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WORKSHOP AND WORKSHOP REPORT ON PFAS MONITORING

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Prepared by	Van Keer I., Hohenblum P., Béen F., Vanermen G., Aus der Beek T., Geerts L., Borchers U., Gemoets J. & Bronders J.
Report submitted by	Umweltbundesamt GmbH
Address	Spittelauer Lände 5 1090 Vienna Austria
Contact	Philipp Hohenblum
Phone	++43 1 31304 5204
E-mail	philipp.hohenblum@umweltbundesamt.at
Website	www.umweltbundesamt.at

PFAS – AN EMERGING POLLUTION CRISIS

Workshop and workshop report on PFAS Monitoring

Final Workshop Report

FRAMEWORK SERVICE CONTRACT “WATER FOR CITIZENS”

ENV.C.2/2016/FRA/0032

Workshop and workshop report on PFAS Monitoring

ABBREVIATIONS

AIX	Anion Exchange Resin
ALARA	As Low As Reasonably Achievable
APCI	Atmospheric Pressure Chemical Ionization
APPI	Atmospheric Pressure Photo Ionization
AOF	Absorbable Organic Fluorine
BCF	Bio Concentration Factor
CEN	European Committee for Standardization
CIC	Combustion Ion Chromatography
CRM	Certified Reference Material
CS-MAS	Continuum Source Molecular Absorption Spectrometry
DGT	Diffusive Gradient in Thin films
DIN	German Institute for Standardization
DWD	Drinking Water Directive
EC	European Commission
ECD	Electron Capture Detector
EEA	European Environmental Agency
EFSA	European Food Safety Authority
EOF	Extractable Organo Fluorine
EPA	United States Environmental Protection Agency
EQS	Environmental Quality Standard
ESI-MS	Electrospray Ionization Mass Spectrometry
FDA	United States Food & Drug Administration
FID	Flame Ionization Detector
GAC	Granular Activated Carbon
GC	Gas Chromatography
GWWL	Groundwater Watch List
HPLC-UV	High Performance Liquid Chromatography-Ultraviolet Spectroscopy
HRMS	High Resolution Mass Spectrometry
ICP	Inductively Coupled Plasma
ICP-MS/MS	Inductively Coupled Plasma Tandem Mass-Spectrometry
IMS	Ion Mobility Spectrometer
INAA	Instrumental Neutron Activation Analysis
IPE	Ion Pair Extraction
ISO	International Organization for Standardization
KS	Keynote Speaker
KWR	Dutch Watercycle Research Institute
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
LoD	Limit of Detection
LoQ	Limit of Quantification
LTQ-Orbitrap	Linear Ion Trap-Orbitrap
MRL	Maximum Residue Limit
MS	Mass Spectrometer
MS	Member States
NF	Nano Filtration
NMR	Nuclear Magnetic Resonance
NTS	Non Target Screening
OECD	Organisation for Economic Cooperation and Development

PIGE	Particle-Induced Gamma-ray Emission spectroscopy
PLE	Pressurized Liquid Extraction
PMT	Persistent, Mobile and Toxic
POCIS	Polar Organic Chemical Integrative Sampler
POP	Persistent Organic Pollutants
ppb	Parts per Billion
PUF	Polyurethane Foam
Q-TOF	Quadrupole Time-Of-Flight
RIVM	Dutch National Institute for Public Health and the Environmen
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RP-HPLC	Reverse Phase-High Performance Liquid Chromatography
RO	Reverse Osmosis
SLE	Solid Liquid Extraction
SPE	Solid Phase Extraction
SVHC	Substances of Very High Concern
TDI	Tolerable Daily Intake
TF	Total Fluorine
TOF	Time-Of-Flight
TOF	Total Organo Fluorine
TOPA	Total Oxidisable Precursor Assay
TWI	Tolerable Weekly Intake
UBA	Umweltbundesamt (German Environment Agency)
UPAE	Ultrasonic Probe-Assisted Extraction
VITO	Flemisch Institute for Technological Research
WAX	Weak Anion eXchange
WFD	Water Framework Directive
WHO	World Health Organization
WWTP	Waste Water Treatment Plant
XPS	X-ray Photoelectron Spectroscopy

CHEMICAL COMPOUNDS

diPAP	Fluortelomer phosphate diesters
EtFASA	Ethyl perfluoroalkane sulfonamide
FASA	Perfluoroalkane sulfonamide
FASE	Perfluoroalkane sulfonamido ethanol
FOSA	Perfluorooctane sulfonamide
FTOH	Fluorotelomer alcohol
FTS	Fluorotelomer sulfonate
FTSA	Fluorotelomer sulfonic acids
HF	Hydrogen fluoride
IF	Inorganic fluorine
OF	Organo fluorine
PE	Polyethylene
PEEK	Polyether ether ketone
PFAA	Perfluorinated alkyl acid
PFAS	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonic acid
PFC	Polyflorinated compound
PFCA	Perfluorocarboxylic acid
PFNA	Perfluorononanoic acid
PFHxA	Perfluorohexane sulfonic acid
PFHxS	Perfluorohexane sulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFSA	Perfluorinated sulfonic acid
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
SBP	Sodium biphenyl
TPSiOH	Triphenylhydroxysilane

TABLE OF CONTENTS

EXECUTIVE SUMMARY

PFAS are a large chemical family consisting of more than 4.700 individual substances with unique chemical properties. It has been demonstrated that they spread into all environmental compartments due to their high solubility in water, low sorption to soil and particulate matter and their resistance to biological and chemical degradation (see I.2 PFAS CHEMISTRY).

Monitoring of PFAS depends on a variety of factors such as the definition of the individual substances, the medium to be monitored and the availability of validated standard analytical methods. To get an overview and a sound discussion among experts in the field of PFAS monitoring, the European Commission brought together global PFAS experts in a workshop to discuss the state-of-the-art and options for future monitoring concepts. The workshop took place on 13 and 14 January 2020 in Brussels. This report summarizes the workshop and in particular, this executive summary anticipates the detailed recommendations provided in chapter II.4 Policy Recommendations.

General recommendations

PFAS accumulate in human beings and animals and some PFAS have properties of toxicological concern (see I.3.4 Toxicology). A considerable proportion of the European population is expected to exceed the tolerable weekly intake due to intake of certain PFAS substances from food and drinking water (EFSA 2018, 2020; see details in chapter II.4.2 Limits for drinking water). These are reasons enough to apply the precautionary principle and to establish restrictions on production and use. As losses into the environment and direct exposure to humans are inevitable, measures at the source are needed rather than advocating end of the pipe measures.

Some of the PFAS have already been restricted or will be restricted in the near future, but still, a multitude of substances is entering the market.

Within EU chemicals legislation, PFOS, PFOS salts and PFOS precursor substances are restricted in the EU according to the Persistent Organic Pollutants (POPs) Regulation (EU 2019/1021). PFOA, its salts and related substances are listed in annex XVII of REACH and will soon be included in Annex I of the POPs Regulation. They will no longer be allowed to be produced or used in the EU as of July 2020 (with some exemptions). PFHxA, its salts and related substances as well as PFHxS, its salts and related substances are under discussion for inclusion in annex XVII of REACH. ECHA is currently evaluating the respective restriction dossiers. The results are expected for late 2020 for PFHxS and for late 2021 for PFHxA. Further regulatory measures on other PFAS are currently being discussed under REACH, like the identification as SVHC or a restriction of C_9-C_{14} PFCAs, for which the opinion of ECHA's committees is already available. In addition, GenX and PFBS have been identified as SVHCs due to a high concern about their mobility (PMT).

The EC initiated two studies on the use of all PFAS and non-fluorinated alternatives in fire-fighting foams and in textile – leather processing. The collected data, including substance identification, benefits, hazards, emissions, potential alternatives, critical uses, costs of restricting the substances as well as costs of contamination of soil and water will be used as a basis for the REACH restriction.

However, concern has been raised by a group of renowned scientists that, while some PFAS have been regulated so far, knowledge about uses and hazards of others are still very limited or missing (Zurich statement).

A socioeconomic analysis of environmental and health impacts linked to exposure to PFAS has been published in 2019. It concludes that substantial socioeconomic costs may result from PFAS exposure in terms of impacts on human health and the environment. Annual health-related costs were estimated at 52 – 85 billion for all EEA countries. Overall non-health costs (e.g. environmental remediation) sum up to 20 – 170 billion Euro for all EEA countries (Nordic Council, 2019)

EU Member States asked to the European Commission to develop an EU strategy to minimize the environmental burden and human exposure to PFAS through regulatory and non-regulatory actions. In line with the timeframe of the UN Global Goals for Sustainable Development, the paper proposes actions to be taken on the EU level to phase out all PFASs at the latest by 2025 and to be in effect by 2030.

To summarize, some regulations are in place and several activities are ongoing. But there is also concern that the measures taken are not sufficient to protect citizens from adverse effects of this group of substances. Because of their persistence, PFAS and their degradation products will remain for a long time in the environment. Substances still in use will lead to irreversible contamination while alternative PFAS substances, which might be regrettable substitutions, are brought on the market. Therefore, the following recommendations were given during the workshop:

- The European Commission should acknowledge the concerns of Member States, summarized in the request to issue a strategy for PFAS, which addresses the entire group of chemicals under the chemicals legislation (REACH), but also using other EU legislations and global initiatives (including non-legislative ones). A comprehensive approach also needs to include plant protection products (EFSA) and pharmaceuticals (EMA) as these are precursors of the short chain PFAS.
- The revision of the DWD does not include PFAS precursors. As illustrated during the plenary session, precursors cannot be ignored. Their inclusion into the DWD needs to be re-evaluated.
- On-going activities at ECHA and EFSA need to be finalised without delay, respecting the deadline set in the legislative processes.
- Regulations and policy acts must address the source rather than react at the end of the pipe. This, however, needs time to be fully implemented and thus measures at the end of pipe are needed while uses are being phased out.
- The effect of replacing long-chain PFAS with short-chain PFAS due to regulation (e.g. fire-fighting foams) regarding persistency, bioaccumulation, and toxicity is largely unknown for different environmental matrices and other media and further research is considered necessary. Short-chain PFAS are suspected to be persistent and mobile.
- Clarification in the issue of “essential” vs. “non-essential” uses in the light of (further) restrictions of relevant substances in order to guarantee a uniform and consistent prioritisation approach.

Limits for drinking water

For the Groundwater Directive, 10 PFAS substances have been proposed to be considered for the annexes review, for which sufficient monitoring data are available through the voluntary watch list process. The regulation of pesticides in drinking water, the new Drinking Water Directive (DWD) sets a limit value of 0.1 µg/l for the sum of the 20 most important substances and a limit of 0.5 µg/L for “PFAS total”. The European Commission needs to establish technical guidelines for measuring all PFAS over the next three years. A limit value (0.5 µg/l) will apply once technical guidelines for monitoring ‘PFAS total’ are available.

An EFSA risk assessment, which has been published after the workshop, proposes tolerable weekly intake (TWI) levels based on epidemiological data to specifically protect infants (EFSA, 2018; EFSA, 2020). The TWI calculates as the sum of PFOA+PFNA+PFHxS+PFOS (which contribute most to human exposure) of 8 ng/kg bw/week.

Table 3 illustrates that the tolerable total intake levels depend on the respective body weight.

Table 1: Tolerable weekly intake calculated for different groups depending on body weight

population	**body weight (kg)**	**Tolerable PFAS intake (total in ng/week)**	**% TWI**
children	10	80	100%
teenager	40	320	100%
adult	70	560	100%

By comparing the total intake values for different scenarios of drinking water consumption (exactly meeting the new DWD limits) for different age groups (assuming body weights of 10, 40 and 70 kg) and assuming the predominant presence of the respective four PFASs it is obvious that the limit of sum of PFAS and of total PFAS are not protective.

Table 2: Proportion of the TWI for the three age groups depending on different daily water consumptions and their proportion of the total weekly intake suggested by EFSA

	Total weekly intake: ng	**% TWI**		
water consumption (L/d)	**DWD: 4 PFAS (0.1µg/L)**	**children**	**teenager**	**adult**
1	700	875%	219%	125%
2	1,400	1,750%	438%	250%
3	2,100	2,625%	656%	375%
water consumption (l/d)	**DWD: 4 PFAS (0.5µg/l)**	**children**	**teenager**	**adult**
1	3,500	4,375%	1,093%	625%
2	7,000	8,750%	2,187%	1,250%
3	10,500	13,125%	3,281%	1,875%

Addressing options to overcome the discrepancy is beyond the scope this report.

Monitoring

In order to measure PFAS and PFAS total, several analytical options are available (for details, see I.4 Analytical methods). Existing targeted methods (LC-MS/MS) for the determination of PFAS are still among the most important analytical tools available, in particular because of their specificity and sensitivity. However, the large number of PFASs to be addressed by ‘PFAS total’ calls for additional approaches to broaden the analytical spectrum. Examples for non specific methods to determine the organic fluorine content and to extend the spectrum to species that cannot yet be measured by targeted methods, have been described and compared (see II.3.1 Characterisation of PFAS in groundwater, surface water & drinking water). The measurement of organic fluorine as surrogate for PFAS is an option, but their sensitivity and selectivity have to be investigated more in detail. Also, economic considerations as high investment costs for a very specific kind of analyses like PIGE should be weighed against the market demand and quality aspects. As a matter of fact, results below the limit of quantification need to be checked/confirmed by additional targeted analyses.

A method to include precursors in monitoring is oxidative conversion of precursor substances (TOP). In contrast to other methods, TOP is specific for PFAS while other unspecific total fluorine methods also include fluorine from organic pesticides and pharmaceuticals. This leads to the need for clear definitions that should be considered under 'PFAS' and 'total PFAS' and how to deal with results from unspecific methods which yield fluorine concentrations as a surrogate for 'PFAS total'. All these aspects have to be included when it comes to the establishment of necessary technical guidelines for the implementation of the Directive. Several recommendations have therefore been identified in the workshop:

- Methods for measurement of organic fluorine as surrogate for PFAS are available but need to be evaluated for their applicability.
- The common terminology recommended by Buck et al. (2011) was updated by the OECD (2018), but there is still confusion. Therefore, one unambiguous terminology needs to be elaborated by globally acting organisations, science and standardizing bodies.
- The panel agreed that for the moment precise definitions for "total PFAS content" are not available and that these need to be defined further on a legislative level. Similarly, the term "total" needs to be defined clearly, based on a consensus and/or a specific method.
- Standard analytical methods do not yet fully address the needs for sampling and analysis of PFAS. For instance, a globally applicable and standardised method for measuring of PFAS in air samples, reference matrices for human biomonitoring or biological monitoring is missing. It is recommended to check the possibility of developing a new CEN standard based on the existing ISO standard (ISO 21675:2019) and to support standardization activities, maybe under a specific mandate.
- The availability of certified reference materials (CRM) for PFAS substances shall be increased to raise the level of confidence for the analytical procedures. For the 20 PFAS listed in the DWD, only 18 are commercially available. Certified reference material with known PFAS concentrations is needed for at least eggs, fish, milk (powder), vegetables, and for packaging material (e.g. paper board). CRM are needed to validate analytical procedures and check the metrological traceability of methods which are used for enforcement of legislation. Therefore, the legislator should be precise in the definition and nomenclature of parameters as pre-requisite to the development of appropriate analytical methods, their standardization and development of CRM by commercial providers.
- Currently, little information is available on past and on-going PFAS production, manufacturing and use on regional and national levels. This is important to derive local sampling and analytical protocols for different environmental matrices. Producers and users should submit the necessary data to authorities, preferably under the JRC's IPCHEM platform.
- Under the same IPCHEM platform, a harmonized European database/inventory should be developed, which includes as many PFAS measured environmental occurrences in different

matrices as possible, from authorities, researchers and others. This will enable to derive hotspots and their sources, risk assessment and measures.

- One problem raised is that the different toxicities of PFAS are not considered when calculating sums of PFAS mass concentrations (harmless PFAS and toxic substances are equivalent in the sums). Therefore, the panel suggested to implement some sort of weighting factor (as is done for PCDD/PCDF) if enough knowledge is available. This has to be assessed by toxicologists.

PART I – STATE OF PLAY

I.1 POLITICAL BACKGROUND

Per- and polyfluoroalkyl substances (PFAS) represent a large number and variety of emerging environmental contaminants. More than 4,700 substances have been listed so far with different levels of knowledge of their behaviour, fate, persistence, environmental burden, health impacts and ecological implications. Due to the level of complexity, no legislative approaches are available to enable an adequate or comprehensive regulation of the entire group of PFAS. The European Commission has proposed to include limit values for PFAS in the recast of the Drinking Water Directive and both the European Parliament and the Council have proposed amendments on the specific issue and agreed on a General approach. Trilogues took place in 2019 and the final compromise has been endorsed by the Committee of Permanent Representatives on 5 February 2020. On 18 February 2020, the ENVI Committee of the European Parliament gave its endorsement to the text. Proposed amendments for the study of "PFAS total" and "Sum of PFAS" include 1) the set-up of technical guidelines regarding analytical methods, 2) the definition of detection limits and parameter values and 3) the determination of the frequency of sampling for monitoring of 'PFAS total' and 'Sum of PFAS'.

In particular, the Directive addresses PFAS in Article 13 (Monitoring) and states that the Commission has to establish guidelines regarding the analytical methods for monitoring of "PFAS total" and "Sum of PFAS".

Monitoring of PFAS depends on a variety of factors such as the definition of the individual substances, the medium to be monitored and the availability of validated standard analytical methods. To get an overview and a sound discussion among experts in the field of PFAS monitoring, the European Commission brought together global PFAS experts who discussed the state-of-the-art and options for future monitoring concepts.

I.2 PFAS CHEMISTRY

Perfluoroalkyl substances (PFAS) are a complex family of about 4,700 man-made fluorinated organic chemicals that have been produced since the mid-20th century, although not all of these may be currently in use or in production. PFAS can typically be produced by electrochemical fluorination, telomerization, or oligomerization. There are basically few limitations on industry to develop new compounds by making slight changes to chemical structures. The most important and recognised PFAS are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) and related products. If not being industrially produced PFAS can additionally emerge by biotic and abiotic degradation and alteration processes from neutral precursor substances, without being detected by recent analytical approaches. These volatile precursor substances can be transported long distances in the atmosphere prior to deposition in regions remote from pollution sources (Sunderland et al. 2019). According to Lassen et al. (2013) examples of those precursors are long-chain fluorotelomer alcohols (e.g. 8:2 FTOH), perfluorinated phosphonic acids and fluorotelomer-based side-chain fluorinated polymers. These precursors may be present in a wide range of consumer products, such as impregnated clothing and carpets.

PFAS are fully (perfluoro-) or partially (polyfluoro-) fluorinated alkane (carbon-chain) molecules. Their basic chemical structure is a chain (or tail) of two or more carbon atoms with a charged functional group head attached at one end. The functional groups commonly are carboxylic or sulfonic acids, but other forms are also detected in the environment. PFAS encompass a wide variety of substances with very different physical and chemical properties, including gases (for example, perfluoroalkyliodides ($F(CF_2)_nI$), liquids (for example, fluorotelomer alcohols), surfactants (for example, perfluorooctane sulfonate), and solid material high-molecular weight polymers (for example, polytetrafluoroethylene (PTFE)). An overview of different PFAS types is provided in Figure 1 (OECD, 2018). The main group of commonly recognised PFASs are PFAAs (perfluoroalkyl/per- and polyfluoroalkylether acids) and their precursors (perfluoroalkane sulfonyl fluorides, perfluoroalkyl iodides, per- and polfyfluoro-ether based substances). Other PFASs are fluoropolymers and perfluoropolyethers. Further, there are other highly fluorinated substances, which are currently not included in the PFASs classification (Figure 1b).

Per- and polyfluoroalkyl substances have been reviewed by Buck et al. (2011) who suggest a common terminology, classification and acronyms for the substances and substance groups. Sha et al. (2019) state that some PFASs are not covered by this common terminology and much that development is needed for future systematic naming of PFASs. Therefore and according to the discussion during the workshop, OECD is planning to revise the current terminology to take into account the different PFAS classifications and related substances as shown in Figure 1.

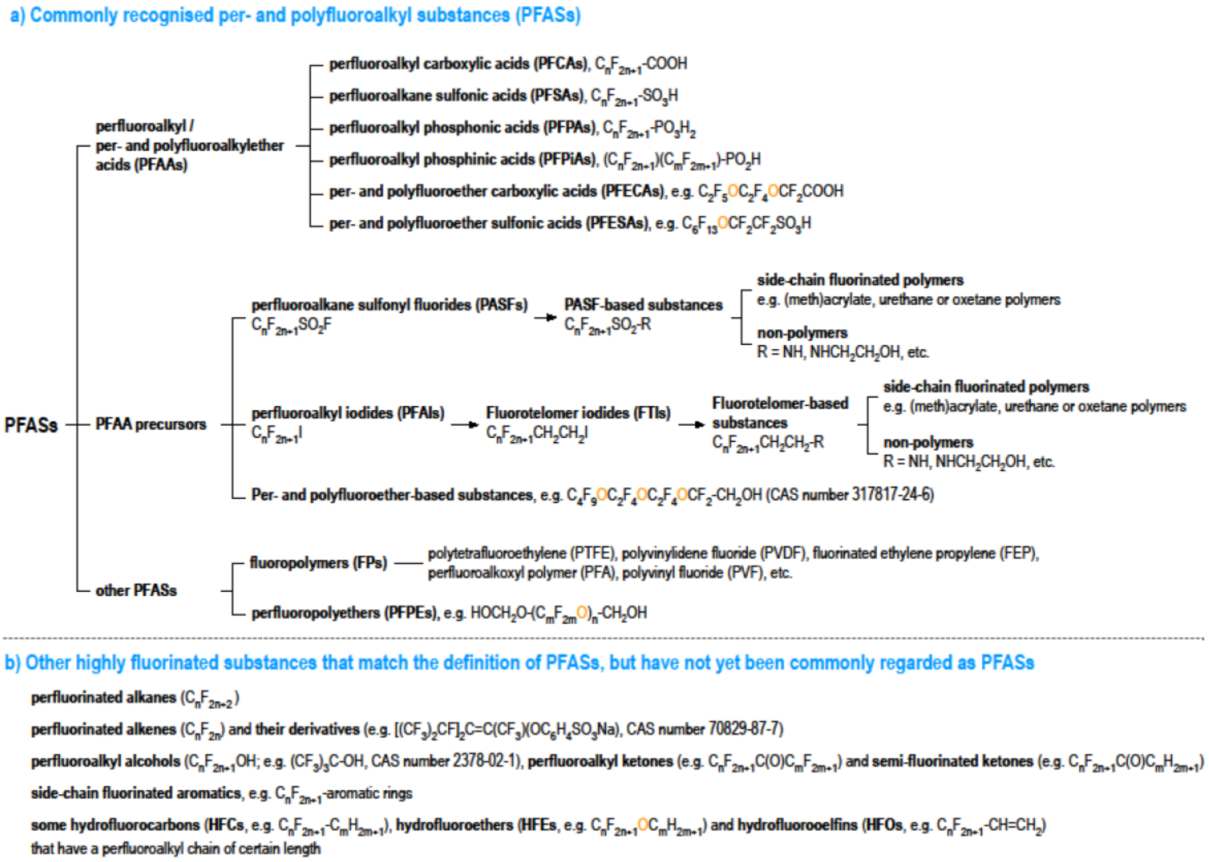

Figure 1: General classification of per- and polyfluoroalkyl substances (PFASs) (OECD, 2018)

As stated by Lassen et al. (2013): “*Fluorotelomers and side-chain-fluorinated polymers account for the major part of the present use of PFAS. The fluorotelomers [are precursors and] do not have fully fluorinated carbon chains but a part of the chain is perfluorinated and may be degraded to a perfluorinated compound. As an example the fluorotelomer alcohol 8:2 (8:2 FTOH) have a perfluorinated part with 8 carbons (and 2 carbons without fluorine) and may degrade to PFOA and PFNA. The formation of more hazardous transformation products has traditionally been a major concern related to these substances. The substances themselves may, however, also have some environmental and health effects, and a proposal for a harmonised classification of 8:2 FTOH as toxic to reproduction has been submitted. The worldwide production of fluorotelomers is estimated at 11,000-14,000 t/y. The largest amount is used as intermediates in the production of side-chain-fluorinated polymers but exactly how much is not reported. No exact data on the use in the EU is available, but the side-chain-fluorinated polymers accounted for 77% of the 3.2 t/y PFAS registered in the Danish Product Register. The polymers are used as surfactants for a wide range of applications and the major uses are all-weather clothing and other impregnated textiles, carpets and various coatings on other materials. As side-chain-fluorinated polymers are polymers, they are exempt from registration under REACH and do in general not appear to have been pre-registered. The status of these polymers under REACH, and particularly side-chain-fluorinated polymers imported from countries outside the EU is not clear. More information on how the use of these substances can be assessed and regulated under REACH is needed.*” Generally, very little data is available on use of PFASs in its various forms on the European level. However, regional studies, e.g. PFASs loads entering the Baltic Sea (Johansson & Undeman 2020) can provide fact-based estimation, e.g. of about 1000 kg/a PFASs via Swedish rivers.

PFASs are used in a wide variety of industrial and consumer products. For water and oil repellent properties, PFASs are found in waxes, carpets, textiles and especially in outdoor gear. For its film-forming abilities and therefore smothering fires, PFASs are an important additive in aqueous firefighting foams. PFAS related surfactants in food packaging and in non-stick coatings in cookware are also of emerging concern as these substances are directly connected to the human food chain. Agricultural products may also contain PFASs such as sulfuramid, an effective pesticide widely utilized in Brazil and China and containing N-Ethyl perfluorooctane sulfonamide which can degrade to PFOS (Liu et al., 2017; Nascimento et al., 2018; Zabaleta et al., 2018). Furthermore, a wide range of PFAS substances are present in food of plant origin, because they enter the agricultural crops via the soil and the water and the food-producing animals via feed and drinking water.

Due to their abundance in consumer goods and products, large PFAS releases can occur from sewage sludge or landfills into soil and groundwater. Wastewater treatment plants are a source of PFAS to surface water. Airports, military bases and firefighting training sites are becoming important sources due to the increased use of firefighting foams containing PFAS.

There is on-going innovation by a large variety of industries to develop PFAS-free consumer goods and products. PFAS-free firefighting foams, such as paraffin-, silicone- and dendrimer-based chemicals have recently been developed and are now on the market (Lassen et al., 2015). Alternatives to long-chain PFAS exist for most applications. Technologically alternatives to long-chain fluorinated chemicals are short-chain chemicals with a carbon chain length of ≤C8 for perfluoralkyl carboxylates and ≤C6 for perfluoroalkyl sulfonates. The short-chain fluorinated alternatives are, as mentioned, still rather persistent and thus problematic from a drinking water perspective (Brendel et al. 2018) but tend to be less bioaccumulative than the long-chain homologues (Lassen et al 2013). However, there are still many gaps in research on the toxicity of short-chain PFAS.

I.3 Properties and behaviour of PFAS

PFASs have become a global concern, due to their persistence, mobility, bioaccumulation in biota (including food) and the environment, and adverse health effects.

I.3.1 Occurrence

Environmental occurrence is from global and local sources i) production of surfactants, polymers and precursors, ii) industrial applications using surfactants and precursors, iii) some emissions from usage, one major is training with AFFF, iv) end-of life emissions, i.e. landfills.

PFASs are ubiquitously found in diverse environmental compartments. National monitoring activities have detected PFASs in the environment across Europe (EEA, 2019). Emerging PFAAs are increasingly detected, as was shown in a review of measured values for surface water between 2006 and 2017, where 455 new PFASs were discovered (Xiao, 2017). The median of published concentrations in sediments was 0.27 ng/g (PFOA) and 0.54 ng/g (PFOS), and 3 ng/l for PFOS and PFOA in surface water (Zareitalabad et al., 2013). In surface water samples of the Faroe Islands, PFOS concentrations were up to 1.18 pg/l, the substance was not detected in Iceland but was found at levels as high as 90 pg/l in Tromsø in Norway. PFOA reached up to 40 pg/l in seawater in Nordic countries. In Greenland, PFCAs were detected in snow with PFOA being the dominant compound (520 pg/l) (DEPA, 2015). Three novel PFECAs were detected in surface waters of countries in Asia, Europe and America, in median concentrations of 0.95 ng/l, 0.21 ng/l and 0.31 ng/l, respectively (Pan et al., 2018). In 59 samples of tap water from countries around the world, the mean concentration of the sum of 29 PFAAs and precursors was 7.1 ng/l (maximum 44 ng/l). The mean for PFCAs and PFSAs was 4.1 and 1.6 ng/l respectively; both groups had high detection frequencies. The highest concentration (39.0 ng/l) was measured for the precursor 5:3FTCA, but the detection frequency was only 7% (Kabore et al., 2018).

Differences between concentrations in soils close to local emission sources (airports) and remotely but in the same region, were 5-10 times for PFOS (226.9 vs 40.2 ng/g and 959 vs 109.9 ng/g), illustrating the importance of local emissions sources (DEPA, 2015).

PFOS and PFOA were detected in the Norwegian Arctic ambient air in very low concentrations (0.02-0.97 pg/m^3 and 0.15-1.51 pg/m^3 respectively); in other air samples from Norway, PFOS concentrations ranged between 0.03-3.32 pg/m^3 (DEPA, 2015).

I.3.2 Distribution

PFASs are usually divided into two categories when it comes to distribution; 1) ionisable and (very) persistent PFCAs and PFSAs that are non-volatile, so transport in the vapour-phase plays a minimal role, and for which sorption is a function of chain length, 2) Neutral, some can be ionisable, precursors that can degrade, some are volatile, and sorption is a function of hydrophobicity.

Depending on the properties of the PFAS, distribution by water or air is taking place, and bioaccumulating PFASs will end up in the food chain, water soluble PFASs in water, volatile PFASs in air. Precursors can undergo biotic and/or abiotic transformation to persistent acids. Polymers are less studied and are assumed to be inert and less transported. Side-chain polymers belong to the group of precursors.

Within the environmentally relevant pH-range (pH 5-9), ionisable PFAAs are normally present as anions and this reduces their sorption potential as the net charge of soils and sediment is usually negative. The retardation in transport in soil and groundwater increases with carbon-chain length and the organic fraction in the soil, with PFSA binding more strongly than PFCA with the same carbon-chain length (CONCAWE, 2016).

Short-chain PFAAs are more mobile in soil and sediment, due to their higher solubility in water and lower sorption to solids; in combination with the high environmental stability, the high mobility implies that the short-chain PFAAs have a high global contamination potential. Criteria for the risk of spreading, i.e. mobility, were developed by UBA (2018) and acknowledged by ECHA in classifying PFBS and GenX as substances of very high concern (SVHC) based on their PMT (persistent, mobile and toxic) properties and their implied risk to waters (ECHA, 2019; 2020). The extent of transport of PFAS via water is influenced by the extent of adsorption to sediment or soil during that transport, the higher the adsorption of PFAS, the slower the transport of PFAS via the water phase. The octanol-water partition coefficient may not be a useful parameter for predicting the adsorption or bioaccumulation of PFAS due to their unusual lipophilic behaviour. It is demonstrated that PFOS and PFOA accumulate in aquatic and terrestrial food chains by partitioning to serum lipoproteins and not to fatty tissues (EFSA, 2018).

