conventions

Screening of fluorine as indicator for PFAS in products

Step 3: Screening of fluorine in the field or laboratory



When applying fluorine screening it needs to be considered that not all fluorine stems from PFAS

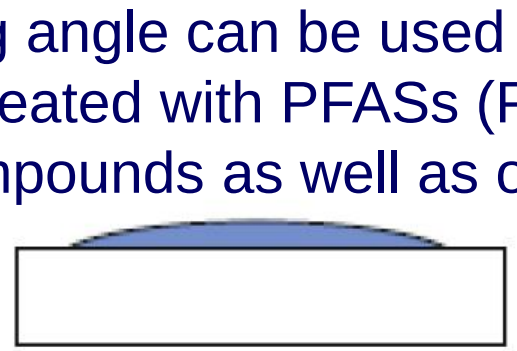
When monitoring for POP-PFASs not only extractable PFAS need to be considered but that a high share of the POPs-PFAS might not be extractable in products due to a high share of POP-PFAS in SCF polymers

Aro et al. (2021). *Iscience*, *24*(9), 102968.

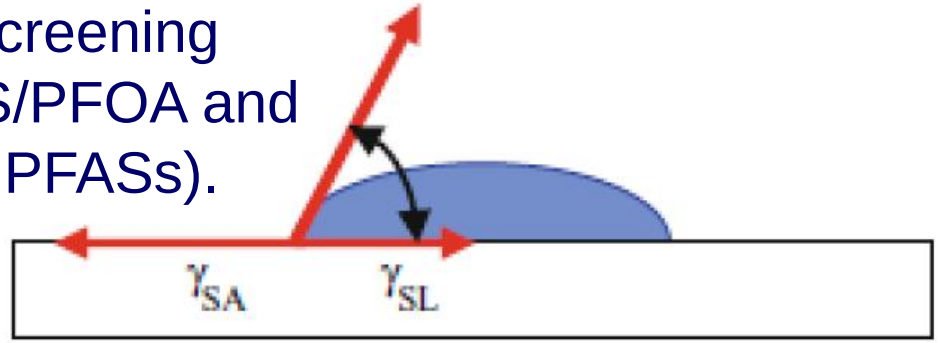
Screening methods as indicator for fluorine or organofluorine

Screening in the field or laboratory – Droplet test

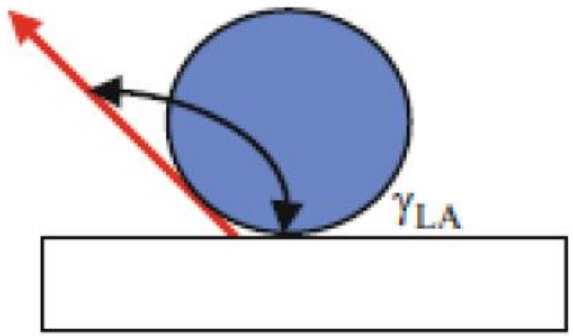
- When PFOS/PFOA and related compounds (or other PFASs) are coated on a textile/carpet substrate and exposed to water (surface tension of 72 mN/m) or oily substances (surface tensions 20 mN/m and more), they will not spread on the surface. Similarly, also for other surface like paper coated with side-chain fluoropolymers. This phenomenon is called “water and oil repellence” and used for water, oil and stain protection of carpets, textiles or leather.
- **Most alternatives cannot achieve a surface energy lower than 22 mN/m, the surface energy for oil. Materials with a high contact angle and low surface energy are therefore likely treated with fluorinated substances**. **Fluorinated surfaces can be distinguished from non-fluorinated surface treatments if both a droplet of water and a droplet of oil put on the surface form drops**. If only the oil droplet flattens out, the surface is likely treated with a non-fluorinated chemical (hydrocarbon surfactant or a silicone coating).
- The wetting angle can be used for screening materials treated with PFASs (PFOS/PFOA and related compounds as well as other PFASs).



$\Theta = 0^{\circ}$ Perfectly Wettable



$\Theta < 90^{\circ}$ +/- Wettable



$\Theta > 90^{\circ}$ Unwettable

Screening methods as indicator for fluorine or organofluorine

Screening in the field or laboratory – Droplet test case studies

The water/oil drop test was performed in the PFOS inventory of Suriname for screening water/oil repellency of synthetic carpets in stores. Most synthetic carpets tested showed repellency properties (droplet angle >90°).