PFAS that are sufficiently volatile are to be considered long-range transboundary air pollutants, implying that world-wide emissions may accumulate in cold areas such as the Artic (EEA, 2019). PFASs are widely distributed in the world's oceans implying long-range atmospheric transport from source regions (Prevedouros *et al.*, 2006; Gonzalez-Gaya *et al.*, 2014; Wang *et al.*, 2015; Yeung *et al.*, 2017; Muir *et al.*, 2019). The Henry-coefficient, the rate of the vapour pressure and the solubility, reflects how easily a substance in solution will partition to the gas phase above the liquid. The Henry-coefficients of PFAS are very diverse; the Henry-coefficient of PFOS is negligible and indicates that PFOS will hardly distribute from water to air; PFOA will partition to the air a little bit easier. Sea-spray aerosols may be an important source of PFCAs to the atmosphere (Johansson *et al.*, 2019).

I.3.3 Degradation

The carbon-fluorine bond is amongst the strongest chemical bonds in organic chemistry, making many PFAAs persistent in the environment. PFAAs have a high thermal, chemical, photolytical and biological stability, hence leading to accumulation in the environment. No significant biodegradation of PFOS was observed in 28 days in a standard test, the half-lives for hydrolysis and photolysis are ≥ 41 year and > 3,7 year respectively (OECD, 2002). Precursors (e.g. alcohol telomers) can degrade to carboxylic acids through oxidation or hydrolysis. Perfluorinated precursors with a sulfon-based functional group can yield PFSA, but also PFCA, depending on the pathway. Several 'novel' PFAAs that substitute regulated PFAA, and their short-chain degradation products are also persistent and accumulate in the environment where they have been found to contaminate surface, ground- and drinking water and accumulate in plants (EEA, 2019). Following the widespread use of PFAAs, their persistence in the environment and their high long-range transport potential, PFAAs are becoming globally persistent in air, soil, surface and ground waters, biota and humans, making PFAAs emerging contaminants of real global concern (US-EPA, 2019). The well-known and regularly monitored PFAAs (mainly perfluorinated acids) account only for a fraction of the chemical burden from PFAAs present in human blood, the environment and wildlife (Koch et al., 2020).

Little data are available for the precursor substances of PFAAs; their physical-chemical properties and fate are likely to be different in comparison with their degradation products.

I.3.4 Toxicology

PFOS and PFOA are highly absorbed after oral intake (Johnson et al., 1979; Kemper, 2003) and inhalation (Kinney *et al.*, 1989; Olsen *et al.*, 2007). Unlike other persistent organic pollutants (POPs), PFOS and other PFAS have a low affinity for fat. In the body, PFOS and PFOA bind to proteins e.g. in the blood or occurring on the surface of cell membranes, resulting in bioaccumulation in organs, especially those with a high blood flow, such as the liver (DEPA, 2015). PFOS and PFOA are hardly metabolised and slowly eliminated from the body, which adds to the bioaccumulation. Throughout their life, people and animals accumulate PFAS in their bodies. Human biomonitoring has detected a range of PFAS in the blood of European citizens (EEA, 2019; Colles et al., 2020). A considerable proportion of the European population is expected to exceed the tolerable weekly intake due to intake of PFAS from food and drinking water (EFSA, 2018). Post-workshop note: in the meanwhile, EFSA published its 2020 opinion on the risk to human health related to the presence of PFAS substances in food for public consultation until April 2020. The final opinion is expected to be adopted in short notice. In this opinion EFSA updated its risk assessment for PFOS and PFOA and it carried out a risk assessment for the sum of PFOS, PFOA, PFNA and PFHxS (ECHA, 2020).

Of the relatively well-studied PFAS, most are considered moderately to highly toxic, particularly for children’s development (EEA, 2019). Epidemiological studies show that certain PFAS can affect the development and birth weight of children, cause a lower antibody response to vaccines, increase cholesterol levels and trigger behavioral changes (neurotoxicity) (Ahrens *et al.*, 2019). Several PFAS have shown to cause liver toxicity in laboratory animals (Zeilmaker et al., 2018). Not all PFAS cause concern, but for most PFAS their potential harmful effects are unknown (Nature, 2019). In the environment, PFAS mostly occur as mixtures, but current knowledge on the potential ‘cocktail effect’ is limited. There is some knowledge on certain PFAS creating additional toxic effects, acting as transport vectors for other toxicants.

Several scientific institutes have derived (or are developing) reference values for mainly PFOS and PFOA. In 2018, the European Food Safety Authority (EFSA) proposed to lower its reference values for oral intake of PFOS and PFOA (Tolerable Daily Intake, TDI), established in 2008 (Johansson et al., 2009)) based on the negative impact seen in epidemiological studies (EFSA, 2018). For PFAS with less toxicological data, it is proposed to set threshold values by using a relative potency factor (Zeilmaker *et al.*, 2018).

All these uncertainties and knowledge gaps add to the difficulties in setting limit values for drinking water, groundwater, soil and food. For well-documented PFAS it may be achievable but given the high number of known PFAS substances and unknown degradation products, it is impossible to set health-based limits for each PFAS substance.

I.4 Analytical methods

I.4.1 Introduction

Per- and polyfluorinated alkyl substances (PFAS) are a very broad group of chemicals, with more than 4.700 individual compounds, having varying physico-chemical properties. Due to this complexity, and the large number of matrices, which can contain PFAS (e.g., environmental, biological, food and consumer goods), a broad range of analytical techniques have been developed and implemented for their analysis. The techniques used can be separated in three broad groups. Firstly, so called non-specific methods, which focus on measuring the total (organic or extractable) fluorine content present in samples. Secondly, targeted methods, which generally involve chromatography hyphenated to mass spectrometry, are used to quantify levels of specific PFAS in various matrices. Finally, suspect or nontarget screening methods, generally also involve the use chromatography but in this case hyphenated to high-resolution mass spectrometers, are used to for broad screening purposes and identification of unexpected or previously unknown PFAS. In the following chapters, these various types of analyses, the sample preparation protocols used, and their advantages and disadvantages will be presented.

I.4.2 Non-specific methods

Several methods have been developed for the determination of the total organofluorine (TOF) or extractable organofluorine (EOF) content. An overview of these methods was recently published by Koch et al. (2020). A distinction is made between methods for environmental samples and methods for consumer products.

I.4.2.1 Analysis of OF/EOF in environmental samples

Defluorination with sodium biphenyl (SBP) followed by various fluoride detection methods

The most commonly used reagent for defluorination is sodium biphenyl (SBP). The reaction can be carried out at room temperature and acceptable recoveries have been reported for PFCA, (Musijowski et al., 2007, 2010). SBP is deactivated by water and for that reason a carbon-based sorbent has been used to concentrate water samples followed by drying of the sorbent, prior to SBP defluorination. The extract was then analysed by a flow injection system with either fluorimetric or potentiometric detection. Another method added an extra step where the fluoride was, after defluorination, derivatized with tri phenylhydroxysilane (TPSiOH) and analysed by gas chromatography (GC) coupled with a flame ionization detector (FID), electron capture detector (ECD) or mass spectrometer (MS) (Koc et al., 2011). The GC methods showed comparable limits of detection (LoDs) to those of fluorimetric or conductimetric methods (~1-100 µg/L). A drawback of the defluorination methods is the high background contamination of commercial SBP by inorganic fluorine (IF) (Trojanowicz et al., 2011).

19F Nuclear magnetic resonance (NMR) spectroscopy

19F Nuclear magnetic resonance (NMR) spectroscopy has been employed for the quantitative determination of PFAS in surface water (Moody et al., 2001). The identification of PFAS is based on the chemical shift of fluorine atoms under NMR. The quantification of total PFASs was carried out using the peak area of the terminal CF3 groups; a response factor was determined by constructing a calibration curve for a single compound (PFOS) (Moody et al., 2000). NMR is selective and can also determine the degree of branched isomers (Weiner et al, 2013). However due to the low sensitivity of the 19F NMR technique, extensive pre-concentration or prolonged acquisition time (45 or 60 min) are required for environmental samples. The limit of detection (LoD) for surface water is 10 µg/l after 200 times concentration (Moody et al., 2000; Ellis et al., 2000).

Combustion ion chromatography (CIC)

The CIC method has been used in several studies to estimate the amount of extractable organofluorine (EOF) in different matrices after sample extraction (Miyake et al., 2007; Trojanowicz et al., 2011; Wagner et al., 2013; Weiner et al., 2013; Koch et al., 2019; Kärrman et al., 2019; von Abercron et al., 2019). CIC can also be applied for direct measurement of total fluorine (TF) in a sample. In CIC a solid, liquid or gaseous sample is introduced in a pyrolysis tube. By thermal oxidation in a moisturized oxygen stream at a high temperature (900-1050 °C) all organic fluorine (OF) is converted into hydrogen fluoride (HF). The HF is then absorbed in aqueous media (e.g. MilliQ water or hydroxide peroxide) and free anions (e.g. F^-) are determined by ion chromatography followed by conductimetric detection. A drawback of the CIC analysis may be the necessity to remove inorganic fluoride prior to the combustion of organofluorine. Also, a high chloride content may interfere with the fluoride peak during IC analysis caused by displacement of fluoride ions in the column by chloride ions. Additionally, devitrification of the combustion tube (quartz) caused by high levels of alkaline earth elements (e.g. potassium, calcium) may affect the combustion process and lead to an underestimation of OF in the sample. LoD values of 1-100 ng F/L have been reported, after 500-800 times sample concentration (Miyake et al., 2007; Wagner et al., 2013; Kärrman et al. 2019).

Continuum source molecular absorption spectrometry (CS-MAS)

CS-MAS uses online pyrolysis and formation of metal monofluorides (e.g. AlF, InF, or GaF) at high temperatures (Qin et al., 2012). Monofluorides absorb light between 200 and 900 nm. Qin and coworkers combined a reverse phase-high performance liquid chromatograph (RP-HPLC) to both ESI - MS (electrospray ionization mass spectrometry) and CS-MAS in parallel to identify and quantify novel PFASs in environmental samples. The detection was based on the molecular formation of GaF at 1150°C after pyrolysis at 550°C. The absorption from GaF was monitored at 211.248 nm. CS-MAS detected the presence of fluorine in chromatographic peaks, one drawback however is the time needed for online pyrolysis and subsequent fluoride detection (90 s), which is much larger than the chromatographic peak width so that the fluoride signal produced may correspond with several different OF compounds. An LoD of 1 µg/L for groundwater has been reported. Recently, Metzger et al. (2019) optimized the SPE procedure for extraction of fluorinated compounds as well as separation of interfering inorganic fluoride. With an enrichment factor of about 1000 and use of high-resolution–continuum source graphite furnace molecular absorption spectrometry (HR-CS GF MAS) EOF values in the range of about 50–300 ng/L were detected for Moselle and Rhine surface water samples.

Inductively coupled plasma tandem mass-spectrometry (ICP-MS/MS)

Detection of monoatomic fluoride with common ICP-MS instruments is not feasible because of the high ionization potential of fluorine (17.4 eV), which leads to insufficient formation of F^+ ions in the argon plasma, and because of the isobaric interferences from polyatomic ions such as $^{38}Ar^{2+}$, $^{16}O^1H^{3+}$ and $^{18}O^1H^+$ (Jamari et al., 2017; Zhu et al, 2017). Attempts have been made to produce polyatomic fluorine ions (e.g. AlF^{2+}, BaF^+) and to reduce interfering polyatomic ions by utilizing a collision cell in MS/MS mode. These polyatomic fluorine ions are formed by mixing either Ba or Al solution with the sample prior to introduction into the nebulizer (Bayon et al., 1999). OF detection using the formation of BaF^+ was first demonstrated by (Jamari et al., 2017) for a fluoroacetate standard. The method was further developed for PFAS detection by coupling RP-HPLC to ICP-MS/MS for specific fluorine detection and simultaneous detection of target PFASs by ESI-MS (Jamari et al, 2018). Sample extraction prior to instrumental analysis was tested for spiked river water (sub-ppb level). To measure trace levels of fluorine with the ICP-MS/MS instrument, the instrument needs to be equipped with an “s-lens” (extraction lens) instead of the more commonly used “x-lens” (Agilent, 2016). Furthermore, to reach higher sensitivity Jamari et al. argued the need for negative mode ICP-MS/MS.

I.4.2.2 Direct analysis of consumer products

Particle-induced gamma-ray emission spectroscopy (PIGE)

In the context of PFAS screening PIGE was recently adapted for the quantitative determination of TF/OF in textiles and paper (Ritter et al., 2017) and food packaging (Schultes et al., 2019). In PIGE, an ion beam of accelerated protons excites the nucleus of atoms in the sample. Distinctive gamma rays are emitted from fluorine and the emission count is proportional to the number of fluorine atoms on the sample surface (PIGE measures surface material to a depth of up to 250 mm). The method has the advantages of being non-destructive; there are no matrix effects and the sensitivity is acceptable (0.25 µg/cm2 for paper (Ritter et al., 2017), 38 µg/g for food packaging (Schultes et al., 2019)). A high throughput (>20 samples per hour) can be realized. In addition, no sample pre-treatment is needed for the analysis of solid surfaces (at the condition that contribution from IF is negligible) (Robel et al., 2017). Some materials however contain IF such as ammonium hydrogen fluoride or sodium fluoride (e.g. from wood treatment agents) which would lead to overestimation of the OF (Granby et al., 2018). PIGE is commonly used for solid samples, although powders can be compressed into pellets and liquid samples could also be analysed when using a solid support (e.g. sorbent) (Ritter et al., 2017). Very recently PIGE has been proposed for high throughput analysis of OF in water samples, concentrated by SPE (Oasis WAX) or on an activated carbon felt filter (Peaslee, 2020). As PIGE is non-selective between IF and OF, the removal of IF is needed for other complex matrices such as soil, sediment and biota for OF analysis. A major drawback is the need for a neutron activation source and highly specialized instrument operators.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is another direct analysis method for the determination of the fluorine content in consumer products (Tokranov et al., 2018). XPS spectra are acquired by irradiating the surface of a material with an X-ray under high vacuum while simultaneously recording the number of electrons emitted and their kinetic energy, which is specific to certain chemical states (e.g. CF_2 at ~292 eV and CF_3 at ~293 eV groups). The technique can confirm the presence of perfluoroalkyl moieties. It was demonstrated (Tokranov et al., 2018) that CF_2 and CF_3 can be selectively quantified with high resolution C 1s scans (1s atomic orbital). This was further confirmed by F 1s scans showing a peak of ~689 eV corresponding to the binding energy of fluorinated carbon groups (CF2 and CF3). Both scans allow differentiation between IF and OF, which gives XPS an advantage compared to PIGE and instrumental neutron activation analysis (INAA). XPS is limited to a surface depth of 0.01 mm, however, depth profiles have been made by intervals of etching followed by XPS analysis (Tokranov et al., 2018). Contrary to PIGE, XPS instruments are more common in research laboratories. Sensitivity is comparable with PIGE (ppm level).

Instrumental neutron activation analysis (INAA)

INAA is a non-destructive multi-element analysis for both major and trace elements and can perform both qualitative and quantitative identification (Glascock 2019). In INAA a bulk sample is bombarded with neutrons and radioactive isotopes are produced. The radioactive emission and the radioactive decay are element specific and can be used to determine the elements. Recently, Schultes and co-workers (Schultes et al., 2019) applied INAA to food packaging materials to measure their EOF, and the results were comparable with those obtained by PIGE and CIC. However, interferences can occur (from e.g. aluminium present in the tested certified reference material (CRM)), making INAA unsuitable for some matrices. INAA has advantages of being a non-selective high throughput method and can measure bulk samples as well as liquid and solid matrices.

Combustion ion chromatography (CIC)

Direct analysis of consumer products by ion chromatography following combustion and trapping of HF (see above) has been described for food packaging (Schultes et al., 2019) and cosmetic products (Schultes et al., 2018).

I.4.2.3 3 Remarks on non-specific organofluorine methods

Fairly low LoDs can be reached by a number of OF methods, but compared to MS/MS methods these LoDs are still high and extensive sample preconcentration may be needed (e.g. 800 times concentration of water resulted in 1 ng F/L (ppt) LoD with CIC (Miyake, 2007) or an intake of 3 L water, transferred to a GAC felt filter, was needed for an LOD of 50 ng/l (Peaslee, 2020) with PIGE.

- Most non-specific methods measure OF indirectly (CIC: OF is converted to fluoride; GC-MS/HPLC-UV: sample is derivatized; CS-MAS: monofluorides; ICP-MS/MS: polyatomic fluorine ions). Only XPS and 19F-NMR are selective between OF and IF. 19F NMR gives structural information on the compound, but unfortunately, low LoDs can only be reached by extensive preconcentration and prolonged acquisition time.
- Direct sample analysis of OF is only possible with PIGE, XPS, INAA and CIC. PIGE, XPS and INAA are non-destructive, high throughput, solid surface analysis methods, but the methods can also be used for liquids on solid supports. LoD are sufficiently low for consumer product analysis but too high for environmental analysis.
- For non-specific methods, EOF can be determined with appropriate sample extraction after the removal of IF. Bias due to extraction may be introduced. For example, IPE has been shown to extract only a portion of OF and coextraction of inorganic fluorine can occur. The choice of the extraction method should be carefully considered. Extracts of liquid and solid samples can be analysed for OF with CIC, ICP-MS/MS, 19F-NMR, CS-MAS, PIGE and GC-MS.
- Combined techniques such as HPLC-CS-MAS and HPLC-ICP-MS coupled to ESI-MS can allow the simultaneous detection of OF and their identification.
- The CIC method has been utilized in most studies on OF analysis. In order to obtain low detection limits contamination from different instrument parts needs to be identified and reduced.
- In general, non-specific methods are less sensitive and less selective than specific methods. Other fluorinated compounds not belonging to the PFAS group (e.g. fluorinated pharmaceuticals or agrochemicals) will also be quantified as part of the total OF in a sample. The methods will therefore not always be appropriate for checking compliance with regulations specific to OF from PFAS. The methods can be used for screening purposes; positive samples can be subject to target

analysis and mass balances of quantifiable and unknown organofluorine can be calculated. Non-target or suspect screening can be used to identify the unknown fraction.

I.4.3 Drinking Water, groundwater and surface water

I.4.3.1 Sampling and sample preparation

a. Bottle/grab sampling

The sampling procedure is an very important part of the overall analytical approach and has therefore to be defined and validated properly. The sampling of water with the purpose of determining PFAS requires in particular the inclusion of blank samples. Many materials in the lab and field (e.g. sample containers, clothes, water/oil resistant notebooks, sunscreens, etc.) may contain traces of PFAS. It is important to thoroughly check the entire process (sampling, storage, transportation, and laboratory analysis) through the inclusion of appropriate blanks (e.g. field, trip, and labortory blanks) and quality assurance standards to evaluate PFAS contamination or loss.

Therefore, all sampling material must consist of glass, stainless steel, polyether ether ketone (PEEK), polypropylene (PP) or polyethylene (PE). Materials, such as polytetrafluoroethylene (PTFE) or other perfluorinated compounds, must be avoided because of potential leaching of PFAS from the surface. If glass bottles are used, they must be cleaned thoroughly with appropriate washing procedures to remove adsorbed PFAS compounds.

The EN ISO ISO 21675 requires that samples have to be stored in a refrigerator at 5 ± 3 °C and that they have to be analysed within four weeks after sampling. Longer-chained (>C8) PFAS compounds tend to partition out of solution during storage, if not preserved, due to sorption on vessel surfaces and sample particulates. A proper storage study should be conducted during the method validation stage for all analytes. For most PFAS analytical methods involving water samples, it is important to extract the entire sample rather than aliquots because of partitioning/sorption issues. If quantification of PFAS precursor compounds is desired, there is evidence that freezing the sample can aid in preventing the transformation of precursors to end products during sample storage (Woudneh et al., 2019)

Some more general guidance for sampling of organic trace contaminants can be found in the ISO sampling standard EN ISO 5667-3. But PFAS are not mentioned in detail in the current version of the standard.

In contrast to the mentioned ISO and the German DIN method DIN 38407-42, the respective EPA and ASTM methods allow only PP and PE sampling materials/bottles to reduce sorption on glass surfaces. Sample volumes vary between 10 mL and 1000 mL, depending on sample treatment and sensitivity of the equipment.

Link to existing norms (EPA, ISO, ASTM)

The following standard and or harmonised methods are currently available:

- **ASTM D7979 – 19 (11/2019):** Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent, and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS).

- **EPA method 8327:2019:** Validated Test Method 8327: Per-and Polyfluoroalkyl Substances (PFAS) Using External Standard Calibration and Multiple Reaction Monitoring (MRM) Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)
- **EN ISO 5667-3:2019-07:** Water quality - Sampling - Part 3: Preservation and handling of water samples (ISO 5667-3:2018); German version EN ISO 5667-3:2018
- **ISO 21675:2019:** Water quality — Determination of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water — Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS);

  A revision of the existing ISO standard ISO 21675:2019 may be necessary to implement all new requirements for the list of substances mentioned in the Annex III of the DWD. In the current version of the standard not all of the 20 substances from the EU DWD are included. It is recommended to develop in the first place a new CEN standard on the basis of the existing ISO standard (ISO 21675:2019) for targeted determination of at least all 20 PFAS of the DWD. A CEN standard for total PFAS can be developed if there is an agreement on the extraction and detection method and if this method is found sensitive and selective enough to meet the LOQ requirement of the DWD. In all future regulation relating to total PFAS reference should be made to this CEN standard as non-specific determinations only generate comparable results when laboratories stick to the same analytical procedure. Contact shall be made to CEN TC 230 to check whether a mandate can be a possible way forward.
- **EPA METHOD 533 (12/2019):** Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry
- **EPA METHOD 537.1 (12/2018):** Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS);
- **DIN 38407-42:2011-03:** German standard methods for the examination of water, waste water and sludge – Jointly determinable substances (group F) – Part 42: Determination of selected polyfluorinated compounds (PFC) in water – Method using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS) after solid-liquid extraction (F 42).

SPE (anion exchange resins, HLB)

Frequently, very low detection limits for PFAS are necessary because guidance and regulatory values are often in, or near, single ng/L ranges. Thus, for many analytical methods, a concentration step is crucial for achieving low detection limits. Solid phase exchange (SPE) can effectively concentrate PFAS from a water sample by capturing the PFAS which are then eluted from the SPE.

Most current solid-phase extraction (SPE) methods are based on anionic exchange materials, which are conditioned at pH 9, subsequently washed at pH 3 and eluted with a mixture of an organic solvent (methanol or acetonitrile) and ammonia solution. The same procedure can be applied to the non-ionic Oasis HLB SPE-material.

Alternatives

The lack of volatility of PFAS also allows for several other enrichment procedures in addition to SPE. Therefore, the removal of water with freeze-drying or evaporation using microwaves or electric heating can be applied as a concentration step. Another option could be the application of liquid-liquid-extraction, which is accompanied with a high solvent demand and a much greater amount of laboratory work.

b. Passive sampling

Principles

Most analytical methods and monitoring approaches for determining concentrations of PFAS in water still rely on collecting discrete samples which are then pre-concentrated using SPE to ensure that PFAS in the (sub) ng/L range can be detected and quantified. Recently, passive sampling techniques have also been employed for the monitoring of PFAS in aquatic environments. Passive sampling relies on the use of sorbents, which once exposed to the environment, for instance surface waters, selectively accumulate pollutants based on their affinity with the sorbent used. When the passive sampling device is operated in its kinetic regime (i.e. the sorbent is far from an equilibrium with the exposure medium), a linear relationship exists between the mass of pollutant accumulated on the sorbent and the exposure time. Passive samplers allow the user to (i) pre-concentrate pollutants on the sorbent and (ii) calculate time-weighted average concentrations in the exposure medium (Kingston et al., 2000). Since there is no need for a power supply, passive samplers can be employed in remote or difficult to access areas (e.g., groundwater monitoring wells). In order to obtain quantitative results, passive samplers need to be calibrated in the laboratory, or preferably, on site, to determine uptake kinetics which often differ between locations.

Applications

Detection of PFAS, in particular PFOA and PFOS, using passive samplers for routine monitoring of organic chemicals in wastewater was first reported by Alvarez et al. (Alvarez et al., 2007). In this study, authors used the so-called polar organic chemical integrative sampler (POCIS). This passive sampling device consists of a sorbent enclosed in two polyethersulfone membranes and was originally developed for relatively polar compounds (log $K_{ow} < 4$) (Alvarez et al., 2004). A similar passive sampler, using a weak anion exchange sorbent, was developed by Kaserzon et al. (2012) to quantitatively determine a selection of perfluorinated alkylcarboxylates (PFCAs) and sulfonates (PFSAs) in seawater. In this particular study, the samplers were calibrated in the laboratory prior to deployment on site. Satisfactory results were obtained for most PFAS, however, equilibrium for the more polar compounds such as PFOS and PFOA was rapidly attained ($t_{1/2}$ of 2.4 to 13 days, respectively), hence this sampler could only be operated in kinetic-regime mode for a relatively short period of time. Moreover, specific conditions and turbulence in the field affect the mass transfer and accumulation of PFAS, and thus, the uptake kinetics likely differed from those calculated during the laboratory calibration, resulting in inadequate estimation of pollutant concentrations. To correct for these environmental factors performance reference compounds (PRCs) can be added to the sorbent prior to deployment. The dissipation rate of the PRCs from the samplers into the exposure medium is then used to correct for environmental factors, which influence the uptake of target analytes (provided that isotropic transfer conditions apply). It is essential that target analytes and PRCs have similar physico-chemical properties (ISO, 2011). An alternative approach to conventional passive sampling is offered by diffusive gradient in thin films (DGT). The advantage of DGT compared to conventional passive samplers is that the accumulation of pollutants on the sorbent is less sensitive to changes in hydrodynamic conditions in the exposure medium, thus allowing for a more robust and reliable determination of pollutant concentrations (Challis et al., 2016). A dedicated DGT device using XAD18 (polymeric adsorbent resin) as a binding agent was developed and used to quantitatively determine time-weighted concentrations of PFOA and PFOS in aquatic systems (Guan et al., 2018). More recently, passive samplers comprised of a microporous PE tube filled with an anion exchange sorbent were deployed for the monitoring of

PFAS and precursors in groundwater (Kaserzon et al., 2019). These were calibrated on site and detected 17 different PFAS and precursors, including 4:2 FTS and FOSA. Only 12 PFAS were reportedly detected using conventional grab/bottle samples. With regards to standardized methods, the ISO 5667 norm contains guidance about the use of passive samplers for sampling organic compounds in surface waters (ISO, 2011). The latter provides information about the principles of passive sampling and the correct handling of samplers, for instance with regards to blanks and controls. However, it is focused on surface waters and thus does not provide information about the deployment of passive samplers for groundwater.

In 2016, a novel sorbent based on a porous cyclodextrin polymer called DEXSORB+, was developed (Li et al., 2016). The polymer outperforms many conventional adsorbents for the removal of organic chemicals from water at environmentally relevant concentrations (Alsbaiee et al., 2016). The polymer is derived sustainably from cornstarch, and characterization studies demonstrate that it exhibits rapid adsorption kinetics, excludes interactions with natural organic matter, and can be regenerated without a loss in performance. The polymeric sorbent has successfully been used in passive sampling of surface water and drinking water. In 2018, DEXSORB+ has been developed specifically to target PFAS compounds (where crosslinkers of the cyclodextrin polymer are substituted by loaded compounds with high affinity for PFAS) (Diego et al., 2019). More recently, since February 2020, the DEXSORB+ sorbent has been implemented in a flux-based passive sampling method technology (iFLUX, 2020). The technology consists of a modular passive flux sampler that provides simultaneous in situ point determinations of a time-averaged target compound mass flux and water flux (Verreydt et al., 2012). The sampler is typically installed in a monitoring well where it intercepts the groundwater flow and captures the compounds of interest. The sampler consists of permeable cartridges which are each packed with a specific sorbent matrix. The sorbent matrix of the water flux cartridge is impregnated with known amounts of water soluble resident tracers. These tracers are leached from the matrix at rates proportional to the groundwater flux. The measurements of the contaminants and the remaining resident tracer are used to determine groundwater and target compound fluxes (Verreydt et al., 2014). Exposure times range from 1 week to 6 months, depending on the expected concentration and groundwater flow velocity. The iFLUX sampler technology has been tested at several field projects with promising results. The PFAS cartridge is currently validated for 14 PFAS compounds on a ng/L level, but since validation of more PFAS compounds is ongoing, the list of PFAS will likely expand.

c. Direct injection

Although direct injection methods (e.g. EPA SW846-8327 and ASTM D7979) use direct injection of water samples and LC/MS/MS detection, the existing and/or proposed limit values and performance data of the EU water directives are possibly going to be lower than detection limits for direct injection methods. The EQS (environmental quality standard) for PFOS in inland surface waters is for example at a low level of 130 pg/L. Depending on the LC/MS/MS instrumentation, detection limits for most PFAS analytes using direct injection methods are in the 1-10 ng/L range.

This means that currently an appropriate enrichment of water samples is still necessary to achieve a determination level that fits to the limit values. The latest developments of mass spectrometers (MS/MS) with enhanced analytical devices (HPLC) and high sensitivity detectors will allow lower detection limits in the near future.

d. Background / blank considerations

LC/MS/MS instruments commonly consists of PTFE, so alternative materials (e.g. polyetheretherketone (PEEK) tubing) have to be used or an appropriate purging of components must be applied.

Interferences arising directly from the analytical instruments can be significant for unmodified commercial LC systems because many parts may contain PTFE and other fluoropolymers. Hence, it is necessary to check for possible blank contamination from individual parts of the analytical system, such as tubing, solvent inlet filters, valve seals and the degassing equipment, and replace these with materials such as stainless steel and PEEK, where possible.

Furthermore, LC-vial caps have to be free of fluoropolymer material. Efforts should be taken to minimize all background levels in procedural blank materials such that the procedural blank, including the instrumental blank, is at least 10-fold below the reporting limit.

I.4.3.2 Targeted methods

a. LC-MS/MS methods

A recent review of the determination of PFAS has been published by (Nakayama et al., 2019). In the past decade, targeted instrumental analysis of PFAS in aquatic matrices has not changed substantially. Most studies used (U)HPLC-MS/MS, operated in multiple reaction monitoring mode (MRM), although some studies used HRMS such as Orbitrap- or time-of-flight (TOF)-MS for quantitative and qualitative analyses (Concha-Graña et al. 2018; Tröger et al., 2018). MS is generally operated in ESI-negative mode since most target PFAS are anionic. For neutral PFAS such as FASAs, FASEs and FTOHs, atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionisation (APPI) have also been tested (Ayala-Cabrera et al., 2018). Signal suppression (or enhancement) by coeluting matrix constituents necessitates the use of appropriate internal standards or quantification by matrix matched calibration (Nakayama et al., 2019).