Contents lists available at ScienceDirect

Ke Ai
ADVANCING RESEARCH EVOLVING SCIENCE

Emerging Contaminants

journal homepage: http://www.keaipublishing.com/en/journals/emerging-contaminants/

https://doi.org/10.1016/j.emcon.2020.10.002

Inventory and action plan for PFOS and related substances in Suriname as basis for Stockholm Convention implementation

Victorine Pinas [a], Carmen Van Dijk [b], Roland Weber [c, *]

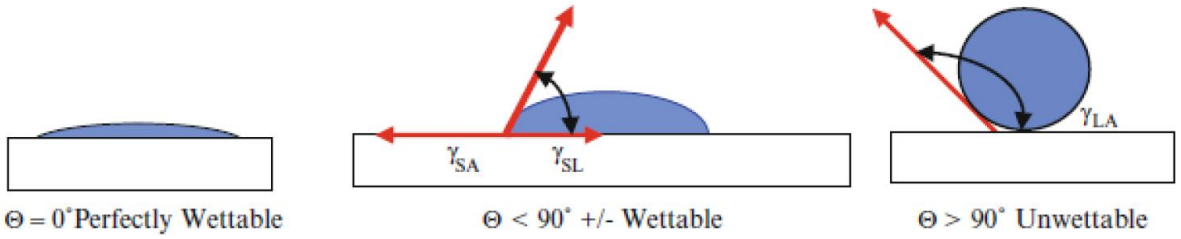
The droplet test has recently been used to assess the efficiency of PFASs on paper repellency to determine intentional PFAS use or presence of PFAS as NIAS (from recycling).

Integrated Environmental Assessment and Management

Brief Communication https://doi.org/10.1002/ieam.4346

Significance of Perfluoroalkyl Substances (PFAS) in Food Packaging

Greg W Curtzwiler, Paulo Silva, Alexander Hall, Alexandra Ivey, Keith Vorst



If compliance for repellancy standard needs to be demonstrated, the contact angle can be measured using DROPImage Advanced software in accordance with ASTM D7334-08(2013) (ASTM 2013).

Screening methods as indicator for fluorine or organofluorine

Screening in the field or laboratory – Sliding spark spectroscopy (SSS)

- The basic principle of the method is the thermal vaporization of a small amount of the sample surface using a train of defined high-current sliding sparks producing a plasma. SSS is normally used for plastic characterization and sorting
- Software analysis of the delivered spectra gives information on the content of elementary fluorine **on top of the surface.**
- For fluorine a typical double-peak at a wavelength of about 350 nm is obtained. By a hardware setup, it is possible to get the absolute intensities of the fluorine emission line.
- The system is portable/mobile and can detect organofluorine (such as PFOS and PFOA related compounds and other PFASs) at a concentration **of ~0.1% (1000 mg/kg).**

http://www.iosys-seidel.de/en/sss3.html

Seidel T, Golloch A, Beerwald H, Böhm G, (1993) Fresenius' Journal of Analytical Chemistry 347, 92-102.
Wolz G, Gruber L, Ewende J, Fiedler D, Schlummer M (2010) Development of screening methods for fluorinated coatings of food contact materials and other everyday commodities. Organohalogen Compounds. 72, 1173-1176. http://dioxin20xx.org/wp-content/uploads/pdfs/2010/10-1444.pdf

Screening methods as indicator for fluorine or organofluorine

Screening in laboratory and field – Optimized XRF spectroscopy

- Handheld XRF for field could not detect the smaller elements like ^{23}Na or ^{19}Fluorine until 2021.
- Recently one company optimized an XRF to detect Na and fluorine: The combination of direct user control of settings, optional helium atmosphere, specific geometry, large-area Silicon Drift Detector (SDD) with 1µm graphene window, and live spectral analysis software enable fluorine analysis with this handheld XRF.
- The fluorine-optimized XRF show a **clear fluorine signal** at 0.677 keV in **PTFE tape**
- Magnification of fluorine-optimized XRF data shows **a clear F signal** in **fluorinated ski wax** samples which makes it possible to distinguish them from fluorine-free ski wax

- The **fluorine-optimized XRF limit of detection (LOD)** is highly dependent on the application; it is typically between **1% to 10%** depending on measured material & measurement conditions.
- **This detection limit is (normally) too high to detect SCF-polymer coated carpets or textiles.**

9	19.00
F	0.001
Fluorine	
Kα	0.677

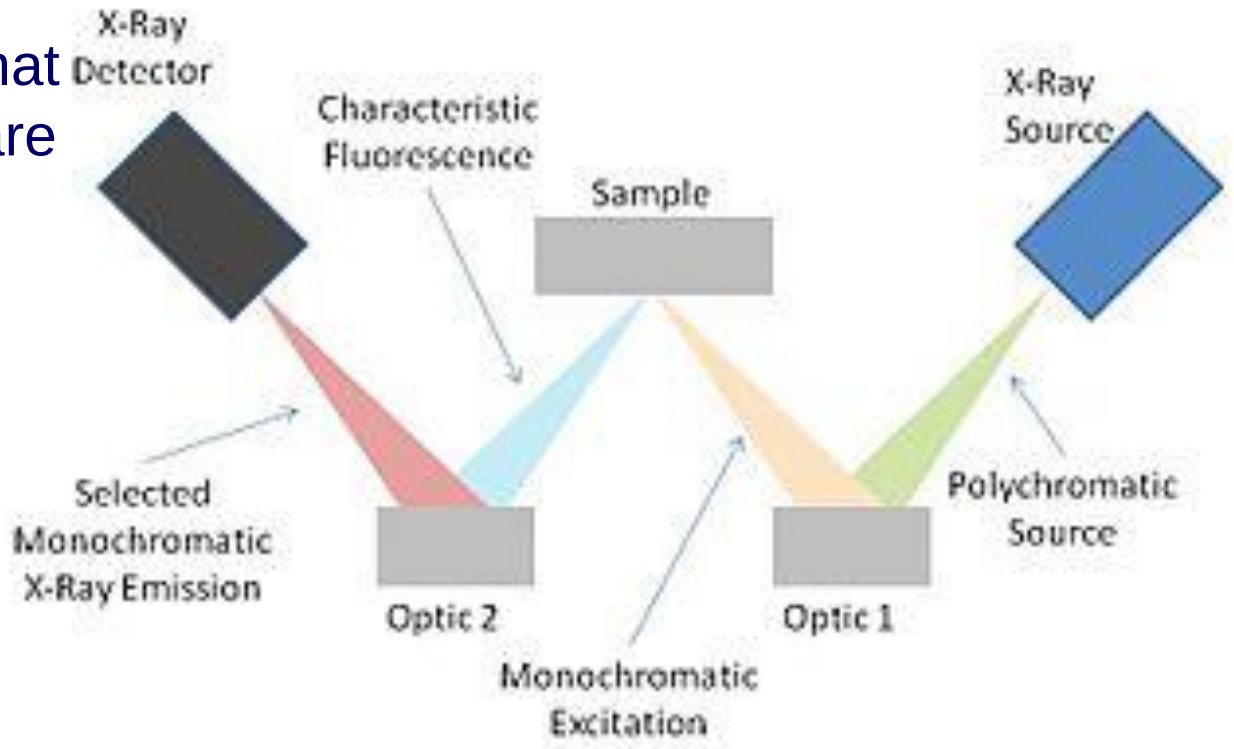
Screening methods as indicator for fluorine or organofluorine

Screening <u>in laboratory</u> – Wavelength dispersive XRF (WD-XRF) spectroscopy

- WD-XRF systems are able to detect fluorine in vacuum mode.
- It is important to understand that **for fluorine** the **depth of signal saturation** is limited to the **first micrometer**, caused by the very low energy of the obtained fluorescence radiation.

- Applying a WD-XRF to the fluorine screening in coated papers an **LOD of 0.05% (500 mg/kg)** fluorine was elaborated. Taking into account, that PFAS side groups of large coating molecules are expected to form the outer shell of the sample matrix, the LOD of 0.05% is sufficient to detect perfluorinated structures (-CnF2n+1).

(UNEP 2021)



Screening methods as indicator for fluorine or organofluorine

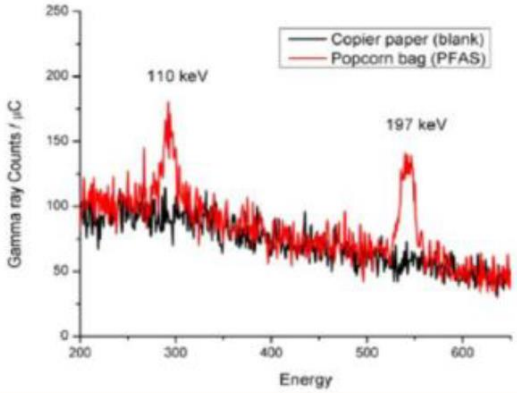
Screening in laboratory: Particle-Induced Gamma Ray Emission (PIGE) spectroscopy

- Particle-Induced Gamma Ray Emission (PIGE) spectroscopy was developed as a rapid screening method for total fluorine and applied to quantify PFASs on consumer textiles and papers. It provides a quantitative measurement of total fluorine on textiles and papers. Samples are irradiated with approximately 10 nA of 3.4 MeV protons for 180 s.