Water samples are generally extracted by solid phase extraction (SPE) on HLB or WAX type cartridges, but also ion pair extraction (IPE) and direct injection have been used. Recovery issues for short-chain resp. very long chain PFAS may arise depending on the chosen extraction method (non-quantitative extraction of very short-chain PFAS by IPE and non-quantitative desorption of very long chain PFAS from SPE adsorbent).

To eliminate instrumental blanks, the use of an in-line isolator column is recommended (see e.g. EPA method 8327). The isolator column is designed to trap PFC contaminants that may be present in the solvent delivery system. The isolator column is installed in the flow path between the mobile phase solvents mixer and the injector. During analysis, the isolator column retains the background PFAS, separating them from the analytes of interest.

Existing international standards for the analysis of water samples are ISO 21675, EPA 537.1 and ASTM D7979-19:

- **ISO 21675:2019:** The scope of the method is drinking, natural and waste waters. Analytes determined are C4-C18-PFCAs, C4-C10 PFSAs, FOSA, MeFOSA, EtFOSA, FOSAA, MeFOSAA, EtFOSAA, 6:2 FTS, 8:2 FTS, 9Cl-PF3ONS, 8:2 FTUCA, 8:2 diPAP, HFPO-DA, ADONA (total of 30 PFAS). Extraction is carried out by SPE on a copolymer-based weak anion exchanger (e.g. Oasis WAX);

FFAS are eluted with methanol and alkaline methanol (0.1% NH3). The extract is injected into an LC-MS/MS system; typically a C18 column is used with a water/methanol/ammonium acetate mobile phase gradient. Quantification is done by the internal standard method (isotope dilution).

- **EPA method 537.1:2018:** The scope of the method is drinking water. Analytes determined are C4-C14 PFCAs, C4-C8 PFSAs, MeFOSAA, EtFOSAA, 11Cl-PF3OUdNS, 9Cl-PF3ONS, 8:2 FTUCA, 8:2 diPAP, HFPO-DA, ADONA (total of 18 PFAS). Extraction is carried out by SPE on a styrene-divinyl benzene sorbent phase ; FFAS are eluted with methanol. The extract is injected into an LC-MS/MS system, equipped with a C18 column. A water/methanol/ammonium acetate mobile phase gradient is used. Quantification is done by the internal standard method. Limits of quantification range from 0.53-6.3 ng/l.
- **EPA method 8327:2019**: The scope of the method is groundwater, surface water and wastewater. The list of target PFAS has been extended to 24 compounds; PFNS, PFDS, 4:2 FTS, 6:2 FTS, 8:2 FTS and FOSA have been added. Water samples are diluted 1:1 with methanol, filtered, and acetic acid (0.1% by volume) is added to adjust pH to ~3 – 4. Acetic acid is added primarily because it improved sensitivity for some target analytes. Samples are then analysed by LC-MS/MS using external standard calibration.
- **ASTM 7979-19:2019:** The scope of the method is non-drinking water (surface water, influent and effluent). Analytes determined are C4-C14 PFCAs, C4-C8 PFSAs, PFECHS; 6:2 FTA, 8:2 FTA, 10:2 FTA, 6:2 FTUA and 8:2 FTUA (total of 21 PFAS). The analysis is done by direct injection (after 1:1 dilution with methanol) into an LC-MS/MS system, equipped with a Phenyl-exyl column. A water/methanol/ammonium acetate mobile phase gradient is used. Quantification is done by the external or internal standard method. For most compounds a limit of quantification <10 ng/l applies.
- **ISO 25101:2009:** Water quality - Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) - Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry.
- **DIN 38407-42:2011-03:** German standard methods for the examination of water, waste water and sludge – Jointly determinable substances (group F) – Part 42: Determination of selected polyfluorinated compounds (PFC) in water – Method using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS) after solid-liquid extraction (F 42).
- **EPA METHOD 533 (12/2019):** Determination of Per- and Polyfluoroalkyl Aubstances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry.

A revision of the existing ISO standard ISO 21675:2019 may be necessary to implement all new requirements for the list of substances mentioned in the Annex III of the DWD. In the current version of the standard not all of the 20 substances from the EU DWD are included. Contact shall be made to CEN TC 230 to check whether a mandate can be a possible way forward.

b. Reference materials

Currently, there are only 18 reference materials from the list of 20 PFAS in Annex III of the DWD commercially available on the market. The two missing reference materials are: perfluoroundecane sulfonic acid and perfluorotridecane sulfonic acid. It can be expected that the providers of reference materials will take this message on board.

Reference substances and standards for target analysis and mass-labelled reference standards can be purchased from Wellington Laboratories and Cambridge Isotope Laboratories. Some native per- and polyfluorinated compounds can also be purchased from other suppliers (e.g. Sigma-Aldrich and Supelco).

There is a need for more standard reference materials (SRMs) that include certified values of a variety of PFAS compounds in relevant environmental matrices (e.g. drinking water, wastewater, solids). The US National Institute of Standards and Technology provides some SRMs (see: https://www-s.nist.gov/srmors/viewTable.cfm?tableid=247). JRC Geel provides IRMM-428 (PFASs in water). SRMs can play a valuable role in ensuring the quality of PFAS analytical data.

c. Combination with Total Oxidisable Precursor assay (TOPA or TOP assay)

The TOP assay was originally developed by Houtz and Sedlak (Houtz et al., 2012). A greater PFAS detection range was realised, but only for substances that can be oxidised by hydroxyl radicals to specific perfluoroalkyl acids (PFAAs). The TOP assay (TOPA) is a method to reveal the presence of any PFCA and PFSA precursors, and several studies have used this approach for surface-, ground- and wastewater (Dauchy et al., 2017; Houtz et al., 2013; Houtz et al., 2016; Houtz et al., 2018; Casson et al., 2018). The method converts PFAA precursors (e.g. N-ethyl perfluorooctane sulfonamidoethanol or fluorotelomer based compounds, such as 6:2 FTSA) into the persistent PFAAs via oxidation using hydroxyl radicals (Houtz et al., 2012; Rhoads et al., 2008). The concentrations of common target PFASs are measured before and after oxidation, and if PFAA precursors are present in the sample, the measured PFAA concentrations will increase after oxidation. The development of a reliable TOPA method can be challenging as the amounts of the base and oxidizing agent (mainly persulfate) need to be optimized for each sample type. Oxidation conversion yields are also PFAS compound dependent (Martin et al., 2019). The sample matrix can affect the pH and/or react with the hydroxyl radicals, which may slow down the persulfate thermolysis or lead to non-quantitative conversion. One option to reduce these matrix effects is to conduct TOPA after sample extraction (Houtz et al., 2013), but additional biases may be introduced as some PFAA precursors may not be extracted from the sample. Another approach can be the addition of a ^{13}C labelled precursor. The reaction is deemed to be complete if all the added mass labelled precursor is consumed. The third approach could be to perform the TOPA in duplicate with one of the extracts being 10 times diluted. If the measured levels of PFAA between the original and diluted samples are the same, then the oxidation process is presumed to be completed. It is clear that a TOPA optimisation study should be conducted prior to the development of a standard.

I.4.3.3 Non-targeted methods

a. Analytical techniques

Suspect and non-target screening (NTS) generally involve the use of high-resolution mass spectrometers (HRMS), such as time-of-flight (TOF) or Orbitrap mass spectrometers. The fast scanning rates, which allow hyphenation with chromatography, and high sensitivity enable the acquisition of accurate mass measurements of trace level compounds in full-scan mode. Hybrid instruments, such as quadrupole-TOF (Q-TOF) and linear ion trap-orbitrap (LTQ-Orbitrap) instruments, have become increasingly common in laboratories as they allow for accurate-mass acquisition of both full-spectrum and product-ion spectrum data. The use of ion mobility spectrometry (IMS) coupled to HRMS, in particular Q-TOF instruments, for the characterization of PFAS and their isomers in aqueous samples has recently also been reported (Dodds et al., 2020). IMS allows for a further separation of ions based on their size, shape and charge in the gas form, thus enabling the discrimination of isomeric, isobaric and, potentially, enantiomeric compounds (Liu et al., 2019). Promising results suggests that IMS can be a useful complement to the separation and identification of PFAS isomers in complex matrices (Dodds et al., 2020). The advantage of NTS compared to conventional target (low-resolution) methods, is that it allows for broad screening of samples without prior knowledge about target analytes. Unexpected or previously unknown compounds can hence be detected and identified. However, NTS analyses are quite complex and require a high degree of analytical expertise. If an unknown compound is tentatively identified, it should be confirmed with an available standard. If a standard is not available, the analyst must rely on fragmentation data and/or comparisons with known compounds/fragments of similar mass to elucidate the structure.

b. Sample preparation and analysis

Although sample pre-processing always bears the risk of losing relevant analytes, NTS for PFAS monitoring in water samples has often been combined with a pre-concentration step due to the expected low concentrations. Most commonly, solid-phase extraction (SPE) protocols used for the extraction of known PFAS (ISO, 2019; Shoemaker & Tettenhorst, 2018) have been implemented. These generally make use of mixed-mode weak anion exchange or hydrophilic-lipophilic balance sorbents (Liu et al., 2019). NTS methods for PFAS generally involve hyphenation with liquid chromatography (LC) to improve separation between structural isomers and increase chances of successful detection/identification. C18 chromatographic columns have been the most widely implemented analytical columns for the separation of PFAS, in both targeted methods and NTS (Liu et al., 2019). Recent studies also used alternative mixed-mode columns, which offer both reversed-phase and weak anion exchange properties, for the separation of smaller and more polar fluorinated compounds (e.g., trifluoromethanesulfonic acid (F_3-MSA)) (Vughs et al., 2019). NTS using HRMS instruments has generally been carried out in negative ionization mode, although some studies reported the identification of cationic and/or zwitterionic compounds using positive electrospray ionization mode (Place & Field, 2012).

c. Data analysis and workflows

Detection and identification of PFAS using NTS generally involves (i) the acquisition of full-scan spectra, (ii) selection of potentially relevant features, (iii) assigning plausible molecular formulas, (iv) product-ion acquisition and eventually (v) confirmation of the compound by analyzing a reference standard (if available) or tentatively propose a structure. Strategies for the identification of PFAS during NTS involve various approaches. Mass defect filtering can be used to detect PFAS features in full-scan spectra. In fact, due to the replacement of hydrogen atoms with fluorine, PFAS generally have low or negative mass defects. Furthermore, homologous series of PFAS can be identified using, for example, CF_2-normalized Kendrick's mass defect plots. Combined with negative mass defects, this approach has been used in various studies to identify PFAS using HRMS instruments (Newton et al., 2017). Investigation of diagnostic fragments (e.g., $C_2F_5^-$) in product-ion spectra can also help detect the presence of PFAS. Selection of precursor ions for further fragmentation has been performed mainly using two modes, namely data-dependent acquisition (DDA) and data-independent acquisition (DIA). Confirmation of the identified PFAS is achieved by comparison with a certified reference standard or by using nuclear magnetic resonance (NMR) spectroscopy. When this is not possible, and structures are being proposed based on the acquired mass spectral information, degrees of uncertainty based on the level of information available, should be expressed. In the case of PFAS, confidence levels ranging from 1 (confirmed structure) to 5 (only an exact mass of interest), as suggested by Schymanski et al. (Schymanski et al., 2014), have often been used. Due to the lack of reference standards, most publications in the field of PFAS report confidence levels between 2 and 3 (Liu et al., 2019).

d. Databases and in-silico tools

Suspect screening approaches are often used to analyse PFAS in environmental samples, including water. These methods make use of existing databases compiling known PFAS, such as those listed by the NORMAN Network (NORMAN Network, 2020) or the US EPA (US EPA, 2020). These databases compile lists of known PFAS, their molecular formula, CAS number and so-called MS-ready SMILES, which can be used to directly derive the structure of the compound of interest in its desalted/neutral form. In certain cases, retention times are also reported, which can further help with the (tentative) identification. Furthermore, databases containing MS/MS data are also available (*MassBank | MassBank Europe Mass Spectral DataBase*, 2020; *MzCloud – Advanced Mass Spectral Database*, 2020) and contain information about some PFAS useful for tentative identification. Finally, *in-silico* tools, which can be used to predict fragmentation patterns (such as MetFrag, CFM-ID or Sirius (*CFM-ID*, 2020; *MetFrag—Home*, 2020; "SIRIUS," 2015)) or retention times (Aalizadeh et al., 2019; Bade et al., 2015) are also available to analysts trying to confirm the structure of detected PFAS. These tools are particularly useful when reference materials are not available.

e. General consideration about NTS

When compared to conventional targeted methods, NTS has the advantage of allowing for broad spectrum screening without prior knowledge about the analytes present. This is particularly useful in the case of PFAS as a large number of chemicals have been and still are being used. Most of these are not available as reference standards, hence limiting the development of broad multi-residue targeted methods. However, NTS is not straightforward and requires skilled personnel, in particular to elucidate the structure of detected compounds. Yet advances in software and workflows in the coming years will further facilitate the use of HRMS instruments, hence promoting the use of NTS even further. The use of non-specific analysis (e.g., OF/EOF), as a preliminary screening, followed by further in-depth investigation with NTS of samples which showed substantial levels of fluorine has been suggested to improve throughput and reduce the number of samples to be processed in NTS (see §I.4.5, Comprhensive workflows; Koch et al., 2020).

I.4.4 Food, crops, feed packaging

I.4.4.1 PFAS contamination in food, crops and packaging materials

Uptake of PFAS through food consumption is one of the main exposure routes for humans (Ericson et al., 2008). Food contamination is thought to occur mainly through two processes, namely (i) bioaccumulation in terrestrial and aquatic food chain and (ii) transfer from food contact material during production and packaging (EFSA Panel on Contaminants in the Food Chain (CONTAM) et al., 2018). In fact, because of their ability to repel oil and water, PFAS have been used in consumer products, including food packaging and cooking ware (Sunderland et al., 2019). Furthermore, the widespread use of PFAS in consumer products and industry means that these will enter the waste stream, will be transported to wastewater treatment plants (WWTPs), making the latter point sources of PFAS contamination (EFSA Panel on Contaminants in the Food Chain (CONTAM) et al., 2018). Besides the risks of contaminating drinking water sources (e.g., receiving waters such as rivers and lakes), sewage sludge or biosolids from WWTPs can be a source of PFAS contamination because it is often used as fertilizer in agriculture. Multiple studies have in fact found PFAS in biosolids (Sepulvado et al., 2011), from where they can be taken up by crops as well as farm animals, thus resulting in contamination of animal products such as meat, dairy and eggs (EFSA Panel on Contaminants in the Food Chain (CONTAM) et al., 2018).

I.4.4.2 Analytical techniques

With regards to analysis of PFAS in food, and in particular PFCAs and PFSAs, LC-MS/MS with electrospray ionisation (ESI) has become the most widespread analytical technique (Jahnke & Berger, 2009). Although still used for neutral and volatile compounds, GC-MS (with or without prior derivatisation) is less common. With regard to OF/EOF measurements, various techniques have been reported in the literature. In particular, combustion ion chromatography (CIC), Particle-Induced Gamma Ray Emission (PIGE) spectroscopy and instrumental neutron activation analysis (INAA) have recently been reviewed and compared specifically for the analysis of food contact materials (Schultes et al., 2019). PIGE and INAA had the advantage of being non-destructive while highest sensitivity was achieved using CIC. However, INAA could not be used for the measurement of materials with high aluminium content. Other techniques, such as inductively coupled plasma (ICP) MS, molecular absorption spectroscopy (Qin et al., 2012) and X-ray photoelectron spectroscopy, 19-fluorine nuclear magnetic resonance spectroscopy (19F-NMR), continuum source molecular absorption spectrometry (CS-MAS), have also been reported for the analysis of total fluorine. However, only X-ray photoelectron spectroscopy has been used to measure fluorine in consumer products and only 19F-NMR can distinguish between organic and inorganic fluorine.

I.4.4.3 Sample preparation protocols

One of the main challenges in analysing PFAS in food, in particular of non-animal origin, is that PFAS are typically present in very low concentrations (i.e., pg/g) (Tittlemier et al., 2007). Due to the low concentrations, contamination in procedural blanks can adversely affect limits of detection when trying to detect trace level compounds (Fromme et al., 2007). Freeze-drying is often used prior to sample processing due to the high-water content, after which samples are stored at -20°C until further processing and analysis. Extraction of PFAAs from food is normally carried out using solid-liquid extraction (SLE) or ion-pairing extraction (IPE). The latter technique has been used for the extraction of PFAAs from vegetables, meat products (e.g., livestock, poultry) and egg using methyl tert-butyl ether, followed by an additional clean-up using SPE (e.g., Fluorisil and ENVI-carb) (Taniyasu et al., 2005; Vestergren et al., 2012; Zhang et al., 2017). SLE generally involves the use of a medium polarity solvent (e.g., acetonitrile or methanol) and has been used in particular for matrices with a high fat content (Berger et al., 2009). An additional clean-up of the extract using SPE is generally used also after SLE (Weiss et al., 2013). Other PFAS, such as perfluoroalkane sulfonamides (FASAs), ethyl perfluoroalkane sulfonamides (EtFASAs) and Ethyl perfluoroalkane sulfonamido ethanols (EtFASEs) have also been extracted using this method (Lacina et al., 2011). SLE with methanol followed by clean-up with EnviCarb, has also been used for the analysis of extractable organic fluorine from food contact materials using CIC, PIGE and INAA (Schultes et al., 2019). Similarly, a method involving the use of methanol and formic acid, followed by QuEChERS extraction has been recently proposed by the US FDA for the analysis of 16 PFAS, including emerging ones such as NaDONA and HFPO-DA (GenX chemical), in bread, lettuce, milk and fish (Genualdi & deJager, 2019). All protocols used for extraction of PFAS from food generally involve the use of isotopically labelled internal standards as well as recovery standards (Weiss et al., 2013). SLE is also often employed for the extraction of PFAS from food contact materials. In particular, methanol or solutions with sodium hydroxide, acetonitrile and ethyl acetate have been commonly used (Szczepańska et al., 2018). The use of pressurized liquid extraction has also been reported as an alternative technique to extract from PFAS from various food packaging (Zafeiraki et al., 2014). Alternatively, ultrasonic probe-assisted extraction (UPAE) using methanol, without any additional clean-up except for filtration and evaporation under a nitrogen stream, has also been successfully implemented for the analysis PFAS and precursors in packaging materials (Zabaleta et al., 2016).

I.4.5 Other matrices

I.4.5.1 Abiotic environmental solid matrices

A summary of recent publications is given in Annex I.1 – Summary of recent publications on analysis of PFAS in abiotic environmental matrices. A review on determinations of PFAS in abiotic matrices has recently been published by (Nakayama et al., 2019).

Sampling tools for sediment, soil and sewage sludge are pre-cleaned before use. Samples are placed in a HDPE or PP bag, bottle or tube and refrigerated at 4°C or frozen at -20°C until analysis. Prior to extraction, samples are generally freeze-, air- or vacuum-dried, then sieved and homogenised. Dust is often collected from houses, offices and shops to estimate human exposure to PFAS. Dust collection is generally carried out using a vacuum cleaner.

Soil, sediment, sludge and dust samples are extracted with soxhlet, pressurized liquid extraction (PLE) or by vortexing/shaking/ultrasonication (van Leeuwen et al., 2007; Jahnke et al., 2009). The usual sample intake is 0.1 g for dust and 1-5 g for other matrices. Mass-labelled PFAS are generally added to the sample as internal or surrogate standards prior to extraction. Extraction solvents are methanol, alkaline methanol and, in a few studies, acidified methanol (Codling et al., 2018; Joerss et al., 2019;). Sometimes acetonitrile is used in combination with water or methanol (Rankin et al., 2016; Guo et al., 2016; Ruan et al., 2015). Sample extracts are cleaned up on graphite carbon or SPE cartridges or by ion pair extraction (IPE). The predominant combination is shaking/ultrasonication followed by centrifugation and cleanup of the supernatant on ENVI-Carb or an SPE cartridge (e.g., OASIS WAX, OASIS HLB or C18) under neutral or basic conditions. The sample extraction procedure should be capable of capturing PFAS with diverse properties, especially highly hydrophobic compounds, cations and zwitterions, which strongly adsorb to solid matrices; methanol with ammonium acetate provided the best option for accurate results (Munoz et al., 2018). Dust samples are analysed for both volatile (neutral) and non-volatile PFAS. These methods tend to be more complex and involve fractionating with different extracting solvents and/or repeated extraction steps (Lankova et al., 2015, Eriksson et al., 2015; Winkens et al., 2018).

GC-PCI-MS is the predominant detection method for volatile PFAS in solids. For ionic PFAS, instruments are similar to those used for analysis of aqueous matrices by (U)HPLC-ESI(-)-MS/MS. A few studies used Orbitrap-MS or TOF-MS (Ruan et al., 2015; Munoz et al., 2016;). LC conditions are generally similar to those adopted for aqueous matrices; C18 columns and water/methanol/ammonium acetate mobile phase gradients are most commonly used. In some studies the mobile phase is acidified and in other acetonitrile is used instead of methanol. LoD and LoQ (Limit of Quantification) values are dependent of matrix and PFAS compound and vary from <0.01 to 10 µg/kg dw.

Existing standards for abiotic matrices are ASTM D7968-17a and DIN 38414-14:

- **ASTM D7968-17a:** The scope of the method is soil. The method is applicable to C4-C14 PFCA, C4-C8 PFSA, PFECHS, FHpPA, 6:2 FTA, 8:2 FTA, 10:2 FTA, 2H-perfluoro-2-decenoic acid and 2H-perfluoro-2-octenoic acid in concentrations above 0.025 µg/kg ds. Samples are vortexed and shaken with methanol/water and methanol/water/NH_3. No cleanup is applied. PFAS are separated on a phenyl hexyl column with a water/acetonitrile/NH_4Ac gradient and detected in MRM mode. Quantification is done by the external standard method.
- **DIN 38414-14:** The scope of the method is soil, sediment and sludge; the method is limited to C4-C10 PFCA and C4-C8 PFSA, with a quantification limit of 10 µg/kg dw. Samples are sonicated with methanol. Clean up on SPE-WAX followed by elution with methanol (0.1% NH_3) is only applied for sludge. PFAS are separated on a C18 column with a water/methanol/NH_4Ac(/HAc) gradient and detected in MRM mode. Quantification is done by the internal or external standard method.

I.4.5.2 Air samples

Recent analytical methods for PFAS outdoor and indoor air samples and airborne particulate matter are summarised in Annex I.2 – Summary of recent publications on analysis of PFAS in air samples.

Outdoor and indoor air samples are usually collected by PUF/XAD/PUF using a high-volume air sampler, or by an SPE cartridge using a low-volume air sampler (Martin 2002, Wong 2018). To sample neutral PFAS in air ISOLUTE ENV+ and Oasis HLB have been widely used. A two-layer SPE consisting of higher carbon (HC)-C18 and weak anion exchange (WAX) material was developed and applied to capture diverse classes of PFAS (Yao, 2018). Typical air sampling volume are 300-2,000 m3 for outdoor air and 20-200 m3 for indoor air (van Leeuwen, 2007]. In recent studies sampling volumes for indoor air have decreased to 0.2-8 m3 (Yao, 2018; Padilla-Sanchez, 2017). Particulate matter is generally collected on a glass- or quartz-fibre filter (Guo 2018; Wong, 2018,). For passive air sampling of PFAS solvent-impregnated polyurethane foam (SIP), developed by Shoeib et al. (2008), has been widely used. The detection of low levels of PFAS in air requires the elimination of background contamination during washing/preconditioning, storage and transport of samplers. To remove contaminants XAD and PUF absorbents are rinsed before use by Soxhlet extraction with organic solvents. SPE cartridges are generally washed with methanol or ethyl acetate and dried with high-purity nitrogen gas before use. After sampling, samplers are typically placed in a polypropylene (PP) container or wrapped with aluminium foil and stored at -20°C until analysis (Martin, 2002; van Leeuwen, 2007; Padilla-Sanchez, 2017; Yao, 2018).

PFAS collected on XAD and PUF are usually extracted with solvents such as acetone and petroleum ether using Soxhlet (Martin 2002, Shoeib 2008) or pressurised liquid extraction (PLE) (Wong 2018). Neutral PFAS collected on HLB or ISOLUTE ENV+ cartridges are generally eluted with methanol (Padilla-Sanchez 2017), whereas ionic PFAS such as PFCAs, PFSAs and diPAPs collected on a WAX cartridge are usually eluted with methanol containing ammonia (Yao, 2018). Soxhlet extraction is also applied for the extraction of PFAS collected on SIP, with appropriate organic solvents such as acetone/petroleum ether (1:1), methanol or ethyl acetate; also cold column extraction with ethyl acetate is applied (Li, 2011; Tian, 2018). Additional clean-up by ENVI-Carb is employed in some cases (Li, 2011; Tian, 2018). Airborne particulate matter collected on filters is generally subjected to Soxhlet extraction with dichloromethane or ultrasonic extraction with methanol (Guo, 2018; Lu, 2018).

Neutral PFAS are usually detected by GC-MS with either electron ionisation (EI) or chemical ionisation (CI) in selected ion monitoring (SIM) mode (Shoeib, 2008; Li, 2011; Yao, 2018,). In most studies a WAX column such as DB-WAX is employed (Martin, 2002; Padilla-Sanchez, 2017; Lu, 2018; Tian, 2018). Ionic PFAS are detected with (U)HPLC-MS/MS with electrospray ionisation (ESI) (Li, 2011; Tian, 2018; Yao, 2018). The method is similar to that used for water samples. Ionic PFAS are generally separated by a C18 column with a water/methanol/acetonitrile gradient containing 5-50 mM ammonium acetate.

Sampling issues are the main challenge when monitoring PFAS in air. Comparison of global studies is hampered by the absence of a standardised methodology. Therefore, the development of a globally applicable sampling method and its standardisation is urgently needed.

I.4.5.3 Products for consumer, professional or industrial use

Recent analytical methods for PFAS in consumer products are summarised in Annex I.3 – Summary of recent publications on analysis of PFAS in consumer products. Diverse consumer products have been analysed: waterproofing and textile finishing agents, fabrics, leather, non-stick baking ware, paints, fire-fighting foams, food contact materials, cleaning agents, lubricants, car and ski waxes, glues, cosmetic products, building materials, etc. Solid samples are generally extracted by sonication with methanol or in case of cosmetic products with alkaline methanol (Schultes et al., 2018); for FTOHs also ethyl acetate has been used (Herzke et al., 2012). Liquid samples are diluted and sonicated with methanol or subject to ion pair extraction with TBAS and MTBE (Kotthoff et al., 2015). Clean up on active carbon or by SPE on a weak anion exchanger is sometimes applied. In case of ski and other waxes aliphatic hydrocarbons and esters can be removed by hexane/methanol partitioning. Neutral PFAS (FTOH) are analysed by GC-PCI-MS or GC-ECNI-MS (Mumtaz et al., 2019). Ionic PFAS are generally analysed by (U)HPLC-ESI(-)-MS/MS, but also HPLC-TOF-MS has been used (Herzke et al., 2012). Results are expressed in µg/kg, µg/l or µg/m^2 depending on sample type.

A CEN technical specification for the determination of extractable PFOS in coated and impregnated solid articles, liquids and fire-fighting foams has been published (CEN/TS 15968:2010). The method is applicable to PFOS, FOSA, MeFOSA, EtFOSA, MeFOSE, EtFOSE. Textile, fabrics, leather and paper are extracted in an ultrasonic bath after addition of internal standards. Clean-up on active carbon or by SPE can be applied. Fire-fighting foams are diluted with water or methanol. Extracts are analysed by HPLC-ESI(-)-MS/MS. It is expected that the method can be adapted easily to other PFAS. The limit of quantification will depend on sample intake, volume of extraction solvent and dilution factor. Typically for solid samples an LOQ <10 ug/kg can be achieved.

To improve comparability of laboratory results EN standards for the determination of ionic and neutral PFAS in consumer products should be developed.

I.4.5.4 Human samples

A summary of recent publications is given in Annex I.4 – Summary of recent publications on analysis of PFAS in human matrices.

Plasma, serum and breast milk represent the major target matrices for human biomonitoring, but some recent studies are also focusing on non-invasive samples such as urine, hair and nail (e.g. Guo, 2013; Wang, 2018). Blood and urine are collected in a PP tube or bottle and stored at -20°C until analysis. Nail and hair samples are collected using pre-cleaned nail cutter or scissors and stored in a PP centrifuge tube at room temperature. Nail and hair samples are often washed with water or acetone to remove external contamination and dried before analysis.

Various pretreatment and extraction methods such as alkaline digestion, acetonitrile protein precipitation, SPE, LLE and IPE have been used. Clean up can be done on a weak anion exchanger (e.g. Oasis WAX) (Kärrman, 2007; Guo, 2013; Wang, 2018). Removal of lipid components can be done by sample freezing after SPE clean-up (Gao 2018) or by graphite carbon (e.g. ENVI-Carb) clean-up (Hanssen, 2013; Berg 2014), but also addition of 1-methyl piperazine to the LC-MS/MS mobile phase (Gao, 2018) has been suggested. A recent trend for human biomonitoring is the simplification of pre-treatment steps and employment of high-throughput on-line SPE techniques and SPE well plates. The sample volume required for PFAS analysis in blood has decreased during the last decade from ml to tens of µl.

(U)HPLC-MS/MS is mainly used for biological sample analysis. The instrumental method is similar to that used for water samples. Sufficient pretreatment is required to eliminate matrix suppression/enhancement by lipophilic components in the samples. Improved quantitation results are obtained using isotope dilution and matrix-matched calibration curve approaches. However not all isotope labelled reference standards are currently available and matrices representative of all samples are also not available. The most promising approach for minimising matrix effects is the use of very sensitive instruments and reducing the volume of the initial sample and the amount of extract injected. Typical LoQ values for serum are 0.01-0.1 ng/ml depending on PFAS compound. PFOS, PFOA, PFNA and PFHxS are the predominant PFAS found in human samples.

I.4.5 Comprehensive workflows

A workflow for a comprehensive organofluorine assessment has been proposed by Koch et al. (2020) and is shown below (Figure 2). As can be seen, this comprehensive workflow involves the use of multiple techniques to assess the total PFAS content of samples and, eventually, identify unexpected or unknown PFAS. Non-specific techniques are used as a first step to screen samples for their (organic or extractable) fluorine content. Samples of interest, i.e. showing high fluorine concentrations, are then selected for further analyses using targeted methods. The combination of non-specific and targeted methods can then be used to assess mass balances. For this purpose, the inclusion of the TOPA could also be considered. Finally, identification of unexpected or previously unknown PFAS in samples of interest can be carried out using suspect and NTS. The implementation of this battery of analytical techniques should provide a more thorough understanding about the amounts and typology of PFAS present in various sample types.