Integrated γ-ray counts in the 110 and 197 keV peaks of ^{19}F per microcoulomb of beam on target (counts per microcoulomb) **can be converted to concentrations of total fluorine (in nanomoles of F per cm²).**

This technique is rapid (ca. 3 min) and sensitive, with a limit of detection (LOD) of 24–45 nmol F/cm² for textiles and 13 nmol F/cm2 for papers, with reproducibility of ±12% RSD.

Fig. 3: PFAS-coated paper sample compared with uncoated paper. Irradiation time of 180 second with 9 nA of 3.4 MeV protons.



Ritter et al. (2017). Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 407, 47-54

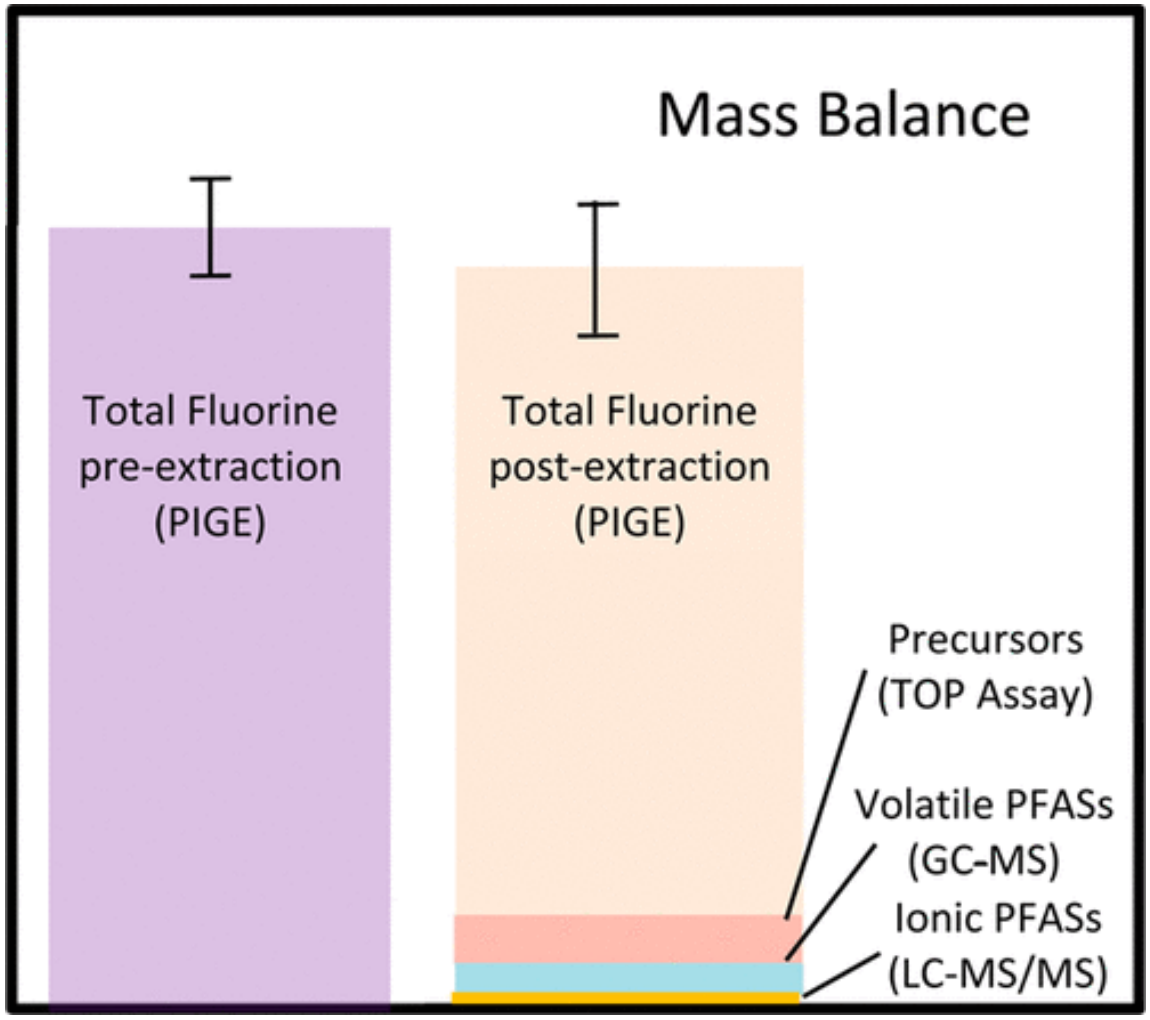
Screening methods as indicator for fluorine or organofluorine