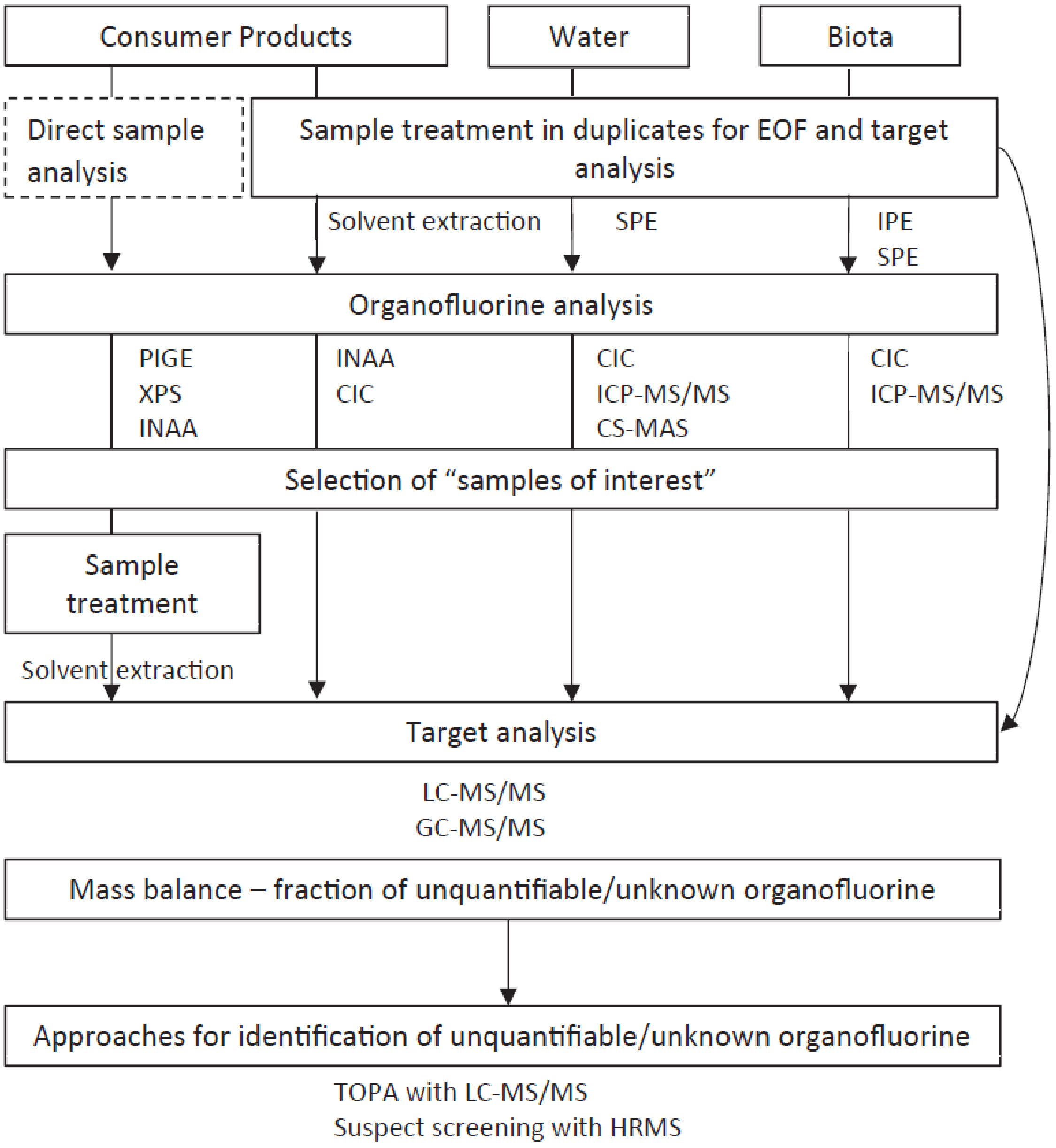

Figure 2: Workflow for a comprehensive organofluorine assessment (Koch et al., 2020)

I.5 PFAS contamination in soil, sediments, ground- and surface water

PFASs have been found at a range of sites including where they are primarily manufactured or used in processing or making various products. The total number of sites potentially emitting PFAS is estimated to be in the order of 100,000 in Europe (Nordic Council of Ministers, 2019). The Nordic Council (2019) has estimated that there are between 12 and 20 PFAS production sites in the EU. PFAS may be used in bulk quantities at facilities for making waterproof textiles and furnishings, locations where leather is treated, in chrome plating industry, photographic development studios, in printing facilities where inks are used in photolithography, where paper coatings are applied and in performance plastics manufacture. Examples of such contaminations are found in Dordrecht (NL), Veneto (It), and Sweden. In Dordrecht, the company Chemours (a spin-off of Dupont) has produced fluorochemicals such as PFOA and Teflon. The Dutch RIVM institute estimated that 750,000 people were exposed to high levels of PFOA originating from this site. PFAS and GenX were detected in vegetable gardens within 1 kilometer of the Dordrecht plants. GenX emissions were required to be reduced from 6,400 to 2,000 kg/y. In Italy, a large-scale contamination of PFAS was discovered in the Veneto Region, directly affecting groundwater, surface water, drinking water and land in an area of over 200 square kilometres (WHO-Europe, 2017). The contamination was attributed to emissions from the company Miteni that produced PFAS-containing products such as herbicides and pharmaceuticals (declared bankrupt in 2018). The highest combined concentration levels of PFAS were estimated to be 1,214 ng/l and estimates for the number of affected people vary from 120.000 to 350.000 (WHO-Europe, 2017). PFCAs have been used as processing aids in the manufacture of fluoropolymers such as PTFE and PVDF (CL:AIRE UK, 2019). They may also enter the terrestrial environment by consumer product use and disposal, by wastewater treatment effluents and biosolids, by leaching from landfills or direct use in the environment, such as by application of firefighting foams (Impelliteri, 2020).

The hazardous substances in aqueous film-forming foams (AFFFs) usually find their way to surface waters through direct runoff, in ground waters through infiltration and in soil through soil diffusion or dispersion. In a case in Sweden, high concentrations of PFAS were detected in the Bredåkra delta (Ronneby), were PFAS contamination (up to 8.000 ng/L of PFOS) was discovered in the outgoing water from one of the two municipal waterworks, Brantafors. The source of the contamination was identified as the fire drill site located in the nearby military airport. Around 6.000 measurements of surface and ground water were compiled by the Swedish EPA, which has shown that all water supplies with contamination levels that exceeded the local safety level were found to be located close to an individual fire fighting training site or to one located within an airport. The use of fire extinguishing foams was identified as the largest direct point source of contamination.

Biosolids and paper sludges that contain PFASs have been applied on land, leading to soil and groundwater contamination. PFAS contaminated sludge containing industrial waste, which was sold under the name of “bio-solids”, was applied at farmland near Ambsberg at the head of the Moehne valley in Germany (Skutlarek et al., 2006). It was estimated that 110.5 kg of PFAS have entered Lake Moehne. This has impacted the whole Ruhr valley catchment and Lake Moehne. An estimated 40,000 people were exposed to drinking water that was contaminated from this source.

In rivers affected by cities, wastewater treatment plants dominate emissions of PFCAs and PFSAs, while for background lakes, rivers, inland seas, atmospheric deposition dominates (Cousins, 2020). For PFCAs and PFSAs, the major global reservoir and sink are the oceans.

Shorter PFAS are generally more hydrophilic and thus more mobile while longer chains will tend to bind more to particles and thus have more potential to bioaccumulate (Ahrens et al., 2010). Because of the heterogeneous properties of the environment, multiple partitioning mechanisms should be considered. Due to head and tail competitions in PFCAs and PFSAs, partitioning at interfaces of environmental media can occur (Brusseau et al., 2019). Most PFCAs and PFSAs are expected to be found in natural waters as anions. Consequently, they are expected to be relatively mobile in groundwater (Xiao et al., 2015). Fluorotelomer alcohols (FTOHs) are on the other hand mostly hydrophobic.

PFCAs and PFSAs are generally considered to be resistant to abiotic and biotic degradation in environmental conditions found in water and soil. Precursors on the other hand are known to transform to PFCAs and PFSAs in environmental conditions. Abiotic processes that transform precursors to perfluorinated alkyl acids (PFAAs) include hydrolysis, photolysis and oxidation. Aerobic biotic transformations of precursors have also been reported, while anaerobic transformation have been studied to a lesser extent (Kucharzyk et al., 2017; ITRC, 2018).

The persistence of PFASs, coupled with their solubility and low/moderate sorption to soils, make many PFASs highly mobile in groundwater, resulting in long contaminant plumes which have the potential to impact groundwater wells and other receptors over a much wider area than conventional contaminants. The extent of migration in groundwater depends on PFAS-specific retardation coefficients (Guelfo and Higgins, 2013).

A lot of attention is being given to the development and implementation of remediation techniques and management strategies (Kucharzyk et al., 2017; Ross et al., 2018). For soils & sediments, the following clean-up and remediation techniques have been considered:

- Capping: prevents contact and further leaching;
- Excavation and off-site landfilling or incineration;
- Sorption/stabilization through ex situ soil mixing;
- Ex situ thermal desorption and off-gas destruction;
- Ex situ soil washing, with disposal or incineration of residual fine and organic fractions.

Disposal to landfills should be carefully considered. In addition to cost, the potential long-term liability of this option (given PFASs persistence) and limited PFASs treatment or monitoring in most landfill leachates are of concern.

Incineration of off-gas from thermal desorption would require very strict operating conditions which may not be fulfilled at many existing facilities and it is very expensive to incinerate PFAS contaminated soil or sediments as such. Thermal desorption can remove PFASs from soil by evaporation, but treatment of the off-gas is subject to the same restrictions as for incineration.

Capping of soil impacts left in situ or containment of excavated soil within engineered stockpiles to prevent infiltration and leaching to groundwater have been undertaken with long-term management, continued liability as well as restrictions on redevelopment being key considerations. Stabilisation and solidification using binding reagents to prevent leaching to groundwater are becoming of increasing focus for source zone impacts, but they have to cope with long-term liability considerations and difficulty to predict long-term performance (CL:AIRE UK, 2019).

For liquids, including various types of waters such as ground-, surface and drinking water, the following treatment process have been implemented or are under development:

- Sorption technologies (e.g. granular activated carbon (GAC) and ion exchange resins);
- Precipitation, flocculation and coagulation in combination with other techniques;
- Liquid-liquid separation technologies (e.g. nanofiltration, reverse osmosis, foam fractionation) and;
- Destruction technologies (e.g. electrochemical degradation, oxidation processes, plasma treatment, UV radiation).

ITRC (2020) has recently published an extensive overview of water treatment technologies for PFAS which are commercially available or in development.

Full-scale treatment facilities in the USA, Europe, and Australia have demonstrated effective removal of PFAS compounds through a variety of treatment technologies, most successfully with activated carbon or membrane filtration (Reade et al., 2020).

GAC is an established technology which can be implemented to remove PFOS and PFOA, but lifecycle operational and maintenance costs are high and costs can increase if other short-chain PFAAs and precursors also require treatment or if natural organic matter levels are high (Ross et al., 2018). The estimated cost of the installation of activated carbon filters for the drinking water treatment plants in the Veneto region was EUR 2 million. Maintaining the carbon filters was estimated to cost EUR 900,000 per year, the short-term cost (5 years) was estimated to be EUR 6.5 million while investment in the medium-term to improve water treatment plants was estimated to be EUR 4.2 million. The spent GAC may be incinerated, but this would require special operating conditions, which are still under investigation (US-EPA, 2020).

Reverse Osmosis (RO) and Nanofiltration (NF) have been shown to be effective in removing PFASs. Removal efficiencies of up to 99% have been reported, even for some PFAS with molecular mass below the membrane cutoff size (Franke et al, 2019). A water reclamation plant in Australia uses membrane processes and advanced oxidation to produce purified recycled water. Influent concentrations of PFOS and PFOA ranging up to 39 and 29 ppt were removed by reverse osmosis (RO) to concentrations below detection and reporting limits (0.4–1.5 ppt) (Thomson et al., 2011). However, these systems are expensive (Higgins and Dickenson, 2016). For surface water and groundwater applications, suspended solids and water geochemistry must be assessed and managed to prevent fouling or deterioration of the membrane. This approach generates a high concentration rejectate (e.g. concentrated brine) which requires further management. Treatment or disposal of RO or NF residuals can be costly and may be problematic if no adequate disposal options are available.

The PFAS Experts Symposium in Arlington, VA (Simon, 2019) concluded that effective PFAS remediation will likely require a combination of treatment technologies and the optimal approaches must ultimately result in complete destruction rather than sequestration.

It has been demonstrated on pilot scale that GAC and AIX (anion exchange resin) treatment could be improved by integrating nanofiltration. Nanofiltration was used to treat drinking water plant feedwater and then GAC and AIX were used to address the concentrated retentate, resulting in increased overall efficiency in the use of GAC and AIX resin (Franke et al, 2019). Another combined technology (Dai et al, 2019) integrated a separation approach (foam fractionation) with destructive treatment by UV/ozonation. This outperformed each individual approach, but the removal of short-chain PFAAs was less efficient in comparison to the long-chain PFAA.

Part II – Workshop report

II.1 WORKSHOP APPROACH

The general aim of the workshop was to facilitate discussions and exchange recent ideas and developments regarding 1) the monitoring and analyses of PFAS in the environment, water, food and other matrices, and 2) the approaches to tackle the pollution.

Therefore, the European Commission decided to bring invited PFAS experts from all over Europe and the USA to facilitate the exchange of the latest information and knowledge on PFAS monitoring and analyses. Special emphasis was given to the monitoring of PFAS in the environment, water, food, and other matrixes, including new approaches to tackle the analytical methods to detect and screen total and individual per- and polyfluoroalkyl substances.

The workshop was attended by approximately 70 invited experts (Annex II.1 – List of participants) with representations from industry, regulators, universities, research institutes, sector organisations and consultants and from different countries. The workshop agenda (Annex II.2 – Workshop agenda) was designed to have in depth discussions and explore creative ideas how to monitor PFAS in the environment, water, food, and other matrixes including new approaches to tackle the whole group e.g. total fluorine methods. Special emphasis was given to the monitoring and analyses of drinking water.

Three different sessions were organized: 1) a plenary session in which Keynote Speakers (KS) provided an overview of the state of play concerning PFAS and monitoring strategies, 2) three parallel break-out sessions to focus on PFAS monitoring methods in different media and 3) a final plenary summarising the findings of the parallel sessions and the conclusions of the workshop.

The workshop started with a half-day plenary session setting the scene. Keynote Speakers (KS) provided an overview of the state of play concerning PFAS and monitoring strategies including the description of the problem, recent developments and political ideas on the way forward.

The 2nd day consisted of parallel outbreak sessions in the morning dealing with the characterisation of PFAS in 1) groundwater, surface water & drinking water; 2) food, crops, feed and 3) other matrices / media, including alternatives substitutes for PFAS. During these parallel sessions PFAS experts were brought together to discuss and exchange current knowledge and creative ideas on technical approaches, analytical solutions and regulatory insights. In the afternoon, the outcomes of the parallel sessions were presented, followed by discussions and the definition of future actions. Via the background document, some guiding questions (Annex II.3 – Guiding questions) were defined and provided to the participants.

Short CVs of the Keynote Speakers, their abstracts and presentations are given in, respectively, Annex II.4 – Keynote Speakers and Annex II.5 – Keynote abstracts and presentations.

Michel Sponar, Head of Unit “Marine Environment and Water Industry” (European Commission, DG Environment, C.2) and Pim de Voogt (Chair of the workshop) opened the workshop and welcomed the participants.

In his opening speech, Michael Sponar emphasized the European Commission's great concern regarding 1) the widespread occurrence of PFASs in the environment, 2) the constantly changing industrial applications and developments whereby long chain PFASs are being replaced by shorter chain PFASs, and 3) the restricted knowledge regarding methods needed for monitoring and analyses. Robust characterization methods are however, extremely important to support policy decisions. Within this respect, 2 paths for which limits will be defined and distinguished, namely characterization of a limited set of 20 PFAS compounds, and/or the characterisation of Total PFAS. However, limits without robust characterisation methods are difficult to enforce. Therefore, it is extremely important to work together, exchange information and increase our knowledge with respect to this very complex group of contaminants in order to achieve the New Green Deal zero pollution approach.

Although PFAS-PFOA only quite recently received a lot of attention in the media Pim de Voogt gave a short overview of past projects from 2004 onwards, including PERFORCE 1 (2004-2006, De Voogt et al, 2007), PERFORCE 2 and PERFOOD (2009-2012; https://ibed.fnwi.uva.nl/perfood/). During the past 15 years a great deal of knowledge and information has been gathered and assessed. Nevertheless, the knowledge regarding pathways of human exposure and the impact of most PFASs on human health remains poor. Consequently, deriving appropriate standards is still a major challenge.

Finally, Tobias Biermann, project officer of the workshop, explained the objectives of the workshop and the role of the European Commission regarding the PFAS threat. The European Commission 1) acts as guardians of treaty, 2) proposes new legislation and 3) manages the implementation of different Directives. Of course the parametric values proposed in the Directives need to be implemented according to legal certainty. Therefore, Tobias Biermann also emphasized the need for robust monitoring and determination methodologies. Since there exists no working group on the monitoring of PFASs, the workshop on PFAS aims to bring together experts working in different domains and countries to exchange experience and knowledge with respect to identification of PFAS in drinking water and other media.

II.2 PLENARY SESSION

Pim de Voogt briefly introduced the plenary session, which was opened by delegates from the European Commission to inform the audience on the European policy strategies regarding the regulation of PFASs.

II.2.1 European Commission perspectives on policy strategies to regulate PFASs at EU level and beyond

Valentina Bertato (EC, DG Env), Tobias Biermann (EC, DG Env), Elisa Vargas Amelin (EC DG Env) and Veerle Vanheusden (EC, DG Sante) gave an overview of the EC action plan on PFASs including 1) the latest approaches in the EC legislation, including proposals to adapt the Drinking Water and the Groundwater Directive annexes, 2) the elements indicating PFAS as a emerging contaminant and 3) the regulatory framework in food.

Long chain PFASs (PFOA, PFOS, PFHxS, C9-C14 PFCA's, including their salts and their precursors) have not only been included as substances of very high concern (SVHC) on the REACH Candidate List, actually, they are all restricted or in the process of being restricted. They have been mostly replaced with short chain PFASs, of which at least some (e.g. PFBS) also have a high contamination potential for food, surface water, ground water and drinking water sources (ECHA, 2020). For this reason, the Netherlands, with support of a few other Member States (MS), has announced the intention to prepare a REACH restriction for the whole group of PFAS for non-essential applications. The European Commission has already initiated studies on the use of all PFAS and non-fluorinated alternatives in fire-fighting foams and in textile–leather processing. The collected data, including substance identification, hazards, emissions, potential alternatives, critical uses, benefits, costs of contamination of soil and water will be used as a basis for the REACH restriction.

Since many PFASs are water soluble and mobile, they are a threat to drinking water resources. Nevertheless, PFASs have not been included in Annex 1 of the EU Drinking Water Directive (DWD). Furthermore, no guidance has been provided covering monitoring campaigns and the frequency of monitoring. Therefore, new limit values for PFAS in the EU Drinking Water Directive were proposed and agreed upon during the final political trilogue on 18-19 December 2019, including a limit value of 0.1 µg/l for a group of 20 individual substances, which will be added to Annex III of the DWD (Table 1), as well as limit values of 0.5 µg/l for total PFAS concentration. The limit value of 0.5 µg/l will only apply once a method for measuring 'PFAS total' is available. Within a time frame of 3 years the European Commission shall develop analytical guidelines, including detection limits, parameter values and frequency of monitoring. The final text of the Directive will have to be adopted and published in 2020.

In parallel to the EU Drinking Water Directive review, an initiative started in 2015 to respond to the need of obtaining information on substances posing a potential risk (emerging pollutants) in groundwater. This work was triggered by the review of the Groundwater Directive Annexes in 2014 and resulted in a voluntary Groundwater Watch List (GWWL) for substances of environmental concern, including pharmaceuticals and PFAS (Lapworth et al., 2019; WFD CIS, 2019, WFD CIS, 2020). Within the PFAS exercise, 11 MS or participating countries provided, on a voluntary basis, monitoring data on PFAS from which PFOA and PFOS are the most frequently detected.

In the period 2008 to present, consumer risk assessments have been carried out including the derivation of tolerable daily intake values (TDI) for PFOS, PFOA and their salts. In 2019, EFSA evaluated new data on toxicity and occurrence, resulting in new values for Tolerable Weekly Intake values (TWI) for four main PFAS (PFOS, PFOA, PFNA and PFHxS). According to these proposed values, the exposure for a considerable part of the population exceeds these TWI. The resulting draft document (EFSA, 2020) is available for public consultation from the end of January until the end of March 2020[1]. The adoption of the EFSA opinion by the Panel on Contaminants in the Food Chain (CONTAM Panel) is foreseen in July 2020. In the 3rd quarter of 2020 discussions will be started with MS in the Working Group on IND and ENV CONTAM on the possible need to set maximum levels for certain PFAS substances in food, taking into account the available data, the possibility of applying mitigation measures and the ALARA (as low as reasonably achievable) principle.

II.2.2 PFAS: Legacy contaminants or still an emerging issue?

Christophe Schulte gave an overview of PFAS terminology, products and uses, hot spots, sources in the environment, worldwide diffuse distribution, and main concerns. He questions why it took 10 years to regulate PFOS (Stockholm Convention) and 10 more years for PFOA after May 2000, when already one company voluntarily ended the production of PFOS. The main concerns are 1) the fact that these long lasting contaminants are still emerging in all environmental media, 2) the WFD only addresses PFOS, and there are no PFAS on the watch list, 3) accumulation of PFAS in food webs and the human body, 4) examples of areas where pristine soil samples were characterised by higher PFAS concentrations compared to rural, urban, and industrial areas, even for precursors and 5) the complexity of sources. Therefore, the following recommendations were formulated: 1) monitoring campaigns need to include long- and short-chains, precursors, metabolites and polymers; 2) regulate the entire group of “safer” alternatives entering the market; 3) a strategic action plan needs to be developed by the European Commission (cf. article 16-9 of the WFD).

II.2.3 PFAS Monitoring and Management in the United States of America

To exchange ideas and knowledge between the EU and the USA, Christopher Impellitteri gave an overview of the PFAS sources, regulations, analytical protocols, drinking and wastewater treatment and research carried out in the USA. Besides manufacturing, industrial applications, consumer products, and direct use in the environment (e.g. firefighting foams), air emissions, landfills (including biodegradable food packages) and the re-use of biosolids are also considered to be the main sources.

PFAS regulations and guidance are currently being developed at the State level, resulting in different rules and standards for PFAS in drinking water that can vary from State to State. The US EPA has provided human health guidance levels for both individual and the sum of PFOA and PFOS of 70 ng/l for drinking water. EPA has also decided to move forward with a regulatory determination for PFOA and PFOS in drinking water.

As in Europe, the main bottlenecks to derive standards are the enormous list of substances and the lack of human and toxicity information for many PFAS of concern. To provide the stakeholders with (eco)toxicity information needed for risk management decisions and communication, the US EPA has

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[1] Extended till 20 April 2020.

initiated 1) a standard toxicity assessment for PFAS of interest via the IRIS process (US-EPA, 2019); 2) the development of new in vitro chemical testing approaches to test 150 PFAS chemicals (https://www.epa.gov/chemical-research/pfas-chemical-lists-and-tiered-testing-methods-descriptions#2); 3) a systematic review of literature on PFAS ecotoxicological data (https://cfpub.epa.gov/ecotox/explore.cfm?cgid=36); and, 4) the development of a research plan including the identification of sensitive taxa, bioaccumulation, benchmarks and thresholds and the use of Adverse Outcome Pathways (AOP) as an organizational framework (US-EPA, 2018) .

Several procedures have been developed regarding the analyses of drinking water (US-EPA 2019b: Method 533; Shoemaker & Tettenhorst, 2018: Method 537:1) and non-drinking water samples (US-EPA 2019c: Method 8327; US-EPA in progress: Method CWA/SW846). In addition to the analyses of individual PFAS components there has also been a great deal of attention to the determination of “total” PFAS, including total oxidizable precursor assay (TOP assay), total organofluorine analysis using combustion ion chromatography (TOF) and non-targeted analysis. Since TOF can be developed on a wide commercial scale, it may become an important technique for a first screening of sites that may be contaminated with PFAS. Non-targeted analyses are applied to explore unknown compounds. The latter technique however requires a high degree of expertise in mass spectrometry. Although cross contamination is a major issue, no specific guidelines exist at the Federal level regarding sampling procedures for PFASs.

An overview of drinking water treatment technology research and cost models was given. The US EPA has developed web-based tools to help with treatment cost determinations and technology selection decisions. (“Drinking Water Treatability Database, TDB)” (https://iaspub.epa.gov/tdb/pages/general/home.do) and “Drinking Water Treatment Technology Unit Cost Models” (https://www.epa.gov/sdwa/drinking-water-treatment-technology-unit-cost-models-and-overview-technologies). Drinking water research also includes studies on the fate and behaviour of PFAS in drinking water treatment media regeneration. Furthermore research is on-going to tackle the treatment of wastewater in combination with end-of-life disposal and/or thermal treatment of PFAS in biosolids and soil. The USEPA is conducting research on biosolids management options (e.g. land application, thermal incineration). More research is needed to ensure the safe management of PFASs in wastewater and residuals.

More information on PFAS data and tools are given via https://www.epa.gov/pfas and https://www.epa.gov/pfas/epa-pfas-data-and-tools.

II.2.4 PFAS pollution, from the artic to the equator. Integrated approaches on characterisation and remediation strategies

Ian Cousins started his presentation with a reflection on the definition of PFAS, referring to the publication of Buck et al. (2011) and the update by the OECD (2018; in progress). Well over 4,000 substances have been identified and provided with a CAS number. Since compounds with aromatic rings and/or hydrophilic and hydrophobic functional groups have been identified, an adapted definition of PFAS has been proposed (OECD, in progress) *“the highly fluorinated ~~aliphatic~~ substances that contain 1 or more C atoms on which all the H substituents …have been replaced by F atoms, in such a manner that they contain at least one aliphatic perfluoro~~alkyl~~carbon moiety, such as* C_nF_{2n}*”*. The question is however “*Do we need a new definition?*”. Still more clarification is needed. The PFAS universe is large, comprising different structures characterised by different mobility and toxicology but one important common characteristic remains "they all break down or form highly persistent substances in the environment".

Several studies (Prevedouros et al., 2005; McLaghlan et al., 2007; Pistocchi and Loos, 2009; Weber et al, 2017) indicate 1) the main global historical emission sources for PFAS are manufacturing and the use of PFAS containing products, 2) the contribution of precursors is relative low, nevertheless locally they can be important, 3) the River Po in Italy contains the highest concentrations of PFAS of all rivers studied in Europe and accounted for 2/3 of the total PFOA concentrations reported for European rivers, likely due to the presence of a fluoropolymer production facility located in the Po watershed, 4) away from manufacturing sources, PFOS and PFOA river concentrations correlate with population density and GDP (i.e. release from waste water), 5) global emissions of some PFCAs and PFSAs have declined substantially but legacy sources remain in the environment, 6) volatilisation as ions is not directly important, 7) atmospheric deposition may be a dominant pathway in remote areas and in areas distant from cities, 8) "sea spray aerosols" explain enhanced concentrations in coastal areas of Norway and the Netherlands, 9) the transport of PFAS in soil and groundwater has been a high priority topic since 2010 and 10) existing soil remediation techniques are energy intensive, costly, and can only be applied for source zones.

Nevertheless, after 2 decades of research there is still a lot of controversy. Since the PFAS release to the environment is irreversible, the production and use of PFAS should be limited. An immediate 100% ban however is practically not feasible. Therefore, a stepwise phasing out concept has been advised (Cousins et al., 2019).

II.2.5 PFAS risk assessment what do we know and what do we want to know?

Arjen Wintersen described the Dutch methodology to derive PFAS background values, risk limits for soil and groundwater, ecological risk limits, risk limits for agriculture and food production and screening levels for re-use of soil and sediment and site assessment (RIVM, 2018; 2019). In the Netherlands more and more attention has recently been paid to diffuse PFAS contamination as a consequence of wide spread occurrence of PFAS in soil, sediments, biota and surface and groundwater. This is due to incidents at and near the airport of Schiphol, the presence of an important PFAS producing plant and the presence of PFAS in landfills. Furthermore, point sources are difficult to delineate and diffuse concentrations can be high. Before 2019 no standards or limit values existed. Instead, quantification limits (LoQ) had to be used, which had a large impact on the reuse of soil and sediments. Thereafter RIVM was asked to provide input for the development of a framework of standards to control human and environmental risks in the framework of the reuse of excavated soil and sediments. Bottlenecks of the preliminary framework are the uncertainties of 1) the analytical performance of commercial laboratories, 2) sources and distribution of PFASs, 3) environmental behaviour and toxicological effects. Therefore, among others, ring tests or interlaboratory tests will be organised, leaching tests will be performed and more data will be explored.

II.2.6 The Role of Total Fluorine Measurements in Monitoring PFAS

Graham Peaslee opened his presentation with the relevant question "Why is a Total Fluorine method (TFM) needed"? TFMs are applicable in screening and monitoring campaigns and in the regulatory framework. If there is no fluorine, there are no PFASs! Target analyses can be minimised, thus saving a great deal of money. Therefore, recently several methods for quantifying TF in different media have been developed, including total oxidizable precursor assay (TOPA), combustion ion chromatography (CIC) and particle induced gamma-ray emission (PIGE) spectroscopy. PIGE is a recently developed technology. Advantages of this non-destructive method are 1) the possibility to measure over 500 samples a day; 2) simultaneous measurements of all known and unknown PFAS components; and, 3) the absence of interferences. The method detection limit depends on the sample volume (e.g. MDL sample volume 3 L = 70 ng/L). Disadvantages are the limited commercial availability of instrumentation and the requirement of experienced lab personnel to operate the specialised PIGE equipment. The cost of the instrument is about 850 k€, with a payback time of approximately 1 year taking into account 100,000 samples / year. According to recent comparisons (Robel et al., 2017; Schultes et al., 2019) these methods (CIC, TPOA, PIGE) correlate well. Nevertheless, more research on F standards, interlaboratory comparisons, QA/QC protocols are needed.

II.2.7 Reflection on the questions and discussions

During the plenary session, the questions and discussions mainly related to 1) nomenclature, 2) risk assessment & limit values, 3) regulation, 4) PFAS in drinking water and 5) communication.

An overview is given in the following paragraphs.

1. Nomenclature

Inconsistencies regarding the nomenclature of PFASs were mentioned during the keynote presentations. Although the common terminology recommended by Buck et al. (2011) was updated by the OECD (2018), there is still confusion not only with the public, regulators and stakeholders but also with researchers. Therefore, there is a need to ensure that there is non-ambiguous terminology. One example of such a misleading terminology is “TOF” or “Total Organo Fluorine”. TOF is defined by the operation of the analyses. It is suggested to use Total Fluorine (TF) instead or even better “EOF” (Extractable Organic Fluorine). “Total fluorine” implies inorganic F as well.

2. Risk assessment & limit values

Due to their physical-chemical characteristics, PFASs are considered persistent chemicals being resistant to degradation. As a result, they accumulate in the environment, increasing exposure to humans and animals over time. Given the high number of PFAS compounds, the risk assessment and the derivation of limit values for each individual substance is an almost impossible task (EEA, 2019). Therefore, next to the derivation of limit values of selected individual substances, also risk assessment and the regulation of PFAS as a whole or as subgroups, based on toxicity and chemical properties, has to be been considered (see above).

With respect to this approach, the following remarks were given:

- The more individual PFAS you measure the higher the possibility to exceed group standard values.
- Is a risk assessment only based on total fluorine feasible?
    - “If F is not detected, there are “no” PFAS. If elevated concentrations of F are measured, a more detailed characterisation and risk assessment is necessary.” (G. Peaslee)
    - Since concentrations below detection limits of “total” measurements do not necessarily imply [F]=0, PFAS may still be present and detected using more sensitive analyses.
- A discrepancy exists between the proposed EU DWD limits which are not based on toxicological data and the EFSA risk assessment. How do the MS have to deal with it?

They have the right to enforce stricter limits taking into account uptake from food and drinking water limits. The starting point can be the limits of the DWD, but currently, there is no consensus on this issue.

- What about the derivation of maximal concentration limits in the context of the DWD?
  Maximal limits have not been derived yet. They will be based on the ongoing EFSA risk assessment.
- When executing risk assessment, it would be better to replace the application of PFAS specific detection limits by another approach if no risk data are available. (A. Wintersen)

3. Regulation

Regarding the regulation of PFAS some elements of concern were mentioned by the group of experts, which need to be considered when further actions are defined:

- The revision of the DWD does not include PFAS precursors. As illustrated during the plenary session, precursors cannot be ignored. Their inclusion into the DWD needs to be re-evaluated.
- Several publications indicate that short-chain PFAS (per- and polyfluoroalkyl substances), which are widely used as alternatives to long-chain PFAS, also accumulate in the environment, causing contamination of surface, ground- and drinking water (EEA, 2019). An element of concern of the experts is the time needed to regulate them. What steps have been proposed?
  Proposed solutions to reduce the application of short chain PFAS are 1) the regulation of the complete group within REACH; 2) only allow permits for essential use; and, 3) for the long-chain compounds a gradual phasing-out is advisable.
- Although several analytical procedures/guidelines have been developed by national and/or regional authorities, there does not exist a European 'Standard' certified by CEN accreditation. As in the WFD guidelines, it is sensible to allow any methodology to be used as long as it meets data quality standards.
- Since the re-use of PFAS contaminated sludge and the recycling of PFAS containing materials may cause "secondary" PFAS pollutions (EEA, 2019), there is a need for the determination of end-of-waste criteria. This is illustrated by the fact that advanced oxidation processes to treat wastewater can generate more available PFAS or daughter products. Consequently, permits for the reuse of treated wastewater should be handled with caution.
- Other important questions are "how to deal with the discharge of membrane filtration residues and the regulation regarding household landfills". Increased release of PFASs have been observed in leachate from landfills containing food packages and paper sludge.

4. PFAS in drinking water

A great deal of efforts has been made regarding the regulation of PFAS in drinking water. Is there enough information available about PFASs in drinking water?

- According to the EEA (2019) National monitoring activities have detected PFAS in drinking water of some highly polluted areas in EU. The percentage of detections in groundwater were highest for PFBA and PFHxS followed by PFPeA, PFBS, PFHxA, PFOA and PFOS. The concentrations of PFBA and PFPeA exceeded 0.1 µg/L at more than 14 % and 12 % of the sites, respectively.
- In Sweden a monitoring campaign has been carried out. More information can be found via https://www.livsmedelsverket.se/en/food-and-content/oonskade-amnen/miljogifter/pfas-in-drinking-water-fish-risk-management.

- In the US, many surveys have been carried out by states indicating the presence of PFAS in drinking water. The EPA carries out drinking water surveys approximately every five years through the Unregulated Contaminant Monitoring Rule (UCMR) process. The next UCMR survey (2021) will likely include PFAS compounds.
- In the Po Valley in Italy biomonitoring studies on 80,000 people have been carried out as a result of a significant PFAS contamination in the environment and in a drinking water production facility.

5. PFAS and communication

Recently, the PFAS problem is not only the concern of scientists and authorities, but it has also has reached the public. Since actions, taken by the authorities, to cope with the PFAS contamination may block economic activities it is very important to communicate with the different stakeholders. Therefore, the EPA PFAS action plan (EPA, 2019d) foresees in a clear communication strategy in which scientific results and recommendations will be translated to an understandable language by comparisons with clear and simple examples. Unfortunately, these days, it is very hard to control communication.

As illustrated in the KN presentation of Arjen Wintersen , based on the precautionary principle, in 2019, a strict standard was applied in the Netherlands for the re-use of soil and site assessment. This has caused a lot of commotion among dredgers and civil engineering contractors who could/would not handle or respect this new imposed standard because of the negative effect on the progress of their projects. A better communication is needed to convince people of the urgency of actions regarding PFAS contamination. Also in Germany “poor” communication has been an issue. Nobody cared about or understood the PFAS problems until a big scandal occurred.

II.3 Parallel sessions

During the 2nd day of the workshop, parallel outbreak sessions were organised in the morning to have in-depth discussions on the characterisation of PFASs in 1) groundwater, surface water & drinking water; 2) food, crops, feed; and, 3) other matrices / media, including alternatives substitutes for PFAS. During these parallel sessions PFAS experts were brought together to exchange current knowledge and creative ideas on technical approaches, analytical solutions and regulatory insights.

II.3.1 Characterisation of PFAS in groundwater, surface water & drinking water

II.3.1.1 Introduction

Parallel Session I focused on the c*haracterization of PFAS in groundwater, surface water and drinking water*. The session was guided by a keynote presentation by Anna Kärrman (Annex II.5.7 Characterization of PFAS in groundwater, surface water and drinking water, including approaches for total assessment of organofluorines. The presentation and related discussions focused on various topics, which are particularly relevant for PFAS monitoring in water:

i) Available sampling methods and protocols were presented and discussed. These involved current standardized protocols such as solid-phase extraction (SPE) and the importance of appropriate sampling procedures to ensure the chain of custody of samples and minimize contaminations during sampling. Alternative and emerging sampling strategies, such as passive samplers and diffusive gradients in thin films (DGT) were also briefly discussed.

ii) ii) Analytical techniques currently available were presented. The discussions involved conventional targeted methods, based on LC-MS/MS, and existing standardized methods, as well as non-specific total organic/extractable fluorine methods and total oxidizable precursor assay (TOPA or TOP). Broad screening methods based on suspect and non-target screening with high-resolution mass spectrometry were also discussed. Advantages and limitations of the various techniques were discussed using examples presented by the keynote.

iii) The session focused on future steps required for the efficient implementation of available techniques, with a particular emphasis on the drinking water directive (DWD). Importance was given to existing standards, quality assurance and control (QA/QC) and clear definitions of PFAS, total PFAS and sum of PFAS.

iv) The discussion briefly focused on groundwater remediation standards which are being applied in various countries across Europe and covered some aspects which were previously discussed in the plenary session.

During the session, specific questions were presented and used as an additional guidance for the discussion. The specific questions are added to Annex II.6 – Parallel sessions, guiding questions.

II.3.1.2 Summary of Keynote presentation

The presentation about *Charaterisation of PFAS in water*, focused on two main aspects, namely (i) sampling, storage and pre-treatment of water sample for PFAS analysis; and, (ii) extraction, analysis using various techniques (targeted, non-specific and non-targeted), as well as quality control.

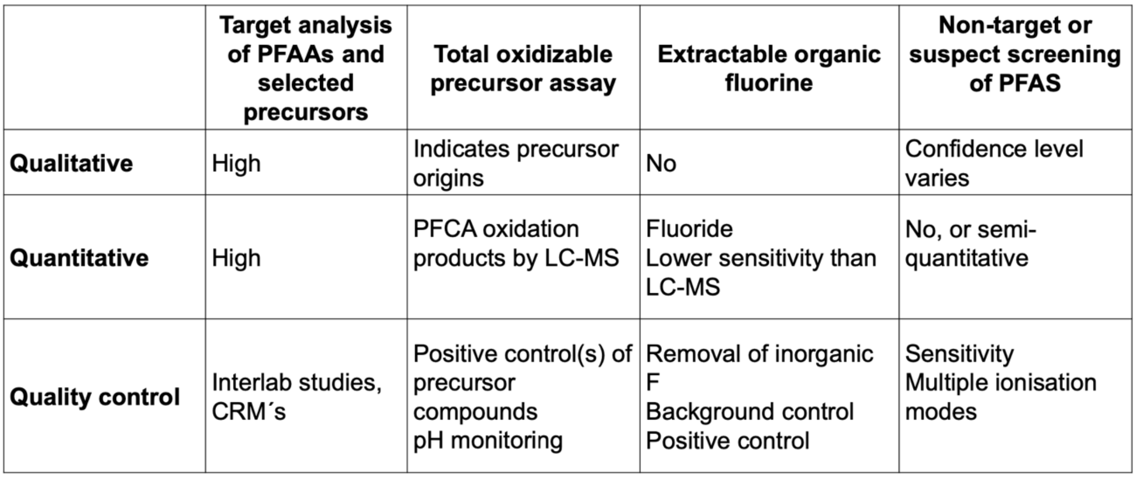
After a brief introduction about the chemical nature of PFAS and fluorine containing chemicals, the presentation focused on aspects related to sampling. The importance of using appropriate sampling equipment on the field to minimize contaminations, as well as the collection of field blanks was highlighted. Furthermore, questions related to sampling variability (i.e. spatial and temporal variability in PFAS concentrations) were also mentioned, together with approaches to account for these (i.e. increased sampling frequency/total number of samples or the use of alternative sampling approaches such as (integrative) passive samplers).

With regard to sampling, the possibilities offered by passive samplers were briefly mentioned and reference was made to existing guidelines, in particular the ISO/FDIS 5667-23 norm which provides general guidance on the use of passive samplers (not specific to PFAS). The focus of the presentation was given to conventional bottle sampling approaches and the associated protocols used to handle and extract PFAS from the latter. Best practices for the storage and pre-treatment of collected water samples were presented. These included sorption on the surface of the used containers, transformation of precursors to their corresponding carboxylic or sulfonic acids during storage, removal of particulate matter (and potential loss of the adsorbed fraction).

Extraction of water samples was also discussed, and emphasis was given to solid-phase extraction (SPE) methods using mixed-mode weak anionic exchange (e.g. WAX) and hydrophilic lipophilic balance (e.g. HLB) sorbents. Advantages (good performances for numerous acids and precursors) and limitations of SPE (full characterization of PFAS content requires more comprehensive extraction approaches) were presented. Existing standard methods for extraction (i.e. ISO 25101 and ISO 21675) were also mentioned.

Analytical methods available were then presented. In particular, the use of conventional targeted approaches based on LC-MS/MS, including the analysis of sulfonic and carboxylic acids, precursors (e.g., FOSA, FOSAA, FTSA, PAPs), phosphonic acids and novel PFAS (e.g., ADONA, HFPO-DA) has been discussed. In total, 73 different PFAS can be analysed with the presented method. Analysis of ultra-short chain PFASs (e.g. C1-C3) using supercritical fluid chromatography (SFC) is an upcoming alternative. Among the non-specific methods is extractable organic fluorine-combustion ion chromatography (EOF-CIC), together with the concept of mass balance. This involves comparing the total mass load of organic fluorine (determined by EOF-CIC) to the fluorine mass load determine by targeted LC-MS/MS analysis. One of the presented examples showed that PFAS determined using the targeted method accounted only for 8% of the total fluorine mass load as determined by EOF-CIC. Careful control of background fluorine concentrations, lower sensitivity and the lack of discrimination between fluorine sources were mentioned among the limitations of the technique. Various examples of the use of EOF-CIC in combination with LC-MS/MS for the determination of fluorine mass balances were presented. The total oxidizable precursor assay (TOP or TOPA) and the protocol used to oxidize precursors to “conventional” (known) alkyl acids was explained. Examples showing the increase in measured amounts of PFAA before and after TOPA in water samples were illustrated as proof of the relevance of the method. Finally, suspect and non-target screening (NTS) methods using LC-HRMS can be used, as well as data mining approaches (i.e., mass defects, fragmentation flagging and available suspect lists of PFAS). Results from various NTS analyses in environmental samples, including water, from Nordic countries were presented. In the particular case of river samples, most detected PFAS compounds were in the PFAA family, whilst some precursors and in particular perfluoroalkyl alcohols were detected but to a lesser extent.

At the end of the keynote, an overview of the various techniques, with their pros and cons was provided (see table below).



	Target analysis of PFAAs and selected precursors	**Total oxidizable precursor assay**	**Extractable organic fluorine**	**Non-target or suspect screening of PFAS**
Qualitative	High	Indicates precursor origins	No	Confidence level varies
Quantitative	High	PFCA oxidation products by LC-MS	Fluoride Lower sensitivity than LC-MS	No, or semi-quantitative
Quality control	Interlab studies, CRM´s	Positive control(s) of precursor compounds pH monitoring	Removal of inorganic F Background control Positive control	Sensitivity Multiple ionisation modes

Figure 3: Overview of various analytical techniques available for the measurement of PFAS and their pros and cons (as presented by Anna Kärrman during the workshop).

II.3.1.3 Discussion

The panel discussion during parallel session I followed the same topics as presented by the keynote speaker. As introduced before, the main discussion points were the following:

- Sampling techniques and protocols;
- Analytical methods and targeted parameters; and,
- Groundwater remediation standards

Sampling techniques and protocols

One of the main topics which was discussed during the session is the risk of contaminations and the importance of having adequate procedures to minimize these, both in the field and in the laboratory (during sample processing). The overall consensus is that the main issue is the contaminations during sample processing and analysis in the laboratory (e.g. laboratory environment, pumping system of liquid chromatography), rather than in the field. Nevertheless, the need for precautions before materials can be used in the field (e.g. validation of materials, such as groundwater sampling pumps and tubing) was stressed, as well as the importance of having a clear communication between laboratory and the field. In particular, procedures used in the field need to be harmonised and clearly explained prior to sampling. Once samples have been collected, preservation and handling protocols need to be available and validated, and a sample chain of custody needs to be ensured. For this purpose, existing norms (ISO 5667-3:2018) should be implemented. Moreover, the importance for accredited laboratories to operate competently and generate valid data by following sampling standards stipulated in existing norms (ISO 17025) was also stressed during the discussion.

Regarding passive sampling methods, the overall experience of the audience with the latter was limited. However, it was suggested that these can be particularly useful for investigative monitoring of PFAS contaminations in water, yet they are currently not suitable for routine surveillance monitoring. The importance and usefulness of implementing guidelines detailed in ISO/FDIS 5667-23 norm was highlighted during the discussion about passive samplers.

Analytical methods and target parameters

Analytical methods, their advantages and limitations, represented the main topic of discussion. In particular, the discussions focused on targeted methods (for LC-MS/MS) highlighted that the available methods, specifically ISO 21675 and 25101, are available for unfiltered water (provided that less than 2 g/l of suspended solids are present). However, the panel agreed that these might need to be revised in view of the modifications of the DWD as the number and type of PFAS included in the methods might not be the same as those reported in the new DWD. With respect to the definitions in the new DWD, discussions focused on the lack of a precise definition of “total PFAS content” from an analytical chemical perspective. The panel agreed that this needs to be defined on a legislative level. Similarly, the term “total” needs to be defined clearly, based on a consensus and/or on a specific method. An additional issue which was raised is that different toxicities of PFAS are not considered when calculating sums of PFAS concentrations/mass loads (i.e., harmless PFAS and toxic substances are equivalent in the sums). As a solution, the introduction of a weighting factor to account for the different toxicity of PFASs was suggested.

The use of TOPA for the analysis of precursors was also discussed. Experts agreed that TOPA can be seen as a pre-treatment step for further analysis, if precursors are also to be considered. However, it was agreed that more thorough validation of the approach is still required, in particular to determine the effect that matrices and other variables have on the oxidation yield. The inclusion of TOPA in methods used for PFAS analysis raises again the question of the definition of PFAS in legal texts. In particular, it was agreed that there needs to be a clear definition of whether total PFAS content also includes precursors (thus that analysis and quantification should be carried out after TOPA). The use of TOPA however also involves increased costs as there is additional sample processing and, most commonly, samples are analysed before and after TOPA (so two samples need to be analysed).

The last point discussed was the total (organic/extractable) fluorine methods, which are currently being used or that are being developed. Sensitivity and selectivity of absorbable organic fluorine (AOF), extractable organic fluorine (EOF) and non-specific methods such as PIGE need to be described and investigated more thoroughly. It is agreed that AOF and EOF methods are currently not suitable for drinking water analysis due to sensitivity issues. PIGE is seen as an interesting and promising approach, however the panel agrees that this method should be considered an AOF method and not a total fluorine one, due to the sample preparation involved. The panel also stressed that there needs to be clarity when reporting results from total PFAS and total fluorine measurements (i.e. fluorine mass loads) as the two are stricto sensu not the same. In fact, total PFAS refers to PFAS concentrations while total fluorine measurements refer to total (organic/extractable) fluorine concentrations. While being very useful for monitoring purposes, AOF and EOF methods are not considered as a preferable approach compared to existing targeted methods (LC-MS/MS). While not able to cover all PFAS, they remain very sensitive and specific for PFAS analysis in water samples. Once again, the panel however stressed the importance of having a clear definition about which PFAS should be included/considered in targeted methods.

The following additional questions were raised during the discussion about EOF/AOF methods and still need to be addressed:

- Can a “total” PFAS method be developed that is selective, sensitive and quantitative for interference-free determination of all PFASs at the required reporting limits?
- Can inorganic fluorine be removed quantitatively?
- What are potential cross-contamination issues?
- Can regulatory limits be set?
- How quickly can validated EN/ISO standards be made available?

Suspect and non-target methods (LC-HRMS) were discussed briefly during the session. These methods are seen as very promising for broad screening of PFAS content in water samples. However, the need for highly experienced personnel and time-consuming data analysis are still the bottleneck of these techniques. Nevertheless, workflows and data analysis tools are constantly improving and will further simply the analysist’s work, thus increasing the sample throughput of LC-HRMS in future.

The following additional questions were raised during the discussion about HRMS and still need to be addressed:

- Is there a need for a standard method?
- Can a suspect list with MS/MS spectra and retention time indices be made available?

<u>Groundwater remediation standards</u>

Aspects related to groundwater remediation standards were covered during the plenary session (see the presentation given by Arjen Wintersen (RIVM, Netherlands)).

II.3.1.3 Conclusion and recommendations

<u>Sampling techniques and protocols</u>

The most important aspects about sampling protocols involve principally the prevention of cross-contaminations, both in the field and, most importantly, during sampling preparation in the laboratory. The latter are in fact considered as the most crucial, although the use of adequately tested and validated sampling material on the field remains vital. Solid phase extraction using mixed-mode weak anion exchange and/or hydrophilic lipophilic balance sorbents remains the method of choice for sample preparation, in particular for mass spectrometric methods. Passive samplers and similar devices are seen as a promising addition for investigative analysis, yet their use for routine monitoring still requires further development/validation. Existing guidelines for sampling, calibration and validation of laboratory results are crucial for the accurate determination of PFAS in water samples and should always be followed.

<u>Analytical methods and target parameters</u>

Existing targeted methods (LC-MS/MS) for the determination of PFAS are still among the most important analytical tools available, in particular because of their specificity and sensitivity. However, the large number of PFASs calls for additional approaches to broaden the analytical spectrum. Moreover, existing standardized methods might need to be revised to reflect new legislations (i.e. the recast Drinking Water Directive). TOPA is a potentially useful sample preparation technique which can enable an increase in the number of PFAS detected (i.e. the precursors) using existing targeted methods. However, further validation is still necessary, in particular to control the oxidation yield in various matrices. EOF/AOF methods are seen as a promising and useful additions to existing targeted methods, in particular as they enable the measurement of PFASs which are not covered by conventional target methods. However, the specificity and sensitivity of these techniques remains an issue, which is the reason why they are not considered appropriate for analysis of drinking water (yet their usefulness for other matrices is not questioned). Furthermore, additional research is still needed to address questions such as interferences, cross-contaminations and removal of inorganic fractions. Suspect and non-target screening methods are also a promising addition to existing methods as they enable the detection and identification of unexpected and previously unknown PFAS. High sample throughput remains an issue due to the complexity of data interpretation, yet as workflows and software improve, this will become less problematic. With respect to analytical methods and legislative texts, there is an urgent need for clear definitions about what should be considered under PFAS (e.g. are precursors included?) as well as what is meant by total PFAS and how to deal with results from EOF/AOF which only report fluorine concentrations/mass loads.

II.3.2 Characterisation of PFAS in food, crops, feed (including packing material)

II.3.2.1 Introduction

There is great uncertainty related to the exposure to PFASs present in food, crops, feed and packaging material. This is related to the fact that once PFASs enter the environment they are persistent and transfer to and accumulate in food and humans. Processes affecting precursor PFASs that can degrade to PFAS over time are important and not well understood. Furthermore, because of the large number of substances, the identification and quantification of PFASs still remains a challenge.

Therefore, Parallel Session II focused on the characterization of PFAS in food, crops and feed. The session was guided by a keynote presentation given by Dorte Herzke from Nilu (Norway). During the workshop participants discussed and raised issues related to human risks, sampling and analytical methods.

II.3.2.2 Summary of Keynote presentation

The keynote presentation was entitled “PFAS in food: risks, sampling, analytical” (Annex II.5.8).

The presentation started by highlighting the many existing questions on the information gap between total organofluorine analysis (AOF) and total oxidizable precursor (TOP) assay on polyfluoroalkyl/perfluoroalkyl substances (PFAS). Sum parameters, such as absorbable organic fluorine (AOF), extractable organic fluorine (EOF) and the total oxidizable precursor (TOP) assay can be applied to assess the amount of unknown precursors by organofluorine mass balance (AOF, EOF) or by molar balance of perfluoroalkyl moieties (PFAAs prior to and after TOP assay). In contrast to AOF and EOF, which can also detect organofluorine from pollutants other than PFASs (e.g. fluorinated pharmaceuticals or pesticides), the TOP assay is specific for perfluoroalkyl moieties (Janda et al., 2019).

It was indicated that there is need for new tools and analytical methods when we want to answer questions related to food safety. This includes sampling approach and design, for which many issues have to be considered and clarified.

Although today’s analytical methods are improving many questions remain – the most important ones are listed here:

- How to evaluate results from different methods?
- How to handle uncertainty and unknowns?
- How to “choose” detection limits (ALARA) and how to achieve this?
- If there are high rates of false negatives: how to solve this?
- How to deal with high variabilities in contamination rates?

An important point related to the questions above is that the food matrix differs from the other matrices, such as water or soil. Effects of storage are different and known to be large and variable, and so might have an impact on the analytical methods used.

The presentation concluded that there is a need for more data on PFAS concentrations in food and feed. This is because of the fact that e.g. reference samples are only available for fish, or that comparison of data is difficult and shows there is need for more types of reference materials. The same is the case for information about dietary exposure and consumption where only limited knowledge is available.

Next to the analytical aspects, other items have to be understood better such as:
- Data availability for PFAS in food and feed;
- Transfer to food and feed (e.g. transfer and accumulation factors);
- Background concentration (only limited numbers are available).

A major conclusion of the introductory presentation relates to challenges for the lab, being "the need for *a standardized method for total PFASs concentrations; defining protocols and the need for QA/QC*".

II.3.2.3 Discussion

During the workshop 4 subjects for discussion where defined:
- Sampling (sample collection) techniques and protocols;
- Analytical methods and target parameters (PFAS total, PFAS sum, individual components);
- Reference samples; and,
- New insights into bioconcentration factors (BCF) & maximum residue limits (MRL).

The discussion was triggered by using a set of questions as given in Annex II.6 – Parallel sessions, guiding questions.

Sampling (sample collection) techniques and protocols

Referring to the overview given during the keynote it was agreed that there is need to consider different types of sampling and methods. Samples should include raw and processed food. For the analyses of these samples Member States with no adequate lab facilities should use labs in other Member States (here there is a role for a reference laboratory network).

It is important to distinguish between hot spots and background, e.g. eggs laid in batteries and those from free-range eggs; farmed fish vs. non-cultivated fish…. This indicates the need for knowledge on accumulation factors also because we need to define transfer data from feed (cattle, fish, chicken, pigs...). Here, the need for extensive databases pops up again since there seems to be very little information available. It was mentioned that all information should be included in a food catalogue including a uniform list of items needed. E.g. for animal feed, information is needed related to accumulation in meat and relations to feed. So, MRL's for feed are necessary and data related to occurrence in feed. There is information available but this it is limited and varies widely.

Risk exposure due to packaging and migration to food is not known. Also, the link to blood concentrations in humans and prepared food/packaging/self-cooking or the need to sample 'pre-prepared' wrapped food (raw and cooked) is not known. It was agreed that a focus on reducing the use of PFASs in different sectors is preferable and can, for example, be achieved by a ban of coatings when alternatives are available (e.g. other types of packaging). However, substitution shall not create new problems, e.g. when plastics are substituted by coated paper material.

Analytical methods and target parameters (PFAS total, PFAS sum, individual components)

An overview of analytical methods is given in Figure 4. A point raised here is that, since we have a combination of TOP and individual component approach, we need to look at different methods enabling us to understand many issues (as defined in 2.1). For example, Total Fluorine (TF) gives a general view, the question here is if this sufficient, or is TOP representing the most "suitable" level?

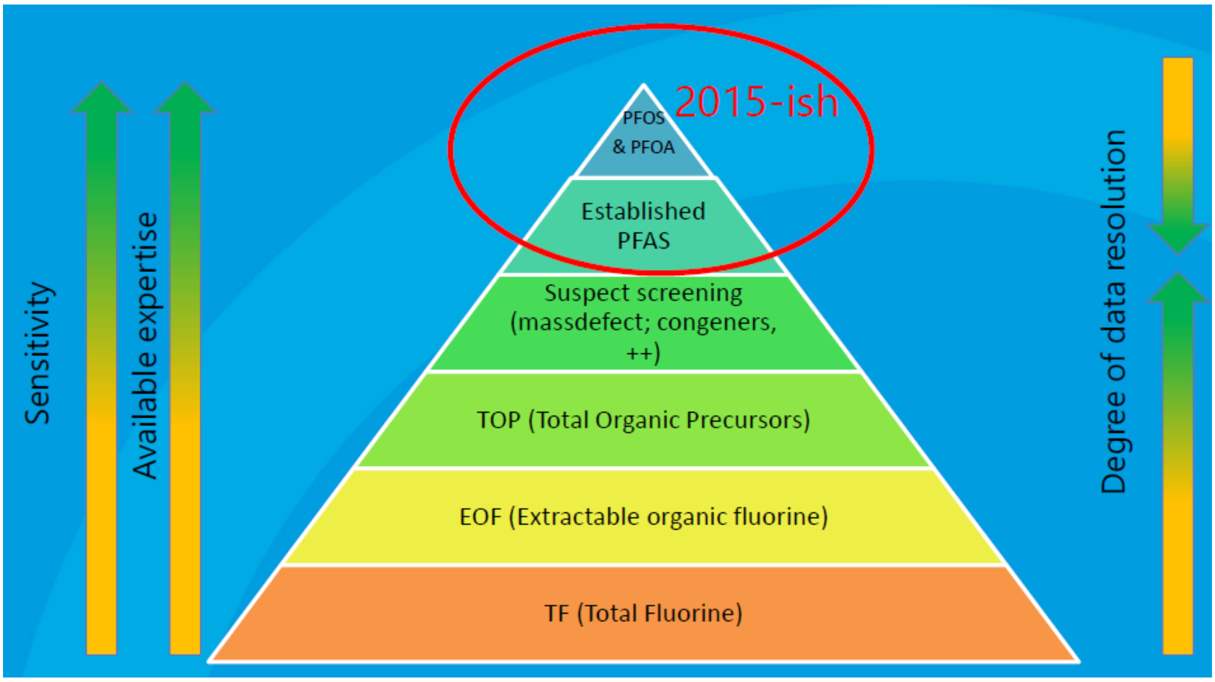


Figure 4: An overview of analytical methods applicable for the determination of PFAS

Related to EOF and TF it is stated that analyses may also include fluorinated pesticides and veterinary medicines which may result in a serious overestimation of PFAS.

Another issue relates to the fact that the TOP assay was never meant to mimic metabolic processes. The oxidation is so strong that it is not representative for what happens in the body. Since all precursors will also be measured, the obtained concentrations will be an overestimation. Nevertheless, the TOP assay could be useful as a conservative estimate of the PFAS content. Furthermore, there is not enough knowledge about over and under estimating packaging material. All this concludes that a harmonised TOP at the EU level is necessary.

Some other points to be taken into consideration were mentioned: 1) is it possible to define limits for individual components? 2) observed PFAS concentrations in blood are higher compared to the concentrations obtained for food, can these be related to accumulation?

Reference samples

As already stated during the keynote presentation, available reference material is limited and only include certified reference materials for the content of perfluoroalkyl substances in fish tissue and drinking water (IRMM-427 and IRMM-428). According to the discussions, certified reference material with known PFAS concentrations is needed for at least eggs, fish, milk (powder), vegetables, and for packaging material (e.g. paper board).

New insights into BCF & MRL

It was agreed in the discussion that a clear proof of the risk is necessary. Maybe an approach linked to the ‘dioxin approach’ needs to be checked as a way forward. Several items have to be taken into account such as the effect of the chain length of the considered PFAS compound. It was stated that longer chains tend not to accumulate in above ground parts of vegetables, as they adsorb to the roots. Furthermore, we also have to be aware that risk limits in crops ≠ risk limits in meat.

At this stage, recommending tolerable total PFAS-concentrations is not possible. It is also not possible to regulate all PFAS substances in food. However, if occurrence data would be gathered for total PFAS it would facilitate further work in that direction.