Step 3: Screening in laboratory - Particle-Induced Gamma Ray Emission (PIGE) spectroscopy – Case study for screening textiles and paper

Total fluorine wes determined by PIGE.

Volatile and ionic PFASs and precursors measured by TOP-Assay accounted for 0–2.2%, 0–0.41%, and 0.021–14%, respectively, of the total nmol F/cm2 determined by PIGE.

After extraction, papers and textiles retained 64 ± 28% to 110 ± 30% of the original nmol F/cm2 as determined by PIGE, indicating that the majority of fluorine remained in the papers/textiles.

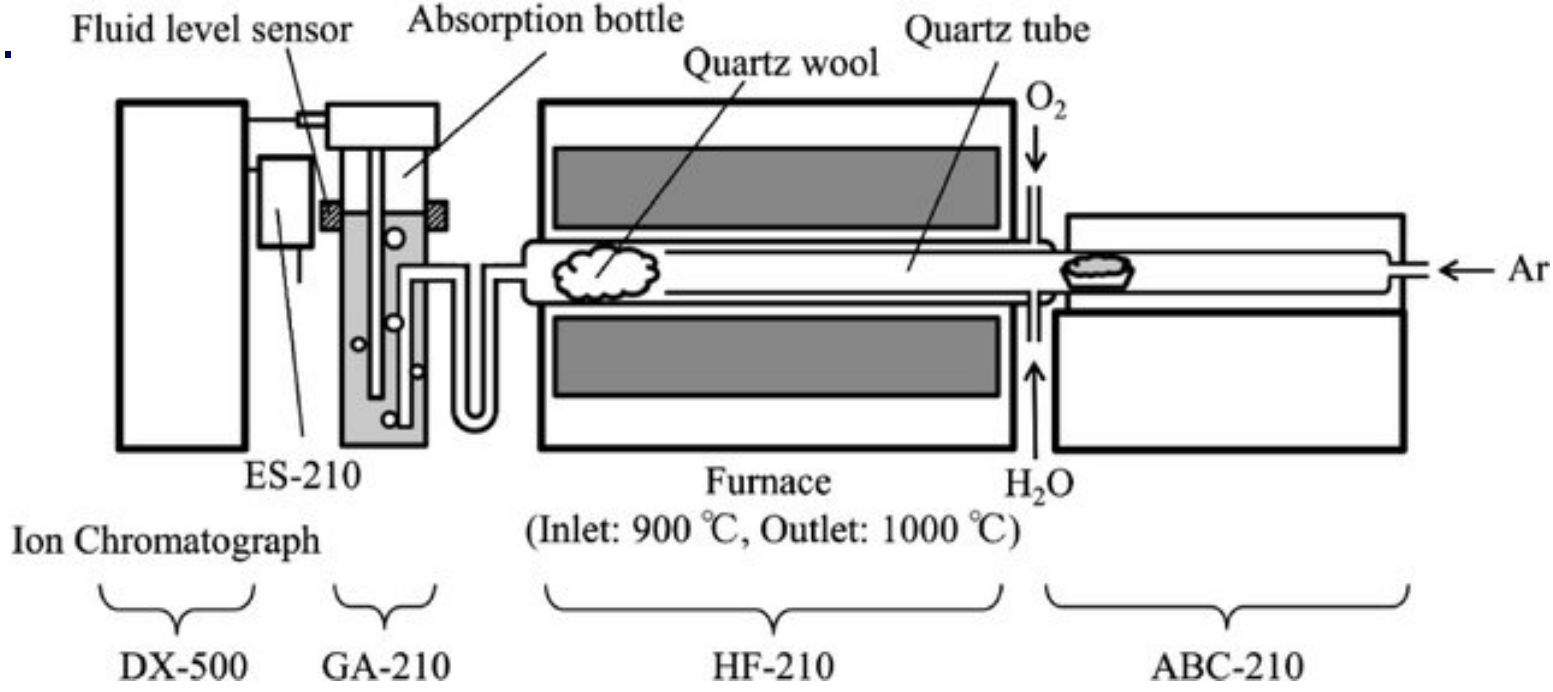


Robel et al. (2017). Closing the Mass Balance on Fluorine on Papers and Textiles. Environ. Sci. Technol. 2017, 51, 16, 9022–9032

Screening methods as indicator for fluorine or organofluorine

Step 3: Screening in laboratory - Combustion ion chromatography (CIC)

- **CIC is a commonly used technique for PFAS sum parameter analysis. Products like textiles or paper are prebaked, inserted into the combustion unit on a ceramic sample boat, and heated gradually to 1100 °C under an oxygen & argon flow**. Combustion gases are absorbed in water, which is then injected into an ion exchange column
- The method can also be used for bromine or chlorine
- The method can aim for extractable PFAS screening (pre-extraction) or for total fluorine (by combustion of total textile or carpet).



Aro et al. (2021). *Iscience*, *24*(9), 102968.
UNEP (2021) POPs in products

Wada et al. (2017). Bunseki Kagaku 64(7):543-549

PFAS in food contact materials in EU (05/2021)

- Study of PFAS in fast food packaging and disposable tableware in 6 EU countries (organised by 9 NGOs).

METHODOLOGY USED .....

- Sample collection .....
- Oil repellency test with droplet of olive oil (bead test) .....
- Quantification of total organic fluorine (TOF) .....
- Detection and quantification of selected PFAS .....
- Fluorine mass balance .....

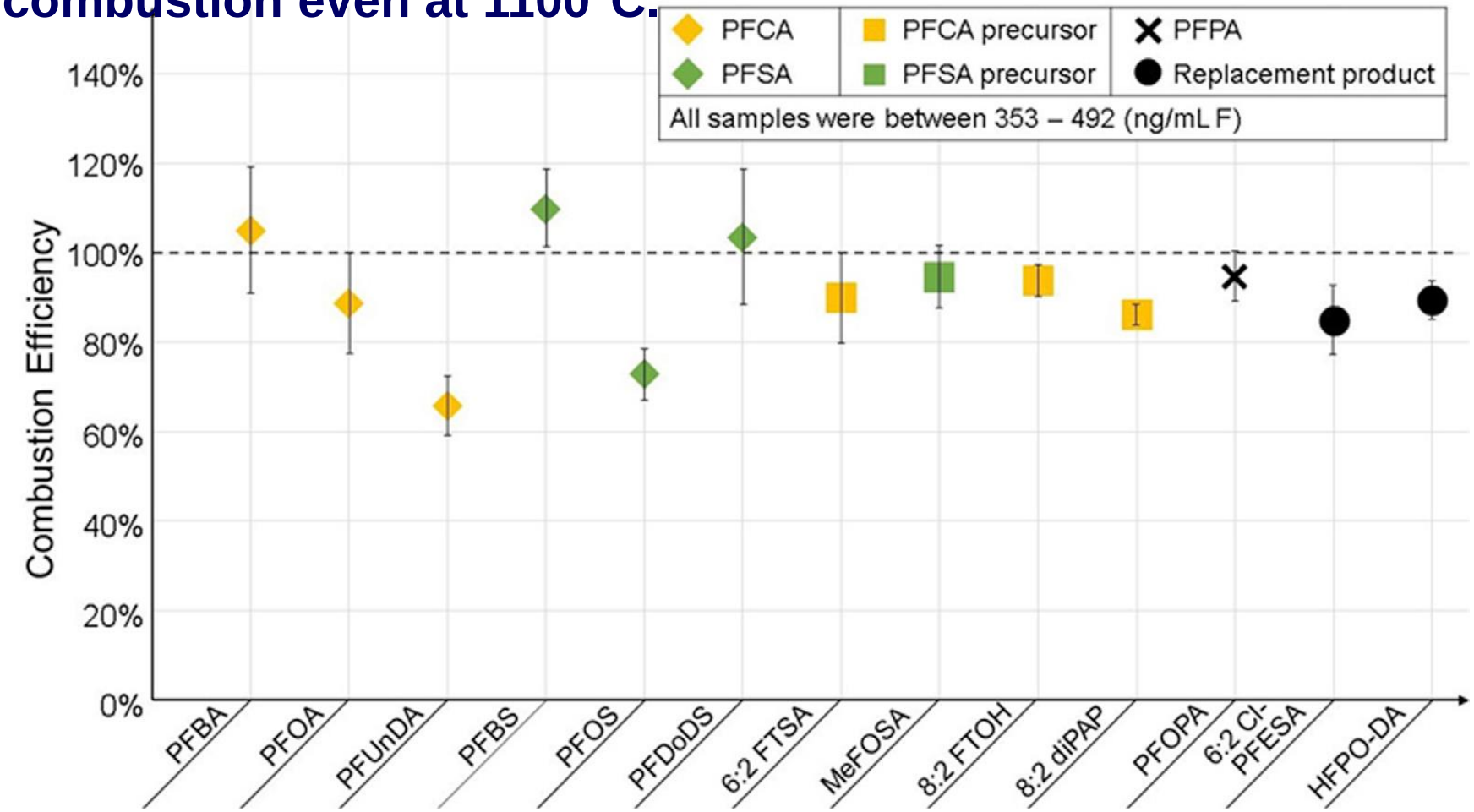
- Study of PFAS in fast food packaging and disposable tableware in 6 EU countries (organised by 9 NGOs).
- 32 out of 42 fast food packages tested in laboratory contained PFAS (KFC, McDonald's; Dunkin Donut, Subway).
- McDonald's fries packaging: In the Czech Republic contained PFAS but in Denmark did not contain PFAS (since 06/2020 there is a PFAS ban in food contact materials in Denmark!).