It is necessary to define MRL and MLs (maximum levels) for contaminants including PFAS. MRL and MLs are mostly set for individual substances and occurrence in specific food item. However, there are cases where MLs have been set for groups of substances e.g. dioxins. Maximum levels are set taking into account occurrence data. MLs are set for commodities, which are high contributors to the exposure. Often these commodities are those, which are consumed in large quantities. Precursors of PFOS/PFOA are an issue related to analytical challenges, but as a conservative approach, they could be taken into account for a consumer risk assessment (e.g. BCF and MLs definition). For PFAS there is still some work needed before such MRL and MLs can be properly defined for individual substances.

If we want to reduce the risk, we need to know the bioaccumulation routes, which are currently not sufficiently understood. Risks have to be reduced in case the consumer risk assessment indicates a health risk (exceedance of the TWI). Regulatory measures need to be defined, including the establishment of maximum levels for contaminants in food items. In some cases food consumption advice can also be considered such as decrease the use of PFAS containing food contact materials (packaging) or if it is known that it is due to one type of food it is advisable to limit its consumption (e.g. dioxins: adult max. 3 eggs/wk). Additional ideas on the reduction of exposure are: 1) referring to the approach applied in Denmark; 2) select some relevant products (food) and advice on the consumption; 3) reduction in packaging material; 4) a ban on the import of foods with high levels (survey needed); and, 5) “improvement” of databases such as the EFSA database.

II.3.2.3 Conclusion and recommendations

Sampling (sample collection) techniques and protocols

To obtain better and more information on the presence of PFAS in foods, crops, feed and packaging material it is proposed to consider sampling campaigns of: 1) raw items randomly selected in supermarkets (Total Diet Study); 2) composite food (ready to eat/cook food items); 3) cauldrons (whole meals, multiple sampling); and, 4) food packaging. Also, the origin of food items needs to be known. As a result databases can be created containing significant information for individual food items, and from scientific reports. Next to this there is a need to do (more) “migration” studies.

Because not every Member State has well-equipped laboratories regarding the analysis of PFAS in the food chain, support from, for instance, reference labs in other MS should be enabled.

Analytical methods and target parameters (PFAS total, PFAS sum, individual components)

Analytical methods for individual PFAS are in place and sufficiently sensitive for food/feed analysis. Important is that when analytical procedures are taken into account there is a large difference between the food matrix compared to soil and water.

Since standard methods are not yet available, it is necessary to define such a standard for TOP, including the appropriate QA/QC. Related to the TOP approach the following have to be considered:

- A combined set of analyses is necessary: individual component approach and TOP;
- TOP requires 2 analyses: before and after oxidation. This gives information about the increase in PFAS-concentration (potential level), which is due to the conversion of precursors;
- For packaging materials, further information must be obtained about the applicability of TOP.

Reference samples

Since only a limited set of CRM exists there is a need for additional material especially regarding meat, eggs, milk (powder) and vegetables. When more information on specific foods are known, it will enable to introduce maximum levels for individual PFAS for all types of food for a larger set of individual PFAS and for TOP.

Insights raised by the participants into BCF & MRL and reduction measures

For a limited number of PFAS substances limited information is available about accumulation in food items (e.g. milk and vegetables). Short chain PFAS tend to accumulate in crops and above ground vegetables while long chain PFAS accumulate in fish and meat and below ground vegetables.

Some ideas to reduce human exposure at a short notice could be: 1) a ban on the use of packaging material (approach in Denmark); 2) not importing food/feed with high levels; 3) consumption advice on selected highly contaminated food items

It would be useful that MRLs are determined for PFAS, it was concluded that these can be achieved with current analytical methods.

II.3.3 Characterisation of PFAS in other matrices / media - alternatives substitutes for PFAS

II.3.3.1 Introduction

PFAS measurements and processes/fate information is mostly available for the aqueous phase (see Chapter II.3.1). However, many PFAS entry pathways into the environment are related to other environmental matrices, such as soil and sludge (Figure 5). Parallel Session III was dedicated to these often neglected occurrences and the according risks. Thomas Knepper from Fresenius Institute, Germany, gave the keynote presentation.

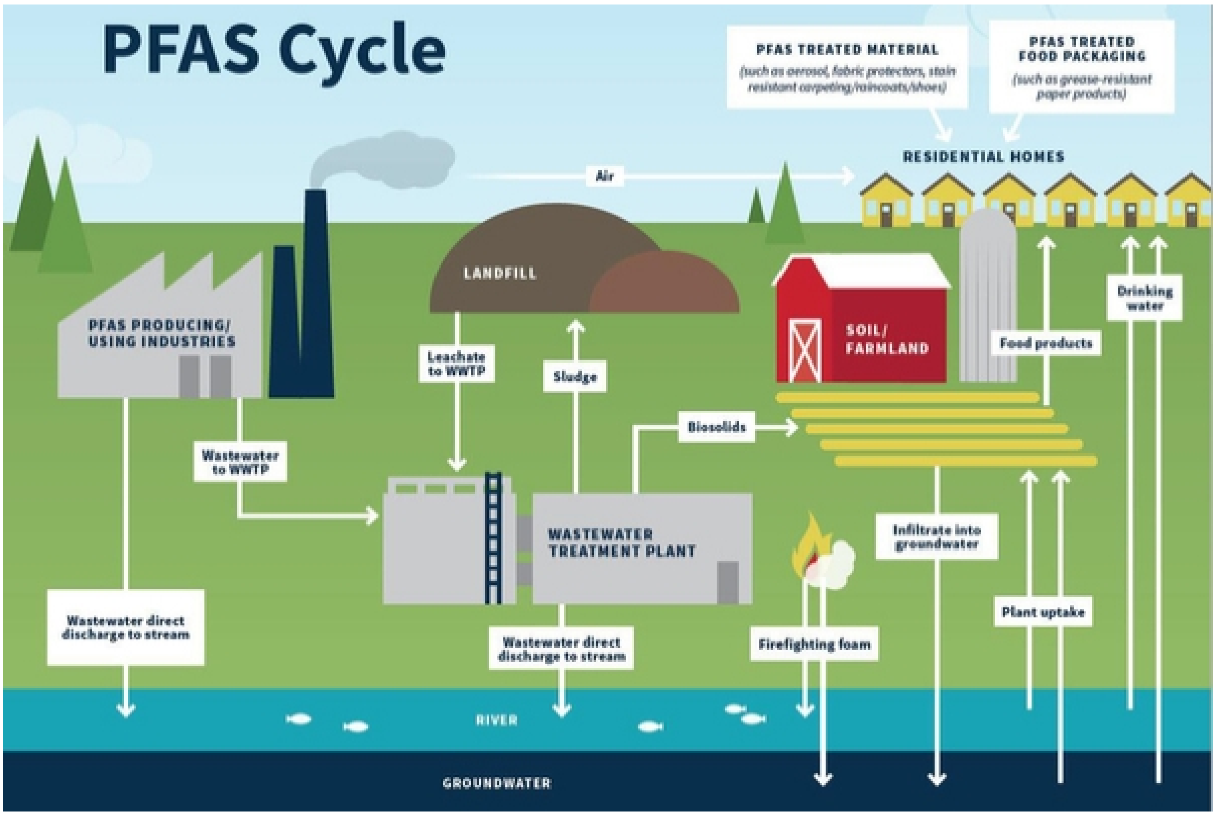


Figure 5: PFAS cycle and entry pathways into the environment (NRWA, 2019)

II.3.3.2 Summary of Keynote presentation

The presentation given by Thomas Knepper (Annex II.5.9) was divided into three parts:

- PFAS in non-environmental media;
- PFAS in other environmental matrices;
- Alternative solutions.

PFAS in non-environmental media

An overview was provided of PFAS detected in multiple non-environmental media, such as outdoor jackets, impregnating sprays, building materials, industrial textile, and ionic liquids. The main conclusions were:

- Numerous potential sources of PFAA and PFSA including precursors exist;
- Analytical methods are extremely challenging due to the different matrices and are not easily comparable to standardized water methods;

- Due to enormous efforts, the first quantitative data about many hitherto scarcely investigated or unknown PFAS such as PM-chemicals have been generated;
- Some of these PFASs cannot be removed with conventional water treatment technologies – applying reverse osmosis seems to be promising;
- Local hotspots may lead to elevated drinking water concentrations when no efficient removal can be achieved (example TFMSA); and,
- Only a fraction of potential intentionally produced and even less transformation-derived PM-chemicals have yet been investigated.

PFAS in other environmental matrices

The second part of this session showed examples of measured PFASs occurrences in grass, leaves, soil, landfills, sewage sludge, wastewater, biosolids, and sediments. The main conclusions were:

- These presented indirect pathways are a highly relevant source for PFAS in groundwater and drinking water;
- PFAS as often persistent and mobile chemicals are problematic for the above mentioned matrices and often provide large storage potential for precursors, including fluorinated polymers;
- Hot spots are difficult to identify, mostly only as a source control after the contamination of (ground)water;
- It is recommended to monitor PFAS producing industrial sites and surrounding areas (air, soil, water cycle), including target, non-target and sum parameter analyses with defined frequencies;
- Highly problematic are the knowledge gaps (occurrence, mobility, chemistry…), missing or inadequate regulation (thresholds, monitoring, standards…), and the costs analysis and remediation methods.

Alternative solutions

In the final part of the presentation examples of PFAS free products and their necessary characteristics, such as reduced surface tension and degradability/mineralization potential were discussed. The main conclusions were:

- PFAS should ideally be ranked according to their need for substitution (e.g. amount used and known toxicity) and then substituted or regulated;
- Knowledge gaps exist on the necessary triggers to encourage producers using PFAS to switch to PFAS free materials;
- It is difficult to recommend specific PFAS free materials from an environmental point of view, as their fate and toxicity are often unknown.

II.3.3.3 Discussion

During the workshop three subjects for discussion where defined:

- Methods and data;
- Risk assessment;
- Policy and regulation.

The discussion was initiated by questions prepared as shown in Annex II.6 – Parallel sessions, guiding questions. The following research, knowledge and regulation gaps were discussed for PFASs in other media:

Methods and data

- There are currently no standardized methods for sample preparation and analysis for all relevant matrices (e.g. water, soil, food, sludge, packaging materials, etc.). It is recommended that we agree on individual methods for specific matrices to make analyses comparable.
- Currently, little information is available on PFAS production and use at the regional level and should be provided at least at the Member State levels. This is important to derive local sampling and analytical protocols for different environmental matrices. Producers and users should submit the necessary data to authorities.
- For several media and products PFAS occurrences and fate are largely unknown. This includes e.g. ionic liquids in batteries. Here, closed loops need to be promoted and life cycle assessments need to be considered. Another example are impregnation sprays, which are difficult to measure due to unreacted monomers, as they may react further. More research is necessary.
- A harmonized European database/inventory should be developed, which includes as many PFAS measured environmental occurrences in different matrices as possible, from authorities, researchers and others. This will enable the identification of hotspots, risk assessments and analytical efforts. Large scale sampling campaigns for regions with few measured data (e.g. Eastern Europe) should be initiated and funded.
- Only a few studies on PFAS contamination via atmospheric deposition are available. They indicate that transport via air cannot be neglected, e.g. top soil PFAS contamination decreasing with distance from production facilities. This also requires further research into current incineration processes, which could lead to further regulation regarding filters and incineration temperatures.
- Non-target analyses of PFASs are useful for detecting unknown substances, but are challenging to perform, especially for non-scientific sampling and analysis. Further innovation on automatization is needed, also on the detection of polymers.

Risk assessment

- There are more than 4700 PFAS in existence, whereas environmental risk assessments, toxicological endpoints, analytical standards and methods are available for only a few of them. Therefore, a discussion is needed on how data can be made available from producers, agencies and researchers. However, as it will be difficult to conduct environmental risk assessments for each PFAS for different matrices, a new strategy needs to be developed. This could result in the development of a new method, which is able to measure Total F concentrations, or of a new list of single PFAS, which represent larger substance groups.
- Current risk assessments and the subsequent regulations are mostly analytically driven (LoQs), and not by toxicological thresholds. Scientists, producers, and regulators should work together to develop a common framework.
- GenX (HFPO-DA) has been detected in plants and water near manufacturing sites. When developing environment-friendly PFAS-free alternatives, they should be less persistent, mobile and toxic than PFOA/PFOS. Further research needs to be conducted about the complete

mineralization of these alternatives, the replacement of requested properties of substances (e.g. reduction of surface tension) and about the design of more environment friendly alternative chemicals.

Policy and regulation

- The effect of replacing long-chain PFAS with short-chain PFAS due to regulation (e.g. fire-fighting foams) regarding persistency, bioaccumulation, and toxicity is largely unknown for different environmental matrices and other media. Further research is considered necessary, as short-chain PFAS are suspected to be persistent and mobile.
- As different PFAS are relevant for different product categories and matrices a PFAS Watch List should be specifically developed for each environmental matrix and other media.
- Based on the chemical structure and known individual characteristics all PFAS substances should be prioritized for future regulation. This should also consider PFAS amounts being produced and used.
- To increase awareness, it is recommended to develop labels which inform consumers about the application of PFAS in certain product groups. However, an overload of labels and information may proof counterproductive. PFAS information could also be integrated in already existing green and eco labels.
- PFAS precursors and intermediates are big challenges in REACH, also in terms of available reference compounds. Further, a robust and clearer definition of polymers in REACH is needed (definition should be based on behavior, not on structure).
- Zero-emission goals for the industry need to be introduced for PFAS for certain product groups (e.g. textiles). Some industries already try to reduce emissions voluntarily, but state that sometimes techniques are missing. For some applications it is difficult to find alternatives, but in some fields it might be easier to reduce the application (non-essential use). Companies ask for further guidance on practical methods on how to test imported products (e.g. pellets) for restricted chemicals like PFOA (sample preparation, not analysis).
- A dialogue with industries producing and using PFAS should be started to define specific goals for certain product groups (round table). Generally, a better communication is necessary between different stakeholders.
- Current applications of clean-up and remediation technologies are often not state-of-the-art. More research and its transfer is recommended.
- The distributing of sewage sludge on top soil of agricultural areas may be an important entry path for PFAS into the environment. The Sewage Sludge Directive (until now only limits for heavy metals) should be revised to include PFAS limits.
- The Industrial Emissions Directive can be useful for issuing environmental permits, BREFS should include PFAS.
- Generally, more innovation from all stakeholders is needed to develop PFAS-free alternatives. More (co-)funding could support this. For example, the substitution of reagents in production processes is difficult for high performance F-polymers and needs to be further investigated. Similarly, for emulsifiers, which are an important source for PFAS in the environment, water-soluble alternatives need to be developed.
- A discussion needs to be started on which uses of PFAS in products are essential and which could be substituted by PFAS-free alternatives. However, society, science and authorities need to be involved and the process should not be driven by market perspectives. Economic factors

should balance out public health and environmental factors. It needs to be considered that "essential uses" can change with time.

- For some applications (e.g. cosmetics) PFAS are not needed. These uses should be restricted.
- Public procurement of PFAS-free alternative products should be promoted at European, national and regional level.
- The development of PFAS-free alternatives should prioritize those products that are used in open applications, such as roof materials, as they are prone to enter the environment quickly on large scales.

II.3.3.4 Conclusions and Recommendations

According to the discussion of the session on PFAS in other matrices/media and alternative solutions to PFAS, the following research needs and options for potential regulatory measures can be summarized:

Methods and Data

To mitigate future PFAS occurrences in other matrices – and their entry into the environment via these matrices - it is necessary to gain more knowledge on substances and their sources, application and fate. Therefore, it was recommended to set up a harmonized European register about PFAS production and occurrences of PFASs in different media to streamline data from different sources and regions. Furthermore, the pathway of PFAS in multiple products and its fate needs to be studied. However, as standardized methods for PFAS in many industrial and consumer products are missing, results are not comparable. Thus, further development of analytical methods, including non-target analytics, needs to be promoted.

Risk assessment

For many PFASs risks for the environment and humans are largely unknown. Toxicological studies on PFASs specific endpoints are needed, including the publication of relevant data from PFAS producers. Also, new risk assessment methods need to be developed, such as PFAS-tailored toxicity assays, as they are considered to be cocktail effects. Even though PFAS alternatives, such as GenX, are now available, studies show that they can cause similar risks as the PFAS substances they are replacing. Therefore, more research on these as well as many short-chain PFAS with unknown effects on the environment and health is required.

Policy & Regulation

Existing regulations, such as REACH, the Sewage Sludge and Industrial Emissions Directives should be improved to better mitigate PFAS occurrences in the environment and other matrices. It needs to be discussed with stakeholders, which product groups can be produced with zero emissions. Also, a prioritization for future regulation of specific PFAS compounds based on their amount and type of usage is recommended. These could also be added to the European Watch List to better monitor their occurrences in Europe. Finally, policy, industry and other stakeholders need to work on the development of PFAS-free substitutes together to consider not only the economic but also the impacts on the environment and health.

II.4 Policy Recommendations

II.4.1 General aspects

PFAS are a large chemical family consisting of more than 4.700 individual substances with unique chemical properties. It has been demonstrated that they spread into all environmental compartments due to their high solubility in water, low sorption to soil and particulate matter and their resistance to biological and chemical degradation (see I.2 PFAS CHEMISTRY). They accumulate in human beings and animals and some PFAS have properties of toxicological concern (see I.3.4 Toxicology). A considerable proportion of the European population is expected to exceed the tolerable weekly intake due to intake of certain PFAS substances from food and drinking water (EFSA 2018, 2020; see details in chapter II.4.2 Limits for drinking water). These are reasons enough to apply the precautionary principle and to establish restrictions on production and use. As losses into the environment and direct exposure to humans are inevitable, measures at the source are needed rather than advocating end of the pipe measures.

Some of the PFAS have already been restricted or will be restricted in the near future, but still, a multitude of substances is entering the market.

Within EU chemicals legislation, PFOS, PFOS salts and PFOS precursor substances are restricted in the EU according to the Persistent Organic Pollutants (POPs) Regulation (EU 2019/1021). PFOA, its salts and related substances are listed in annex XVII of REACH and will soon be included in Annex I of the POPs Regulation. They will no longer be allowed to be produced or used in the EU as of July 2020 (with some exemptions). PFHxA, its salts and related substances as well as PFHxS, its salts and related substances are under discussion for inclusion in annex XVII of REACH. ECHA is currently evaluating the respective restriction dossiers. The results are expected for late 2020 for PFHxS and for late 2021 for PFHxA. Further regulatory measures on other PFAS are currently being discussed under REACH, like the identification as SVHC or a restriction of C_9-C_{14} PFCAs, for which the opinion of ECHA's committees is already available. Also, GenX and PFBS have been identified as SVHCs due to a high concern about their mobility (PMT).

The EC initiated two studies on the use of all PFAS and non-fluorinated alternatives in fire-fighting foams and in textile – leather processing. The collected data, including substance identification, benefits, hazards, emissions, potential alternatives, critical uses, costs of restricting the substances as well as costs of contamination of soil and water will be used as a basis for the REACH restriction.

However, concern has been raised by a group of renowned scientists that, while some PFAS have been regulated so far, knowledge about uses and hazards of others are still very limited or missing (Zurich statement).

A socioeconomic analysis of environmental and health impacts linked to exposure to PFAS has been published in 2019. It concludes that substantial socioeconomic costs may result from PFAS exposure in terms of impacts on human health and the environment. Annual health-related costs were estimated at 52 – 85 billion for all EEA countries. Overall non-health costs (e.g. environmental remediation) sum up to 20 – 170 billion Euro for all EEA countries (Nordic Council, 2019).

EU Member States asked to the European Commission to develop an EU strategy to minimize the environmental burden and human exposure to PFAS through regulatory and non-regulatory actions. In line with the timeframe of the UN Global Goals for Sustainable Development, the paper proposes actions to be taken on the EU level to phase out all PFASs at the latest by 2025 and to be in effect by 2030.

To summarize, some regulations are in place and several activities are ongoing. However, there is also concern that the measures taken are not sufficient to protect citizens from adverse effects of this group of substances. Because of their persistence, PFAS and their degradation products will remain for a long time in the environment. Substances still in use will lead to irreversible contamination while alternative PFAS substances, which might be regrettable substitutions, are brought on the market. Therefore, the following recommendations were given during the workshop:

- The European Commission should acknowledge the concerns of Member States, summarized in the request to issue a strategy for PFAS, which addresses the entire group of chemicals under the chemicals legislation (REACH), but also using other EU legislations and global initiatives (including non-legislative ones). A comprehensive approach also needs to include plant protection products (EFSA) and pharmaceuticals (EMA) as these are precursors of the short chain PFAS.
- The revision of the DWD does not include PFAS precursors. As illustrated during the plenary session, precursors cannot be ignored. Their inclusion into the DWD needs to be re-evaluated.
- On-going activities at ECHA and EFSA need to be finalised without delay, respecting the deadline set in the legislative processes.
- Regulations and policy acts must address the source rather than react at the end of the pipe. This, however, needs time to be fully implemented and thus measures at the end of pipe are needed while uses are being phased out.
- The effect of replacing long-chain PFAS with short-chain PFAS due to regulation (e.g. fire-fighting foams) regarding persistency, bioaccumulation, and toxicity is largely unknown for different environmental matrices and other media and further research is considered necessary. Short-chain PFAS are suspected to be persistent and mobile.
- Clarification in the issue of “essential” vs. “non-essential” uses in the light of (further) restrictions of relevant substances to guarantee a uniform and consistent prioritisation approach.

II.4.2 Limits for drinking water

For the Groundwater Directive, 10 PFAS substances have been proposed to be considered for the annexes review, for which sufficient monitoring data are available through the voluntary watch list process. The regulation of pesticides in drinking water, the new Drinking Water Directive (DWD) sets a limit value of 0.1 µg/l for the sum of the 20 most important substances and a limit of 0.5 µg/L for “PFAS total”. The European Commission needs to establish technical guidelines for measuring all PFAS over the next three years. A limit value (0.5 µg/l) will apply once technical guidelines for monitoring ‘PFAS total’ are available.

An EFSA risk assessment, which has been published after the workshop, proposes tolerable weekly intake (TWI) levels based on epidemiological data to specifically protect infants (EFSA, 2018; EFSA, 2020). The TWI calculates as the sum of PFOA+PFNA+PFHxS+PFOS (which contribute most to human exposure) of 8 ng/kg bw/week.

Table 3 illustrates that the tolerable total intake levels depend on the respective body weight.

Table 3: Tolerable weekly intake calculated for different groups depending on body weight

population	body weight (kg)	Tolerable PFAS intake (total in ng/week)	% TWI
children	10	80	100%
teenager	40	320	100%
adult	70	560	100%

By comparing the total intake values for different scenarios of drinking water consumption (exactly meeting the new DWD limits) for different age groups (assuming body weights of 10, 40 and 70 kg) and assuming the predominant presence of the respective four PFASs it is obvious that the limit of sum of PFAS and of total PFAS are not protective.

Table 4: Proportion of the TWI for the three age groups depending on different daily water consumptions and their proportion of the total weekly intake suggested by EFSA

	Total weekly intake: ng	**% TWI**		
water consumption (L/d)	**DWD: 4 PFAS (0.1µg/L)**	**children**	**teenager**	**adult**
1	700	875%	219%	125%
2	1,400	1,750%	438%	250%
3	2,100	2,625%	656%	375%
Water consumption (l/d)	**DWD: 4 PFAS (0.5µg/l)**	**children**	**teenager**	**adult**
1	3,500	4,375%	1,093%	625%
2	7,000	8,750%	2,187%	1,250%
3	10,500	13,125%	3,281%	1,875%

Addressing options to overcome the discrepancy is beyond the scope this report.

II.4.3 Monitoring

In order to measure PFAS and PFAS total, several analytical options are available (for details, see I.4 Analytical methods). Existing targeted methods (LC-MS/MS) for the determination of PFAS are still among the most important analytical tools available, in particular because of their specificity and sensitivity. However, the large number of PFASs to be addressed by 'PFAS total' calls for additional approaches to broaden the analytical spectrum. Examples for non specific methods to determine the organic fluorine content and to extend the spectrum to species that cannot yet be measured by targeted methods, have been described and compared (see II.3.1 Characterisation of PFAS in groundwater, surface water & drinking water). The measurement of organic fluorine as surrogate for PFAS is an option, but their sensitivity and selectivity have to be investigated more in detail. Also, economic considerations as high investment costs for a very specific kind of analyses like PIGE should be weighed against the market demand and quality aspects. As a matter of fact, results below the limit of quantification need to be checked/confirmed by additional targeted analyses.

A method to include precursors in monitoring is oxidative conversion of precursor substances (TOP). In contrast to other methods, TOP is specific for PFAS while other unspecific total fluorine methods also include fluorine from organic pesticides and pharmaceuticals. This leads to the need for clear definitions that should be considered under 'PFAS' and 'total PFAS' and how to deal with results from unspecific methods which yield fluorine concentrations as a surrogate for 'PFAS total'. All these aspects have to be included when it comes to the establishment of necessary technical guidelines for the implementation of the Directive. Several recommendations have therefore been identified in the workshop:

- Methods for measurement of organic fluorine as surrogate for PFAS are available but need to be evaluated for their applicability.
- The common terminology recommended by Buck et al. (2011) was updated by the OECD (2018), but there is still confusion. Therefore, one unambiguous terminology needs to be elaborated by globally acting organisations, science and standardizing bodies.
- The panel agreed that for the moment precise definitions for "total PFAS content" are not available and that these need to be defined further on a legislative level. Similarly, the term "total" needs to be defined clearly, based on a consensus and/or a specific method.
- Standard analytical methods do not yet fully address the needs for sampling and analysis of PFAS. For instance, a globally applicable and standardised method for measuring of PFAS in air samples, reference matrices for human biomonitoring or biological monitoring is missing. It is recommended to check the possibility of developing a new CEN standard based on the existing ISO standard (ISO 21675:2019) and to support standardization activities, maybe under a specific mandate.
- The availability of certified reference materials (CRM) for PFAS substances shall be increased to raise the level of confidence for the analytical procedures. For the 20 PFAS listed in the DWD, only 18 are commercially available. Certified reference material with known PFAS concentrations is needed for at least eggs, fish, milk (powder), vegetables, and for packaging material (e.g. paper board). CRM are needed to validate analytical procedures and check the metrological traceability of methods which are used for enforcement of legislation. Therefore, the legislator should be precise in the definition and nomenclature of parameters as pre-requisite to the development of appropriate analytical methods, their standardization and development of CRM by commercial providers.
- Currently, little information is available on past and on-going PFAS production, manufacturing and use on regional and national levels. This is important to derive local sampling and analytical protocols for different environmental matrices. Producers and users should submit the necessary data to authorities, preferably under the JRC's IPCHEM platform.
- Under the same IPCHEM platform, a harmonized European database/inventory should be developed, which includes as many PFAS measured environmental occurrences in different matrices as possible, from authorities, researchers and others. This will enable to derive hotspots and their sources, risk assessment and measures.
- One problem raised is that the different toxicities of PFAS are not considered when calculating sums of PFAS mass concentrations (harmless PFAS and toxic substances are equivalent in the sums). Therefore, the panel suggested to implement some sort of weighting factor (as is done for PCDD/PCDF) if enough knowledge is available. This has to be assessed by toxicologists.