https://www.env-health.org/wp-content/uploads/2021/05/FINAL_pfas_fcm_study_web.pdf

Screening methods as indicator for fluorine or organofluorine

Step 3: Screening in laboratory - Combustion ion chromatography (CIC)

- Aro et al. discovered that the combustion efficiency differed for different PFAS (1100°C) with a **fluorine recovery between 66%** and 110%. **The reason is that some of the C-F bonds survive the combustion even at 1100°C.**



Aro et al. (2021). Combustion ion chromatography for extractable organofluorine analysis. *Iscience*, *24*(9), 102968.

Screening methods as indicator for fluorine or organofluorine

Screening in laboratory - Fluorine screening with ^{19}F Nuclear Magnetic Resonance (NMR) spectroscopy

- Fluorine has an uneven number of protons, and hence has an unpaired proton which couples electromagnetically when exposed to a magnetic field.
- Fluorine is furthermore monoisotopic and has a high sensitivity (81% compared to Hydrogen).
- **This, together with the high numbers of fluorine present in PFOS, PFOA and other PFASs, makes ^{19}F-NMR a sensitive screening technique, capable of screening PFAS down to ~300 ng/g (ppb) in samples.**
- **The instrumentation is costly and immobile.**
- **One measurement can take one day.**

Wikipedia: Mike25

Trier X (2011) PhD Danish Technical University, Copenhagen/Denmark.
UNEP (2021) Monitoring POPs in products and recycling

Screening of PFAS in products

Step 3: Screening of POPs PFAS in laboratory

Some screening technologies can screen POPs-PFAS in products

UNEP (2021) Monitoring POPs in products and recycling

Thank you for your attention !

More Information

UNEP Chemical in Plastics: www.unep.org/resources/report/chemicals-plastics-technical-report

UNEP Plastics Treaty: https://www.unep.org/about-un-environment/inc-plastic-pollution

Basel Convention: www.basel.int

Stockholm Convention: http://chm.pops.int/

Rotterdam Convention: www.pic.int

SAICM: http://www.saicm.org/

IOMC/OECD: https://iomctoolbox.org/; http://www.oecd.org/chemicalsafety/

Science: www.ipcp.ch; www.foodpackagingforum.org/; www.isde.org/; https://ikhapp.org/scientistscoalition/

Industry: https://endplasticwaste.org/; https://plasticseurope.org/; http://www.suschem.org/

NGO: www.ipen.org; www.ciel.org/; www.ban.org; www.chemsec.org; www.wecf.org; https://chemtrust.org/

Better-world-links: http://www.betterworldlinks.org/; https://www.plasticstreaty.org/scientists-declaration/

IPCP International Panel on Chemical Pollution

UN environment programme

gef