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Annexes

Annex I.1 – Summary of recent publications on analysis of PFAS in abiotic environmental matrices

Reference	PFAS	Intake dw	Extraction	Clean up	Measurement	Matrix and reported levels (in µg/kg ds)	LoD/LoQ
DIN 38414-14	C4-C10 PFCA C4-C8 PFSA	1 g	Sonication with MeOH	SPE WAX (optional) Elution with MeOH 0.1% NH3	HPLC-ESI(-)-MS/MS	Soil Sediment Sludge	LoQ: 10 µg/kg
ASTM D7968-17	C4-C14 PFCA C4-C8 PFSA PFECHS FHpPrA 6:2 FTCA 8:2 FTCA 10:2 FTCA 2H-perfluoro-2-decenoic acid 2H-perfluoro-2-octenoic acid	2 g	Vortexing and shaking with 50:50 MeOH/water and 50:50 MeOH/water/NH3 (pH 9-10)	-	UPLC-ESI(-)-MS/MS,	Soil	LoQ: 0.01-0.25 µg/kg RL: 0.25 µg/kg
Munoz 2016	C5-C18 PFCA C4-C10 PFSA FOSA 6:2 FTUA 8:2 FTUA 5:3 FTCA 7:3 FTCA PFOAB PFOSB PFOANO PFOSNO PFOAAmS PFOSAmS PFOSAm	1 g	Vortexing and sonication with MeOH (20 mM NaOH) (2x)	ENVI-Carb Washing with MeOH	UPLC-HRMS (Q-Exactive, Rs 70.000)	Sediment <LOD-4.2 µg/kg dw	LoD: 0.0006-0.46 µg/kg
Huset 2018	C4-C8 PFCA C4-C8 PFSA	5 g	Sonication with MeOH (1% NH3) (3x)	ENVI-Carb	HPLC-ESI(-)-MS/MS	Soil	LoQ: 0.01-0.03 µg/kg
Joerss 2019	C4-C14 PFCA C4-C10 PFSA PFECHS HFPO-DA HFPO-TrA HFPO-TeA	5 g	Vortexing and sonication with water (1% HAc) and MeOH/water (1% HAc)(2x)	Oasis WAX Elution with 80/20 MeOH/water and MeOH (0.1% NH3)	HPLC-ESI(-)-MS/MS	Sediment <LoQ-2 µg/kg	LoQ: 0.006-0.5 µg/kg

	ADONA 6:2 Cl-PFESA 8:2 Cl-PFESA 6:6 PFPiA 6:8 PFPiA FOSA 4:2 FTSA 6:2 FTSA 8:2 FTSA						
Rankin 2016	C6-C14 PFCA C6-C10 PFSA n:2 FTSA n:2 FTUCA (n = 6-14, even) m:3 FTSA m:3 FTUCA (m = 5-13, odd)	5 g	Addition of 400 µl NaOH 2M and vortexing and sonication with 90/10 ACN/water	IPE with TBAS/MTBE	UHPLC-ESI(-)-MS/MS	Soil Europa: ΣPFCA: 0.06-3.6 µg/kg ΣPFSA: LOD-3.3 µg/kg	
Shen 2018	C5-C18 PFCA C4-C10 PFSA	5 g	Shaking and sonication with MeOH	ENCI-Carb	UHPLC-ESI(-)-MS/MS	Sediment ΣPFAS: 0.08-0.3 µg/kg	LoQ 0.002-0.01 µg/kg
Zhang 2018	FOSA EtFOSA FOSAA EtFOSAA EtFOSE SAmPAP diester SAmPAP triester	1 g	Shaking with MeOH (3x)	ENVI-Carb Washing with MeOH (0.5% NH3) and MeOH/DCM 1/1	UHPLC-ESI(-)-MS/MS	Sediment ΣPFAS: 0.3-18 µg/kg SAmPAP diester: <LOD-4 µg/kg SAmPAP triester: <LOD-1.1 µg/kg	LoD: 0.03 µg/kg
Codling 2018	C4-C14 PFCA C4-C10 PFSA MeFOSAA EtFOSAA MeFOSE EtFOSE	2.5 g	Sonication with MeOH (1% HAc)(3x)	Oasis HLB Elution with MeOH and toluene	UHPLC-ESI(-)-MS/MS	Sediment ΣPFAS (mean): 11 µg/kg	
Kikuchi 2018	C4-C18 PFCA C4-C10 PFSA FOSA, MeFOSA, EtFOSA, FOSAA, MeFOSAA,	2 g	Shaking with MeOH (0.1M NaOH) (2x)	Oasis WAX Elution with MeOH and MeOH (0.1% NH3)	UHPLC-ESI(-)-MS/MS	Soil PFCA: <LOD-8.3 µg/kg PFSA: <LOD-1.7 µg/kg FASA:	LoD: 0.005-9 µg/kg

	EtFOSAA, MeFOSE, EtFOSE, n:2 FTSAs (n = 6, 8, 10)					<LOD-0.65 µg/kg FASAA: <LOD-0.88 µg/kg FASE: <LOD FTSA: <LOD-3 µg/kg	
Guo 2016	C5-C13 PFCA C6-C10 PFSA n:2 diPAPs (n = 6, 8, 10), PFPAs (n = 6, 8, 10), 6:6 PFPiA 6:8 PFPiA 8:8 PFPiA	1 g	Shaking with water (0.2M NaOH)/ACN	IPE with TBAS/MTBE	UHPLC-ESI(-)-MS/MS	Sediment ΣPFAS: 13 µg/kg (mean)	LoD: 0.004-0.2 µg/kg
Ruan 2015	C4-C10 PFSA n:2 FTSA (n= 6, 8) n:2 Cl-PFESAs (n = 6,8,10)	0.5 g	Shaking with ACN:water (1M NaOH)	ENVI-Carb	UHPLC-ESI(-)-MS/MS UHPLC-ESI(-)-HRMS (Orbitrap)	Sludge ΣPFSA: <LOD-220 µg/kg ΣPFSA: <LOD-19 µg/kg ΣCl-PFESA: <LOD-240 µg/kg	LoQ: 0.025-0.14 µg/kg
Winkens 2018	LC: C4-C15 PFCA C4-C10 PFSA FOSA MeFOSA EtFOSA MeFOSAA, EtFOSAA n:3 FTCA (n = 3,5,7) ADONA n:2-PFESAs (n= 6, 8) n::2 FTSAs (n= 6, 8) n:2 monoPAPs (n = 4, 6,8,10) n:2 diPAPs (n = 4,6,8,10) m:2/n:2 diPAPs	Ca 0.1	GC-fraction: vortexing and sonication with ethyl acetate and ENVI Carb, centrifugation LC-fraction: vortexing, sonication with methanol (0.3% NH3) and ENVI-Carb, centrifugation	ENVI-Carb	UHPLC-ESI(-)-MS/MS	Dust PFCA: <0.1-779 µg/kg PFSA: <0.1-1117 µg/kg monoPAP: <12-5946 µg/kg diPAP: 1.6-4841 µg/kg FTCA/FTUCA: <0.1-26 µg/kg FASA/FASE: <0.1-6772 µg/kg 6:2 FTSA: <2.0-20 µg/kg FOSA: <1.4-28 µg/kg	LoD: 0.005-24 µg/kg

	(m = 4,6,8, n = 6,8,10,12,14) GC: 6:2 FTAC 6:2 FTMAC n:2 FTOHs (n = 4,6,8,10) MeFOSA EtFOSA MeFOSE EtFOSE						
Lankova 2015	C4-C14 PFCA C4-C10 PFSA	0.05 g	Matrix solid phase dispersion (MSPD) with florisil Me/EtFOSA: Hex:DCM 15:85 Other PFAS: MeOH		UHPLC-ESI(-)-MS/MS	Dust Σ18PFAS: 1.6-240 µg/kg	LoQ: 0.25-1 µg/kg
Eriksson 2015	C4-C18 PFCA C4-C10 PFSA FOSA MeFOSA EtFOSA MeFOSE EtFOSE 6:2 FTSA n:3 FTCA (n = 5,7) n:2 FTUCAs (n = 6,8,10) n:2 monoPAPs (n = 6,8,10) n:2 diPAPs (n = 6,8,10) m:2/n:2 diPAPs (m = 2,4,6,8; n = 6,8,10,12,14) n:2 triPAPs (n = 6,8) 6:2/6:2/8:2 triPAPs	0.1 g	Sonication with MeOH:NaOH 0.2 M	Oasis WAX and HLB	UHPLC-ESI(-)-MS/MS	Dust PFCA: <0.1-779 ng/g PFSA: <0.1-1,177 ng/g monoPAP: <12-5,946 ng/g diPAP: 1.6-4,841 ng/g FTCA/FTUCA: <0.1-26 ng/g FASA/FASE: <0.1-6,772 ng/g 6:2 FTSA: <2.0-20 ng/g FOSA: <1.4-28 ng/g	LoD: 0.005-24 µg/kg

Annex I.2 – Summary of recent publications on analysis of PFAS in air samples

Reference	PFAS	Matrix	Sample volume	Sampling device	Absorbent	Elution/clean up	Instrument	LoD/LoQ	Reported levels
Wong 2018	C4-C14 PFCA C4-C10 PFSA n:2 FTOH n:2 FTAC (n = 6,8,10) FOSA MeFOSA EtFOSA MeFOSE ETFOSE 6:2 FTSA	Outdoor air	1200, 2000 m^3	High-volume sampler	GFF, XAD	PLE, sonication with MeOH	GC-PCI-MS UHPLC-ESI(-)MS/MS UHPLC-ESI(-)TOF-MS	0.008-4.2 pg/m^3	FTOH (median): 3.8 pg/m3 FASE (median): 0.49 pg/m3 FASA (median): 0.13 pg/m3 FTAC (median): 0.24 pg/m3 FOSA (median): 0.12 pg/m3
Padilla-Sanchez 2017	n:2 FTOH (n = 6,8,10) MeFOSA EtFOSA MeFOSE ETFOSE	Indoor air/ personal air	7.2/1.44 m^3	Low volume sampler	SPE (ENVI+)	MeOH	GC-PCI-MS	0.03-71 pg/m^3 (indoor air) 1.4-350 pg/m^3 (personal air) (MDL)	FTOH: 170-446,000 pg/m^3 FASA: <MDL-78,300 pg/m^3 FASE: <MDL-38,800 pg/m^3
Yao 2018	C4-C12 PFCA C4-C8 PFSA MeFOSA EtFOSA MeFOSE ETFOSE n:2 FTOH (n = 6,8,10) n:2 FTUCA n:2 di PAP (n = 6,8)	Indoor air	0.172-8.33 m^3	Low volume sampler	SPE (WAX/HC-C18)	Ethyl acetate 0.5% NH3 MeOH	GC-PCI-MS HPLC-ESI(-)MS/MS	0.9-26.3 pg/ average 3 m^3 (MDL)	ΣFTOH: 249-62,100 pg/m^3 ΣPFCA: 121-8,670 pg/m^3 ΣPFSA: 71.2-1,780 pg/m^3 ΣdiPAP: ND-125 pg/m^3 ΣFASA/E: ND-2,460 pg/m^3 ΣFTUCA: ND-413 pg/m^3
Li 2011	8:2 FTO n:2 FTOH (n = 4,6,8,10,12) n:2 FTAC (n = 6,8) MeFBSA MeFOSA EtFOSA MeFBSE MeFOSE EtFOSE	Outdoor air		Passive sampler	SPE (SIP disk)	Ethyl acetate (cold column extraction) ENVI-Carb	GC-PCI-MS	0.09-1.85 pg/m^3	ΣFTOH: 51.4-1,210 pg/m^3 ΣFTAC: 0.20-15.3 pg/m^3 ΣFASA: 3.22-831 pg/m^3 ΣFASE: 7.44-172 pg/m^3

Tian 2018	C4-C12 PFCA C4-C8 PFSA MeFOSA EtFOSA MeFOSE ETFOSE n:2 FTOH (n = 6,8,10) n:2 di PAP (n = 6,8)	Outdoor air		Passive sampler	SPE (SIP disk)	Soxhlet: EtOAc, MeOH ENVI-Carb	GC-PCI-MS HPLC-ESI(-)MS/MS	0.02-0.22 pg/m^3	ΣFTOH: 58-2,100 pg/m^3 FASA: ND-13 pg/m^3 ΣPFAS: 280-820 pg/m^3 diPAP: <MDL-12 pg/m^3 TFA: 1.4-3.0 ng/m^3

Annex I.3 – Summary of recent publications on analysis of PFAS in consumer products

Reference	PFAS	Matrix	Extraction	Clean up	Measurement	Main detected PFAS
Herzke 2012	C4-C14 PFCA C4-C10 PFSA FOSA n:2 FTOH (n = 4,6,8,10)	Waterproofing agents Paint Coated fabrics (paper, textile; leather, carpets) Non-stick ware Electrics and electronics Fire-fighting agents (AFFF)	Sonication with MeOH (ionic PFAS) and ethyl acetate (FTOH)(3x)	ENVI-Carb/acetic acid (FTOH)	HPLC-ESI(-)TOF-MS GC-PCI-MS	PFSA: AFFF (max 900 mg/l) FTOH: AFFF (max 27 mg/l) and water proofing agents (max 330 mg/l)
Blom 2015	C4-C14 PFCA C4-C8 PFSA n:2 FTSA (n = 4,6) n:2 FTOH (n = 4,6,8) n:2 diPAP (n = 6,8)	Table cloths Baking paper Sandwich papers Car waxes Dishwashers Waterproofing agents Ski waxes Lubricant Dental flosses Non-stick baking ware	Vortexing and sonication with MeOH	-	HPLC-ESI(-)MS/MS GC-PCI-MS	PFCA: table cloths (max 6.3 µg/m^2), ski waxes and lubricants (max 92 µg/kg) PFOS: ski wax (53 µg/kg) FTOH: table cloths (max 370 µg/m^2), food packaging paper (max 5.2 µg/m^2), waterproofing agents (max 260 mg/l), non-stick baking ware (max 95 µg/m^2)
Van de Veen 2016	C4-C14 PFCA C4-C8 PFSA FOSA	Textiles	Sonication with MeOH (2x)	-	HPLC-ESI(-)MS/MS	
Borg 2017	C4-C10 PFCA C4-C8 PFSA MeFOSA EtFOSA MeFOSE EtFOSE n:2 FTOH (n = 4,6,8,10) n:2 FTA (n = 6,8,10) TOF	Popcorn bags and cupcake forms Rinse aids Waterproofing agents (leather, textile) Waxes (shoe, floor, furniture, car) Textiles	Sonication with matrix-dependent solvents	-	HPLC-ESI(-)MS/MS GC-PCI-MS CIC	6:2 FTOH: shoe/textile/leather treatment, floor polish (max 120 mg/m^2)
Kotthoff 2015	C4-C14 PFCA C4-C10 PFSA n:2 FTOH	Cleaning agents Carpets Water proofing agents	Liquids, sprays, outdoor textiles, glue: IPE (TBAS/MTBE)	-	UHPLC-ESI(-)MS/MS GC-PCI-MS	FTOHs: impregnating sprays: (max 700 mg/kg) and

	(n = 4,6,8,10)	Outdoor textiles Gloves Leather Paper-based food contact materials (FCM) Ski waxes Wood glue	Carpets, leather, FCM: vortexing and sonication with MeOH Ski wax: vortexing with hexane/methanol, centrifugation and discard of hexane phase			cleaning agents (max 550 mg/kg) PFCAs: FCM (PFOA max 660 µg/kg) and ski-waxes (PFOA max 2000 µg/kg) PFBA and PFPA: leather (max 240 µg/kg)
Schultes 2018	C4-C13 PFCA C4-C11 PFSA FOSA n:2 FTSA (n = 4,6,8) n:2 monoPAP (n = 4,6,8,10) n:2/m:2 diPAP (n = 4,6,8,12,14) ADONA 9Cl-PF3ONS 11Cl-PF3OUdS TF and EOF	Cosmetic products (Cream, foundation, pencil, powder, shaving foam)	Vortexing and sonication with MeOH (0.2 M NaOH), repeat with MeOH, neutralize with HCl CIC	ENVI-Carb/acetic acid	UHPLC-ESI(-)MS/MS	6:2/6:2 diPAP (max 410 µg/g) and 6:2 monoPAP (max 62 µg/g): foundations EOF: foundations (max 1.7 mg/g) TF: cream (max 11 mg/g) and powder (max 19 mg/g)
Janousek 2019	C4-C14 PFCA C4-C12 PFSA n:2 FTSA (n = 4,6,8) FOSA n:2 FTOH (n = 6,8,10)	Building materials (coatings, OSB, sealants, wood glue, foils, …) Industrial fabrics (awnings, seat covers, truck trailer cover, tent material, maritime applications …)	Sonication with MeOH		UHPLC-ESI(-)MS/MS	ΣFTOH: coatings (max 4.3 g/l), awnings (max 4.2 g/kg), seat covers (max 0.65 mg/kg), maritime applications (0.69 mg/kg) ΣPFAA: coatings (max 0.9 mg/kg), awnings (max 0.28 mg/kg), seat covers (0.048 mg/kg)
Mumtaz 2019	C4-C11 PFCA C4-C10 PFSA n:2 FTOH (n = 4,6,8,10)	Textile finishing agents	Ionic PFAS: SPE (Oasis WAX) FTOH: dilution with methanol		UHPLC-ESI(-)MS/MS GC-ECNI-MS	ΣFTOH: max 1.37 g/l

Annex I.4 – Summary of recent publications on analysis of PFAS in human matrices

Reference	Compound	Region	Matrix	Sample intal	Pre-treatment	Extraction	Clean-up	Instrument	LOD/LOQ	Reported levels
Goralczyk 2015	PFOS, PFOA, PFHxS, PFNA, PFDA, PFUnDA, PFDoDA	Poland	serum	100 µl serum	addition of IS enzymatic pretreatment (glucuronidase)	digestion at 37 °C for 90 min.	protein precipitation with ACN	HPLC-ESI(-)MS/MS	0.06-0.3 ng/ml	mean of women and males PFOS 8.42 ng/mL 18.49 ng/mL PFOA 2.83 ng/mL 5.12ng/mL, PFNA 0.67 ng/mL 1.29 ng/mL, PFDA 0.24 ng/mL 0.4 ng/mL, PFHxS 2.34 ng/mL 1.22 ng/mL PFUnDA 0.14 ng/mL 0.17 ng/mL PFDoDA 0.06 ng/mL 0.04ng/mL
Karrman 2007	PFBuS PFHxS PFOS THPFOS PFDS PFHxA PFHpA PFOA PFNA PFDA PFUnDA PFDoDA PFOSA	Sweden	breast milk serum	500 µl serum 1 ml milk	addition of IS and formic acid/water (1:1) sonication centrifugation		SPE (Oasis WAX)	HPLC-ESI(-)MS/MS	LOD serum: 0.1-1.1 ng/ml milk: 0.005-0.1 ng/ml	mean serum concentrations: PFOS 20.7 ng/mL PFHxS 4.7 ng/mL PFOA 3.8 ng/mL PFNA 0.80 ng/mL PFDA 0.53 ng/mL PFUnDA 0.40 ng/mL PFOSA 0.24 ng/mL mean milk concentrations: PFOS 0.02 ng/ml PFHxS 0.085 ng/mL PFOSA 0.013 ng/mL PFNA 0.017 ng/mL
Guruge 2005	PFBS PFHS PFOS PFPeA PFHxA PFHpA PFOA PFNA PFDA PFUnA PFDoA PFOSA 6:2 FTS	Sri Lanka	serum seminal plasma (SP)	1 ml	-	IPE with TBAS/MTBE	-	HPLC-ESI(-)MS/MS	LOQ: 0.002-0.02 ng/ml (PFOA 0.07 ng/ml)	mean (ng/mL) serum SP PFOS 5.03 0.118 PFHS 0.565 0.032 PFDoA 0.011 <0.004 PFUnA 0.112 0.003 PFDA 0.088 0.004 PFNA 0.172 0.007 PFOA 6.38 0.323 PFHpA 0.132 0.014 PFHxA 0.300 0.013

Inoue 2004	PFOS PFOA PFOSA	Japan	cord blood maternal blood	1 ml	-	on-line SPE (Oasis HLB)	-	HPLC-ESI(-)MS/MS	PFOS < 0.5 ng/mL PFOA < 0.5 ng/mL PFOSA <1.0 ng/mL	(ng/mL) maternal fetal PFOS 4.9 - 17.6 1.6-5.3 PFOA <0.5-2.3 ND PFOSA ND ND
Calafat 2007	PFOSA Me-PFOSAA Et-PFOSAA PFBuS PFHxS PFOS PFHpA PFOA PFNA PFDeA PFUA PFDoA	**NHANES** US	serum	1 ml	addition of IS	on-line SPE (Oasis HLB)	-	HPLC-ESI(-)MS/MS	LOD: 0.1 - 1.0 ng/ml	detected in > 98% of the samples: PFOS < 0.4 -435 ng/mL PFOA < 0.1-77.2 ng/mL PFHxS < 0.3-82.0 ng/mL PFNA < 0.1-11.5 ng/mL Detected at lower frequencies: PFDeA (31.3%) Me-PFOSAA (27.5%) PFOSA (22.2%) PFUA (9.7%) PFHpA (6.2%) Et-PFOSAA (3.4%)
Gao 2017	n:2 FTSA (n= 6,8,10) 6:2 PAP 8:2 PAP 6:2 diPAP 6:2/8:2 diPAP 8:2 diPAP PFOPA 6:6 PFPiA 6:6/8:8 PFPiA 8:8 PFPiA FOSA N-MeFOSA N-EtFOSA FOSAA N-MeFOSAA N-EtFOSAA 6:2 Cl-PFAES 8:2 Cl-PFAES C4-C18 PFCA C4-C12 PFSA	Japan	serum	25 µl	dilution with water addition of IS centrifugation	on-line SPE (Oasis HLB)	on-line removal of lipids with IPA	HPLC-ESI(-)MS/MS	LOD: 0.013 - 0.089 ng/mL	mean (ng/mL) ordinary- occupational worker PFOA 3.59 - 325 ng/ml PFHxS 10.7 - 523 ng/ml PFOS 13.9 - 1064 ng/ml FTSA 1.49 - 64.1 ng/mL PFOSA 0.06 - 0.15 ng/ml

Yeung 2013	C6-C14 PFCA 6:2-diPAP 8:2-diPAP	Germany	blood plasma	1 - 3 ml	-	IPE with TBAS/MTBE	-	HPLC-ESI(-)MS/MS		PFHpA 0.0191−2.24 ng/mL PFOA 0.092−39.4 ng/mL PFNA 0.200–2.70 ng/ml PFDA 0.020–0.880 ng/ml PFUnDA 0.003–0.555 ng/ml PFTriDA <0.005 - 0.0484 ng/ml 4:2/4:2-diPAP<0.0007− 0.0948 ng/ml 6:2/6:2-diPAP <0.0002–0.687 ng/ml 8:2-diPAP <0.0010–0.285 ng/ml 4:2/6:2 diPAP 0.0007–2.38 ng/ml 6:2/8:2 diPAP <0.0002–0.113 ng/ml
Berg 2014	C4-C18 PFCA C4-C10 PFSA C6-C10 PFPA n:2-FTSA (n = 4,6,8) PFOSA	Norway	serum	0.25 ml	-	sonication-facilitated LLE	ENVI-Carb	UHPLC-ESI(-)MS/MS	LOD: 0.001-0.07 ng/ml (PFBA 0.2 ng/ml) (PFOS 0.3 ng/ml)	concentration range (ng/mL) PFHxS <LOD-14.8 PFHpS <LOD - 1.10 ∑PFOS 0.30 - 35.8 PFOS Linear <LOD-19.1 PFOS Branched <LOD - 18.2 % linear PFOS 36.0-80.0 FOSA <LOD - 0.38 PFHpA <LOD - 0.45 PFOA 0.28 - 11.0 PFNA 0.15 - 4.36 PFDA 0.05 - 2.34 PFUnDA 0.03 - 1.46 PFDoDA <LOD - 0.2
Hanssen 2013	C4-C10 PFSA FOSA C4-C14 PFCA	Russia and Uzbekistan	blood plasma (maternal and umbilical cord samples)	0.5 - 1 ml	addition of 4 ml MeOH	-	ENVI-Carb	UHPLC-ESI(-)MS/MS	MDL: 0.03-0.1 ng/ml	
Lee 2018	C5-C18 PFCA C4-C10 PFSA	Korea	breast milk	2 ml	-	IPE with TBAS/MTBE	-	HPLC-ESI(-)MS/MS	LOQ: 0.01-0.05 ng/ml	predominant PFAS: conc range - detection rate PFHxS <10-133 ng/L (35%) PFOS 14.8-380 ng/L (100 %) PFHxA <10-129 ng/L (40%) PFOA <10-657 ng/L (88%) PFNA <10-127 ng/L (63%) PFunDA <10-119 ng/L (86%)

Poothong 2017	6:2 PAP 8:2 PAP 6:2 diPAP 8:2 diPAP C6-C10 PFPA C4-C10 PFSA C5-C14 PFCA FOSA MeFOSA EtFOSA	Norway	serum plasma whole blood	50 µl	addition of IS protein precipitation with MeOH centrifugation	on-line SPE	-	UHPLC-ESI(-)MS/MS	MDL: 0.002-0.09 ng/ml	
Kato 2009	PFOSA EtPFOSAA MePFOSAA C4-C8 PFSA C4-C12 PFCA		serum	100 µl serum	addition of HCOOH 0.1M addition of IS sonication centrifugation	on-line SPE (C18)		HPLC-ESI(-)MS/MS	LOD: 0.1-0.4 ng/ml	
Huber 2015	C4-C14 PFCA C4-C12 PFSA FOSA	Norway	serum	50 µl	addition of HCOOH	automated SPE (Oasis WAX)		UHPLC-ESI(-)MS/MS	LOD: 0.013-0.089 ng/ml	ΣPFOS 0.13-118 ng/ml ΣPFOA 0.53-3.44 ng/ml PFHxS 0.18-11.6 ng/ml PFNA 0.03-2.06 ng/ml
Guo 2013	PFOA PFOS	China	serum urine hair nail	1 ml 1 ml 0.1 g 0.1 g	- HCOOH addition, sonication, centrifugation rinsing with water, aceton, air-drying, grinding	IPE with TBAS/MTBE - sonication with ACN digestion with MeOH/NaOH	- SPE Oasis WAX - -	UHPLC-ESI(-)MS/MS	0.02 ng/ml (LOD) 1.1-2.1 ng/ml 0.03 ng/g 0.05 ng/g	0.26-35 ng/ml <LOQ-160 ng/l <LOQ-6.7 ng/g <LOQ-5.1 ng/g
Wang 2018	C4-C14 PFCA C4-C8 PFSA n:2 Cl-PFESA (n=6,8,10)	China	urine hair nail	50 ml 0.1 g	dilute with water rinsing with water, aceton, air-drying, grinding	SPE Oasis WAX shaking with ACN alkaline digestion, shaking with MeOH	- SPE Oasis WAX SPE Oasis WAX	HPLC-ESI(-)MS/MS	0.003-0.035 ng/l (LOQ) 0.005-0.11 ng/g 0.018-0.339 ng/g	<LOQ-64 ng/l <LOQ-51 ng/ml <LOQ-29 ng/g
Li 2020	C5-C12 PFCA C4-C8 PFSA	Sweden	serum	25 µl	dilution with water digestion with glucuronidase protein precipitation with CAN centrifugation			HPLC-ESI(-)MS/MS	0.1 ng/ml (LOD)	Exposed group (median): PFOS 160 ng/ml PHHxS 140 ng/ml PFOA 1.6 ng/ml Control group (median): PFOS 4.8 ng/ml PFHxS 0.98 ng/ml PFOA 1.6 ng/ml

Nakayama 2020	C4-C18 PFCA C4-C10 PFSA C6-C10 PFPA n:2-FTS (n = 4,6,8) MeFOSA EtFOSA 6:2 diPAP 8:2 diPAP diSAmPAP	Japan	serum	100 µl	ACN addition centrifugation clean-up on Oasis MCX	on-line SPE (Oasis WAX)		HPLC-ESI(-)MS/MS	0.02-0.16 ng/ml (LOD)	<LOQ-4.5 ng/ml (median)
Salihovic 2020	C4-C14 PFCA C4-C12 PFSA FOSA PFECHS	Sweden	serum	20 µl	mixing with ACN (1% HCOOH)	SPE (well plate)		HPLC-ESI(-)MS/MS	0.02-0.15 ng/ml	<LOQ-17 ng/ml
Ingelido 2020	C4-C12 PFCA C4-C8 PFSA	Italy	serum	250 µl	addition of ACN			HPLC-ESI(-)MS/MS	0.01-0.5 ng/ml	Exposed group (median): 0.06-40 ng/ml Control group (median): 0.03-5.8 ng/ml

Annex II.1 – List of participants

Name	Surname	Affiliation	Country
Ahrens	Lutz	Swedish University of Agricultural Sciences	SE
Aus der Beek	Tim	IWW Water Centre	DE
Béen	Frederic	KWR Water Research Institute	NL
Bémelmans	Stéphanie	Institut Scientifique de Service Public	BE
Bertato	Valentina	European Commission (DG Environment)	
Biermann	Tobias	European Commission (DG Environment)	
Blume	Malene Teller	Coop Danmark	DK
Bonte	Matthijs	Shell - Concawe	NL
Borchers	Ulrich	IWW Water Centre	DE
Brambilla	Gianfranco	Istituto Superiore di sanità	IT
Brandt	Marc	German Federal Ministry for the environment	DE
Bronders	Jan	Flemish institute for technological research (VITO)	BE
Campling	Paul	Flemish institute for technological research (VITO)	BE
Carr Kaljo	Cassandra	European Commission (DG Environment)	
Chauveheid	Eric	VIVAQUA	BE
Cousins	Ian	ACES, Stockholm University	SE
de Voogt	Pim	KWR Water Research Institute	NL
Eisenreich	Steven	Free University Brussel (VUB)	BE
Feder	Maja	European Commission (DG Environment)	
Geerts	Lieve	Flemish institute for technological research (VITO)	BE
Geertsen	Gitte	Danish Veterinary and Food Administration	DK
Gemoets	Johan	Flemish institute for technological research (VITO)	BE
Göckener	Bernd	Fraunhofer IME	DE
Hansen	Helle Rüsz	Danish Environmental Protection Agency	DK
Haug	Line Småstuen	Norwegian Institute of Public Health	NO
Herzke	Dorte	Norwegian Institute for Air Research (NILU)	NO
Higgins	Trudy	European Commission (DG Environment)	
Hjort	Marcus	Concawe	
Hohenblum	Philipp	Environment Agency Austria (UBA)	AT
Impellitteri	Christopher	US EPA	US
Jahnke	Anne	German Federal Institute for Risk Assessment	
Jans	Anne	Rijkswaterstaat	
Kämpfe	Alexander	German Environment Agency (UBA)	DE
Kärrman	Anna	Örebro University, Sweden	SE
Knepper	Thomas	Hochschule Fresenius	DE
Königsmann	Herbert	Dyneon GmbH	DE
Kozel	Ronald	Swiss Federal Office for the Environment	CH
Lange	Frank Thomas	Technologiezentrum Wasser (TZW)	DE
Lekatos	Stylianos	European Commission (DG Grow)	
Mackay	Karen	European Food Safety Authority (EFSA)	
Mader	Brian	3M	US
Magaton	Alberto	VIACQUA SpA	
Mouratidis	Pavlos	European Commission (DG Environment)	
Neulen	Sabine	German Federal Ministry for the Environment	DE
Nicol	Liz	Wood plc	UK

Name	Surname	Affiliation	Country
Pancras	Tesse	Arcadis	NL
Peaslee	Graham	University of Notre Dame	US
Pedersen	Gitte Alsing	Danish National Food Institute	DK
Peeters	Bavo	European Commission (DG Environment)	
Posner	Stefan	Independent researcher	SE
Rabaey	Jonas	Witteveen+Bos	BE
Riemenschneider	Christina	EURL - CVUA	DE
Ronco	Paolo	Centro RIVE - Water Resources of Veneto	IT
Scaglia	Elisabetta	UNIC-Concerie Italiante	IT
Schmid	Cora	IWW Water Centre	DE
Schulte	Christoph	German Environment Agency (UBA)	DE
Schwerdtle	Tania	University of Potsdam	DE
Slenders	Hans	Arcadis	NL
Strassburger	Thomas	German Ministry For The Environment	GE
Touchant	Kaat	Flemish institute for technological research (VITO)	
van Bentum	Elisabeth	Expertisecentrum PFAS	NL
Van Gestel	Griet	Flemish Waste Agency (OVAM)	BE
Vanheusden	Veerle	European Commission (DG Sante)	
Van Keer	Ilse	Flemish institute for technological research (VITO)	BE
van Leeuwen	Stefan	University of Wageningen	NL
Vargas Amelin	Elisa	European Commission (DG Environment)	
Vis	Remco	Witteveen+Bos	NL
Voorspoels	Stefan	Flemish institute for technological research (VITO)	BE
Wang	Zhanyun	ETH Zurich	CH
Wilson	Alan	Element Materials Technology	
Wintersen	Arjen	RIVM	
Winther	Toke	Danish EPA	DK

Annex II.2 – Workshop agenda

Workshop on PFAS monitoring in water and other media

DG Env - Borschette Conference Centre, Froissartstraat 36 / Rue Froissart 36 - 1040 Brussels,

13 January 2020

	Registration & Welcome	
13:30 – 14:00	**Security & Registration (Coffee)**	
14.00 – 14:15	Welcome European Commission	Michel Sponar, DG ENV
	Welcome	Pim de Voogt
14:15 - 14:30	Objectives of the workshop	Tobias Biermann, DG ENV
	Plenary Session - Setting the Scene	**Keynote speakers**
14:30 - 15:00	European Commission perspectives on policy strategies to regulate PFASs at EU level and beyond	Tobias Biermann, Valentina Bertato, Elisa Vargas Amelin, (DG Env) & Veerle Vanheusden (DG Sante)
15:00 - 15:30	PFAS: Legacy contaminants or still an ermerging issue?	Christoph Schulte (UBA, DE)
15:30 - 16:00	PFAS monitoring and management in the United States of America	Christopher A. Impellitteri (US-EPA)
16:00 - 16:30	Coffee break	
16:30 - 17:00	PFAS pollution, from the Arctic to the equator. Integrated approaches on characterisation and remediation strategies	Ian Cousins (Stockholm University, SE);
17:00 – 17:30	PFAS risk assessment (properties & behaviour), what do we know and what do we want to know?	Arjen Wintersen (RIVM, NL)
17:30 - 18:00	The role of total fluorine measurements in monitoring PFAS	Graham Peaslee (U. Notre Dame, USA)
18:00 - 18:30	Questions and panel discussion	Pim de Voogt (moderator)
19:30	**Business Dinner**	

14 January 2020

9:00 - 12:00	**Parallel session I: Characterisation of PFAS in groundwater, surface water & drinking water**	
	* Sampling techniques and protocols; active versus passive sampling	**Keynote Speaker:**
	* Analytical methods and target parameters (PFAS total, PFAS sum, individual components)	Anna Kärrman (ÖREBRO University, SE)
	* Groundwater remediation standards - Parametric values	Moderators: Frederic Béen (KWR) / Stefan Voorspoels (VITO / UGent)
		Rapporteurs:
		Ulrich Borchers (IWW)
		Paul Campling (VITO)
9:00 - 12:00	**Parallel session II: Characterisation of PFAS in food, crops, feed (including packing material)**	
	* Sampling techniques and protocols	**Keynote Speaker:**
	* Analytical methods and target parameters (PFAS total, PFAS sum, individual components)	Dorte Herzke (NILU, NO)
		Moderator: Pim de Voogt (KWR)
	* Reference samples	Rapporteurs:
	* New insights into BCF & MRL	Jan Bronders (VITO)
		Kaat Touchant (VITO)
9:00-12:00	**Parallel session III: Characterisation of PFAS in other matrices / media - alternatives substitutes for PFAS**	
	* PFAS in other environmental matrices (e.g. soil, manure)	**Keynote Speaker:**
	* PFAS in non-environmental media (e.g. fire-fighting foams, textiles, coatings)	Thomas Knepper (Fresensius, DE)
		Moderator: Tim aus der Beek (IWW)
	* Alternative solutions (e.g. PFAS free products, substitution, relinquishment)	Rapporteurs:
		Johan Gemoets (VITO)
		Cora Schmid (IWW)
12:00 - 13:15	**Lunch**	
	Final plenary session	
13:15 - 13:50	Presentation outcome parallel session I + discussion	moderator + rapporteurs
13:50 - 14:25	Presentation outcome parallel session II + discussion	moderator + rapporteurs
14:25 - 15:00	Presentation outcome parallel session III + discussion	moderator + rapporteurs
15:00 - 15:30	Definition of future actions	Pim de Voogt, Chairman
15:30 - 16:00	Wrap up and Closing remarks	Tobias Biermann, DG ENV

Annex II.3 – Guiding questions

- **Analytical issues**
    - How do we define a uniform "total PFAS content" in an analytical chemical context. (i.e., which members of the PFAS family are included? Total PFAS before or after applying TOPA?
    - How feasible and how accurate are the total F/Fluorine methods under development, and what are their timeframes?
    - Methods for the targeted analysis of PFAS, using LC-MS/MS and GC-MS, are very selective, sensitive and accurate. EN/ISO standard methods however only exist for the water matrix; can standard methods for other matrices be made available quickly? Is there a need to develop reference materials for method validation and quality control? As replacement PFAS are put on the market very quickly and a quick adaptation of standard methods will be desired; how can the continuous extension of the parameter list by novel PFAS and the unavailability of (expensive) reference substances and corresponding mass labelled analogues be addressed?
    - Will the combined targeted analysis of PFAS before and after TOPA (total oxidisable precursor assay) cover sufficiently the amount of PFAS present in the sample? How robust is TOPA: is there sufficient knowledge of conversion yields depending on PFAS compound, matrix type and reaction conditions. Can a standard procedure and reference test sample be made available quickly?
    - Are non-specific methods for the determination of organically bound fluorine (EOF, AOF, …) a more preferable approach for the monitoring of PFAS? Are these methods sufficiently selective, sensitive and quantitative for the interference-free determination of all per- and polyfluorinated compounds at the required reporting limits? Can inorganic fluorine be removed quantitatively and are system blanks and cross contamination well under control? Which regulatory limits can be set? Standardisation of AOF and EOF is a prerequisite, how quickly can validated EN/ISO standards be made available?
    - Should PFAS suspect screening, using HRMS analytical techniques, be included in the analytical workflow for the comprehensive organofluorine assessment in case of organofluorine results (EOF, AOF) not covered by targeted PFAS analyses (i.e. identification of unknown organofluorine fraction)? If yes, is there a need for a standard method to be developed and can a suspect list including MS/MS fragmentation data and retention time indices be made available?
- **Limit values for drinking water, groundwater , and residues in food**
    - What are background levels in soil (in Europe)? At what level do we consider soil to be contaminated (so that remediation is required)?
    - As described in paragraph 3, several bottlenecks hamper the development of limit values. Could a generic limit value for each PFAS and a limit value for the total group of PFAS-substances give solace? If yes, on what basis to set these values?

- **Remediation techniques**

  A number of clean-up technologies have been identified for the remediation of contaminated soil and (ground)water. Which can be considered as proven and available technologies and what uncertainties are there still about them?

- **Parallel session I - Characterisation of PFAS in groundwater, surface water & drinking water**
    - *Sampling techniques and protocols; active versus passive sampling*

  Passive sampling techniques have been proven to be an added value in monitoring campaigns to the so-called classic pumping methods. What about passive sampling in relation to determination of PFAS concentrations / fluxes. Which samplers are already available on the market ? What are their benefits? What's the risk for cross contamination.
  - *Analytical methods and target parameters (PFAS total, PFAS sum, individual components)*
    See guiding questions "analytical issues".
  - *Groundwater remediation standards - Parametric values*
    To what extent can cross-contamination during sampling and chemical analyses influence observed concentrations and risk assessment? Are existing sampling and analytical procedures sufficiently elaborated to minimize it?

- **Parallel session II - Characterisation of PFAS in food, crops, feed (including packing material)**
  - *Sampling techniques and protocols*
    To what extent can cross-contamination during sampling and chemical analyses influence the measured concentrations? Are existing sampling and analytical procedures sufficiently elaborated to minimize it?
  - *Analytical methods and target parameters (PFAS total, PFAS sum, individual components)*
    See guiding questions "analytical issues".
  - *New insights into BCF & MRL*
    EFSA (2018) concluded recently that considerable proportions of the European population exceed the newly established tolerable weekly intakes of both PFOS (13 ng/kg bw/wk) and PFOA (6ng/kg bw/wk). How do we realize a reduction in human exposure on short notice?

- **Parallel session III - Characterisation of PFAS in other matrices / media - alternatives substitutes for PFAS**
  - *PFAS in other environmental matrices (e.g. soil, sediments, manure)*
    Which are the dominant entry pathways of PFAS into the non-aquatic environment, their associated risks and potential measures? How do we identify hot spots and manage risks?
  - *PFAS in non-environmental media (e.g. fire-fighting foams, textiles, coatings)*
    Which PFAS in non-environmental media are prone to enter the environment and how? How can stakeholders (e.g. producers, society, ...) reduce risks?
  - *Alternative solutions (e.g. PFAS free products, substitution, relinquishment)*
    Which PFAS alternatives exist, which are being developed, which are substantially being used, and which PFAS are currently indispensable? What is necessary for producers using PFAS to switch to PFAS free materials? What are the future (research) questions for chemical science, governance, and regulation?

Annex II.4 – Keynote Speakers

Mr. Tobias Biermann (EC, DG ENV) studied chemical engineering in Clausthal and Berlin. He worked nine years for the German Land Baden-Württemberg in different areas of environmental protection, and three years for the Mexican government on industrial environmental audits. Since 2003 he works for the European Commission in Brussels, first in the field of civil protection and accidents (Seveso Directive), and then in the field of eco-design and energy efficiency, responsible for various product groups. Since 2014, he is responsible, among other things, for the implementation and further development of the EU Drinking Water Directive in the Directorate-General for the Environment.

Mrs. Elisa Vargas Amelin (EC, DG ENV) worked for over ten years in the private sector as a consultant and independent expert for Spanish administrations in the water sector and the European Commission. She is Policy Officer in the Directorate-General for Environment of the European Commission (Brussels, Belgium) since 2015. She works mainly on the implementation of the Water Framework Directive, the Groundwater Directive, water scarcity and indicators. She holds a B.S. in Natural Resources and Environmental Studies from (U. of Minnesota, US), and a joint PhD in Economics (UNED, Madrid) and Hydrology and Engineering (VUB, Brussels). As co-leader of the EU Working Group on Groundwater, she coordinates on-going works on emerging pollutants in groundwater bodies including PFAS.

Mrs. Veerle Vanheusden (EC DG Sante) holds a PhD in Pharmaceutical Sciences (medicinal chemistry) from the University of Ghent (Belgium), where she graduated in 1999 as a Pharmacist. Between 1999 and 2013 she worked in the private pharmaceutical sector (organic chemistry and analytical chemistry). Veerle joined the European Commission in 2013, where she worked for 4 years as a policy officer in the Unit "Pesticides and Biocides" of the Directorate General for Health and Consumers. Since September 2017 she moved to the DG SANTE unit dealing with Food processing and novel foods, where her main areas of activity are the EU policy and legislation on residues of veterinary medicinal products and contaminants.

Mr. Christoph Schulte is head of the Water and Soil department at the German Environment Agency (Umweltbundesamt, UBA). Christoph does research in Ecotoxicology, Environmental Chemistry, Water and Soil Science. He has been involved in the management and regulation of PBT-chemicals and especially PFAS for more than 10 years. With the REACH-Team UBA proposed a number of PFAS regulations already enforced (i.e. the restriction of PFOA) or in preparation by the Commission.

Mr. Christopher A. Impellitteri serves as the Associate National Program Director for EPA Office of Research and Development's Safe and Sustainable Water Resources Research Program. He leads EPA research on water treatment and infrastructure that focuses on comprehensive water management in support of EPA's Program and Regional Offices and State partners for protecting water resources. He also directs EPA-ORD's stormwater management research which provides innovative ways for managing storm water and combined sewer overflows. Chris is currently leading cross-agency efforts for developing EPA methods and management of PFAS in water resources.

Mr. Ian Cousins is a Professor at the Department of Environmental Science at Stockholm University. His research comprises a combination of experimental and theoretical (e.g. modelling) approaches to investigate the sources, transport, fate and exposure of chemical contaminants. Recently, much research has been focused on per- and polyfluoroalkyl substances (PFAS) which due to their unique environmental chemistry offer exciting new research opportunities. Ian works closely with analytical chemists in his department to better understand the behaviour of PFAS and other substances.

Mr. Arjen Wintersen is an environmental researcher at RIVM (Nl), specializing in the risks and behavior of soil and groundwater contaminations. He is involved in the assessment of PFAS in soil and groundwater in various projects since 2010. At the moment Arjen is the coordinator of the projects at RIVM aimed at substantiating the national framework for PFAS in soil, sediments and groundwater, that is due to come into effect in 2020.

Mr. Graham Peaslee is a professor of Physics at the University of Notre-Dame (USA) who's research interests lie at the interface between any nuclear or atomic physics measurement method and materials that impact society. Most of these methods are accelerator-based (known as Ion Beam Analysis), where light charged particles are used to bombard the surface of some solid material. The resultant x-rays, gamma-rays or UV-Vis light emitted, plus the scattering of charged particles can yield important information about the elemental content and distribution within a sample. These measurements have applications when they determine the presence of lead in paint, or halogenated flame-retardants in furniture, or the occurrence of per-and polyfluorinated compounds (PFAS) in the environment.

Mrs. Anna Kärrman is deputy head of School of Science and Technology and associate professor in environmental chemistry conducting research in the Environment and Health group at MTM Research Centre (SE). Her main research agenda is to unravel the identity of drivers of toxicity by seeking relevant and sensitive methods including non-targeted methodologies. Focus is on analytical chemistry and emerging organic pollutants, their distribution in the environment, sources, and human exposure. Among her research work are studies of per- and polyfluoroalkyl substances and microplastics. Most of her work is conducted within the Environmental Forensic Laboratory (EnForce), of which she is the deputy manager. Among her external assignments are the Swedish Chemical Society editorial board and The Toxicological Council, the latter an expert group acting as an early warning system for the identification of chemical substances that can be harmful to human health or the environment.

Mrs. Dorte Herzke currently works as senior researcher at the Department of Environmental Chemistry, Norwegian Institute for Air Research (NILU). She has been working in the position of Head of Section for Arctic Environment in Tromsø, Norway in the last 8 years. In 2019 she became assoc. prof. at the University of Tromsø. Dorte does research in Analytical Chemistry and Environmental Chemistry with focus on the Arctic. Her current projects are covering both the role of urbanisation as a source of pollution, impact on top predators and humans with an emphasis on emerging PFAS as well as plastic litter as a carrier for pollutants. Among her external assignments are member of the Board of POLARIA, Exhibition Centre of the FRAM center in Tromsø, Norway, Viceleader of research program Plastic in the Arctic of the FRAM center, member of board for ethically advice at University of Tromsø.

Mr. Thomas Knepper is Vice President for Research and Research Funding at Hochschule Fresenius gGmbH in Idstein, Germany and professor in analytical chemistry. He is also founder and director of the Institute for Analytical Research (IFAR). His main research fields are developing analytical methods for monitoring and fate studies of polar organic micro pollutants in the environment as well as other matrices. Among his research work are various studies of per- and polyfluoroalkyl substances and synthetic polymers. He has participated as coordinator or partner in numerous research projects, both national and international. He and his group are also performing contract work for the chemical industry within the mentioned research field.

Annex II.5 – Keynote abstracts and presentations

II.5.1 European Commission perspectives on policy strategies to regulate PFASs at EU level and beyond

Tobias Biermann, Valentina Bertato*, Elisa Vargas Amelin* and Veerle Vanheusden***
*European Commission, *DG Environment & **DG Sante*

PFAS emissions into the environment can be reduced at the source by restricting their manufacture and use under REACH, the European Chemicals Legislation. Some PFASs are also restricted globally with the Stockholm Convention on Persistent Organic Pollutants (POPs). These instruments have until now addressed the so-called long-chain PFAS, such as PFOS, PFOA, PFHxS. This has led industry to replace the restricted substances with structurally similar ones, still belonging to the PFAS group, the so-called short-chain PFAS. REACH is now looking also at these alternatives, with the identification as Substances of Very High Concern (GenX, PFBS) or the restriction process (PHFxA). A new approach is also emerging. Seen the very high number of PFASs on the market, the limited information available in many cases on their identity and hazard and the hazard posed by some degradation products, there are proposals to regulate them as a group. The Commission has launched two studies, looking at the hazard and uses of PFASs and their alternatives in fire-fighting foams and textiles and leather. The studies are also looking at identifying the essential uses of PFASs, taking into account the availability of alternatives, the benefits they bring to the society and the cost of contamination.

The growing concern on anthropogenic organic contaminants extends to groundwater, given its importance as drinking water source and to sustain ecosystems. While the priority should focus on reducing pollution at source, it is essential to understand the degree of pollution by PFAS in groundwater resources. Several measures have been introduced for regulating substances that impact groundwater (e.g. nitrate and pesticides). However, additional substances that pollute groundwater, such as PFAS, are not yet covered. Monitoring for these unregulated substances is also limited. To address this, the European Commission launched in 2015 a voluntary watch list mechanism to facilitate the identification of substances, for which groundwater quality standards or threshold values should be set. The methodology, supported by EU Water Directors, has been tested for PFAS and also for pharmaceuticals. The specific exercise on PFAS was developed through the collection of data from 11 Member States and participating countries, and is summarised in a technical report[2]. The resulting watch list agreed in 2019 contains eleven compounds, two of which are PFAS. In parallel, 10 PFAS for which there is sufficient monitoring data and which are considered the most persistent, have been proposed for potential regulation through the Groundwater Directive annexes.

For the revision of the EU Drinking Water Direcitve, the WHO recommended adopting parametric values for two individual perfluorinated substances: perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). However, there is a wider range of substances with varying chain lengths found in water. PFOA and PFOS, the most common substances, have been substituted by similar per- and polyfluoroalkyl substances (PFASs) often with shorter chains. Therefore the Commission recognised the need to regulate the whole family of these substances, also because there is no conclusive list of all the substances available. The proposal of 2018 was to regulate the group of PFASs, and to suggest values of 0.1 µg/l for individual PFAS and 0.5 µg/l for PFASs in total, as is done

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[2] The draft technical report is available at https://circabc.europa.eu/ui/group/9ab5926d-bed4-4322-9aa7-9964bbe8312d/library/fe202d23-a93f-4e89-96ee-2eb4f20f60ef/details

for pesticides. In the provisional new Drinking Water Directive (final political trilogue on 18/19 December 2019), a limit value of 0.1 µg/l was for agreed for the sum of the 20 most important substances. Furthermore, the Commission has to develop a method for measuring all PFAS over the next three years. A limit value (0.5 µg/l) will apply once a method for monitoring ‘PFAS total’ is available. The final text will have to be adopted and published in the course of 2020.

The EU regulatory framework for contaminants in food (Council Regulation (EEC) No 315/93) states that food containing a contaminant in an amount which is unacceptable from the public health viewpoint shall not be placed on the market. In order to protect public health the Commission establishes where necessary maximum levels (MLs) for specific contaminants in Commission Regulation (EC) 1881/2006. These maximum levels are set on the basis of occurrence data, using the ALARA (As Low As Reasonably Achievable) principle. So far no MLs have been established for PFAS substances in food. A new EFSA opinion the risk to human health related to PFAS substances in food is foreseen to be adopted mid-2020. If needed, taking into account the outcome of the opinion, a discussion on the possible need for setting MLs for specific PFAS substances in specific food commodities can be started.

Workshop in PFAS monitoring in water and other media.
13-14 January 2020

European Commission perspectives on policy strategies to regulate PFASs at EU level and beyond.

Veerle Vanheusden
DG SANTE

Valentina Bertato, Tobias Biermann, Elisa Vargas Amelin
DG ENVIRONMENT

PFAS in the chemicals legislation

Council

June 2019: conclusions

The Council of the European Union:

UNDERLINES the increasing health and environmental concerns posed by highly persistent chemicals; NOTES in specific the growing evidence for adverse effects caused by exposure to highly fluorinated compounds (PFAS), the evidence for wide spread occurrence of PFAS in water, soil, articles and waste and the threat this may cause to our drinking water supplies; CALLS on the Commission to develop an action plan to eliminate all non-essential uses of PFAS

December 2019: NL announces the intention to prepare a REACH restriction on the whole PFAS group.
8 MSs support a EU PFAS action plan.

At EU level

Green deal

- zero-pollution ambition for a toxic-free environment;

- chemicals strategy for sustainability;

- address risks posed by very persistent chemicals.

Member States: asking the Commission for a PFAS action plan

- **to look at PFASs as a group;**
- **use all available regulatory and non regulatory instruments**

Concerns of PFAS

Long-chain PFAS (PFOA, PFOS, C9-C14 PFCAs and their salts): included in the Candidate List/restricted e.g. because of:

- Extreme persistence
- Bioaccumulation
- Toxicity for reproduction

Short-chain PFAS: High contamination potential of food, surface & ground water and drinking water sources

- Mobility in the environmental compartments
- No efficient techniques available for removal from sewage, drinking water and contaminated sites due to low adsorption potential;
- Accumulation in (edible) plants; bioaccumulation potential; protein binding potential
- Found in humans and in the environment despite of limited volumes
- Long-range transport potential – wide geographical scale

PFASs also result from degradation of precursors (side-chain fluorinated polymers and fluorotelomers)

REACH activities on PFAS

- PFOS, PFOA, C9-C14 PFCAs, PFHxS: all restricted or in the restriction process.
- GenX, PFBS: recently identified as a Substances of Very High Concern because of
  - persistency, mobility, potential for long range transport, observed adverse effects, bioavailability for uptake via drinking water
  - very high potential for irreversible effects.
- Restriction intention for PFHxA
- NL announced the intention for a group restriction on PFAS (except essential uses)

Commission studies on PFAS

- COM + ECHA: use of all PFAS and non-fluorinated alternatives in fire-fighting foams
- COM: use of all PFAS in textiles and leather
- Data collected: substance identification, hazard, emissions, potential alternatives, critical uses, benefits, costs of contamination of soil and water
- To be used as a basis for the REACH restriction.

Regulatory measures to protect human health

- EU Drinking Water and Groundwater Legislation
  - DG ENV
- EU Legislation on Contaminants in Food.
  - DG SANTE

EU Drinking Water Directive

Since 1980, latest: 1998 (98/83/EC)

High compliance, all MS > 99%

- Annex I: list with parameters (so far no PFAS)
- Annex II Monitoring/Minimum frequencies
- Annex III: No specific methods: Minimum performance characteristics ‘Uncertainty of measurement’

2018/19: Revision

- Commission initial proposal: “family” approach (PFAS total)

-Council General Approach: “list” approach restricted to 16 PFASs substances

-Last-minute compromise 18th December 2019 by co-legislators:

  - family approach as an alternative to the list approach, as soon as the relevant monitoring method becomes available.
  - list of substances expanded to 20, to be kept under monitoring

Draft PFAS Parameter Annex I

'Sum of PFASs 0.1 µg/l	'PFASs Total' 0.5 µg/l
'Sum of PFASs' means the sum of all per- and polyfluoroalkyl substances considered a concern for drinking water ***listed in Annex III***. This is a subset of PFAS substances that contain a perfluoroalkyl moiety with three or more carbons (i.e. –CnF2n–, n ≥ 3) or a perfluoroalkylether moiety with two or more carbons (i.e. –CnF2nOCmF2m−, n and m ≥ 1).	'PFASs Total' means the totality of per- and polyfluoroalkyl substances. • **This value shall only apply once technical guidelines for monitoring this parameter are developed.** • **Member States may then decide to use either one or two of the parameters 'PFAS Total' or 'Sum of PFAS'** (wording under review!)

PFAS Substances List Annex III

Perfluorobutane sulfonic acid (PFBS)	Perfluorobutanoic acid (PFBA)
Perfluoropentane sulfonic acid (PFPS)	Perfluoropentanoic acid (PFPA)
Perfluorohexanesulfonic acid (PFHxS)	Perfluorohexanoic acid (PFHxA)
Perfluoroheptane sulfonic acid (PFHpS)	Perfluoroheptanoic acid (PFHpA)
Perfluorooctanesulfonic acid (PFOS)	Perfluorooctanoic acid (PFOA)
Perfluorononane sulfonic acid (PFNS)	Perfluorononanoic acid (PFNA)
Perfluorodecane sulfonic acid (PFDS)	Perfluorodecanoic acid (PFDA)
Perfluoroundecane sulfonic acid	Perfluoroundecanoic acid (PFUnDA)
Perfluorododecane sulfonic acid	Perfluorododecanoic acid (PFDoDA)
Perfluorotridecane sulfonic acid	Perfluorotridecanoic acid (PFTrDA)

Input NEEDED:

Article 11 (6)

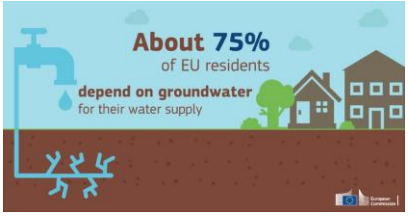
The Commission shall, no later than 3 years after entry into force of this Directive, **establish technical guidelines regarding the analytical methods**, including detection limits and parameter values and frequency of sampling for monitoring of' PFAS total' and 'Sum of PFAS'.

(wording under review)

PFAS as emerging concern in groundwater

Background: Directive 2014/80/EU amended annex II of the **Groundwater Directive**. Recital 4: <u>need of a groundwater watch list to increase monitoring data on substances posing risk, including emerging pollutants</u>.

Process launched in 2015 within the Water Framework Directive, Common Implementation Strategy. **Pilot exercise on PFAS in 2017**. Group of volunteers: COM, MS, stakeholders, industry, academia…



Pilot exercise in Groundwater, results:

- A total of 11 Member States or participating countries provided monitoring data on voluntary basis on PFAS (and 13 on pharmaceuticals). (PFOA and PFOS the most frequently detected. Both substances were analysed and detected in all countries performing PFAS monitoring).
- List facilitating Annex I and II (i.e. possible substances to be considered for the future review of the Groundwater Directive Annexes): 2 pharmaceutical and **10 Per- and Polyfluoroalkyl Substances (PFAS)**.
- First voluntary watch list, **2 PFAS** and 9 pharmaceuticals.
- Draft report on PFAS pilot study.
- The group will carry out future data collections on non-relevant metabolites and PMT (Persistent, Mobile, Toxic) compounds.

DWD PFAS Substances List Annex III vs Groundwater technical works (watch list 'WL', list facilitating 'LF')

Perfluorobutane sulfonic acid (PFBS) (LF)	Perfluorobutanoic acid (PFBA) (LF)
Perfluoropentane sulfonic acid (PFPS)	Perfluoropentanoic acid (PFPA) (LF)
Perfluorohexanesulfonic acid (PFHxS) (LF)	Perfluorohexanoic acid (PFHxA) (LF)
Perfluoroheptane sulfonic acid (PFHpS)	Perfluoroheptanoic acid (PFHpA) (LF)
Perfluorooctanesulfonic acid (PFOS) (LF)	Perfluorooctanoic acid (PFOA) (LF)
Perfluorononane sulfonic acid (PFNS)	Perfluorononanoic acid (PFNA) (LF)
Perfluorodecane sulfonic acid (PFDS)	Perfluorodecanoic acid (PFDA) (LF)
Perfluoroundecane sulfonic acid	Perfluoroundecanoic acid (PFUnDA) **(WL)**
Perfluorododecane sulfonic acid	Perfluorododecanoic acid (PFDoDA) **(WL)**
Perfluorotridecane sulfonic acid	Perfluorotridecanoic acid (PFTrDA)

Regulatory framework contaminants in food

- Council Regulation (EEC) No 315/93
  - Food containing a contaminant in an amount which is unacceptable from the public health viewpoint shall not be placed on the market.
  - Contaminant levels shall be kept as low as can reasonably be achieved by following good practices at all the stages,
  - In order to protect public health the Commission may where necessary establish the maximum tolerances for specific contaminants.
- Commission Regulation (EC) 1881/2006
  - Establishes maximum levels for certain contaminants in food
  - So far no MLs established for PFAS substances

➔ MLs can be established when evidence becomes available, which indicates a **risk to human health**

➔ MLs are established on the basis of **occurrence data** according to the ALARA principle

Consumer risk assessment

- 2008 EFSA opinion on perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts
  - Establishment of a TDI
  - The available occurrence data were limited
  - Unlikely that adverse effects of PFOS or PFOA are occurring in the general population
- 2012 EFSA scientific report on perfluoroalkylated substances in food: occurrence and dietary exposure
  - Occurrence data gathered under Commission Recommendation 2010/161 were evaluated
  - No health risks were identified taking into account the 2008 TDI

Consumer risk assessment

- 2019 EFSA opinion risk to human health related to the presence of perfluorooctane sulfonic acid and perfluorooctanoic acid in food.
    - New information on toxicity and occurrence was evaluated
    - A new TWI was put forward
    - Conclusion: the exposure for a considerable part of the population exceeds the TWI
    - Discussion between EFSA and national risk assessment bodies on the need to apply a mixture approach and on the nature of the uncertainties and on how they should be dealt with.
    - Disclaimer added to the opinion:

      The conclusions of this assessment will be reviewed in parallel with the finalisation of the EFSA scientific opinion on the risks to human health related to the presence in food of perfluoroalkylated substances other than PFOS and PFOA. The indicative timeline for this is December 2019. Until such time, the conclusions and derived ***tolerable weekly intakes shall be considered provisional****.*

Consumer risk assessment

- EFSA opinion risk to human health related to the presence of perfluoroalkylated substances in food.
    - Will cover PFOS, PFOA and other PFAS substances.
    - Endorsement by the CONTAM panel foreseen end of January 2020.
    - Public Consultation: end of January to end of March 2020
    - Stakeholder meeting: end of February 2020
    - Opinion Adoption by CONTAM Panel: target July 2020

Regulatory measures

- Q3 2020: start of discussions with Member States in the Working Group on IND and ENV CONTAM on the possible need to set maximum levels for certain PFAS substances in food taking into account:
  - Occurence data
  - The possibility of applying mitigation measures
  - ALARA principle
- Exploration of options for the development of good practices for mitigation of the contamination
- Follow up on the recommendations made in the EFSA opinion
  - Need for more occurence data for certain PFAS substances
  - Need for more toxicological information on certain PFAS substances

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Questions?

Tobias.BIERMANN@ec.europa.eu
Valentina.BERTATO@ec.europa.eu
Elisa.VARGAS-AMELIN@ec.europa.eu
veerle.vanheusden@ec.europa.eu

II.5.2 PFAS: Legacy contaminants or still an emerging issue?

Christoph Schulte, Annegret Biegel-Engler & Jan Koschorreck
German Environment Agency (Umweltbundesamt, UBA), Department Water and Soil

According to an OECD- survey, more than 4,000 per- and polyfluorinated alkyl substances (PFASs) are known. Some of the substances have been in use for decades, such as PFOS and PFOA. Due to the extreme persistence, PFASs are ubiquitously present in the environment, including remote areas. Sources of environmental emissions include manufacturing of PFAS, production and processing of fluoropolymers and side chain fluorinated polymers, use of treated articles and waste disposal. Over the last decades the compounds have been distributed world-wide mainly via surface water and air.

Not all of the identified PFAS are of commercial relevance, but may be relevant for environmental or human exposure, e.g. as by products in manufacturing of transformation products. Some PFAS are well known. The mechanisms of environmental distribution and effects on man and environment are object of worldwide research.

PFAS provide unique properties: they are stable against heat and chemical degradation and are water and grease repellent. Thus, the substances are used in a wide variety of applications, i.e. for textile and paper treatment, in aqueous firefighting foams (AFFF), and in semiconductors. Other PFAS and PFAS-based materials are widely used for surface protection in aqueous mixtures or as side-chains to introduce the repellent properties in polymers. Some of the brands are well known by consumers and preferred because of their unique combination of properties. Many uses are not well knows, but may lead to a widely distribution in the environment, e.g. PFAS-based chain lubes for bicycles of ski-waxes.

Due to the stability against heat and chemical degradation and the surface-activity, PFOS was used for many years as ingredient in aqueous firefighting foams (AFFF). The substance was also used in semiconductor manufacturing and galvanic industry. The other PFAS which is well investigated is PFOA. PFOA was used as an auxiliary in the production of certain fluoropolymers, mainly Polytetrafluorethylene (PTFE). Another long-chain PFCA, PFDA was also used in the fluoropolymer production. These substances were still produced in certain countries which were not involved in the regulatory activities yet

PFOS, PFOA were subject to regulatory activities, e.g. under the EU REACH legislation and the International Stockholm-Convention due to the widespread contamination of the environment and known human health effects as carcinogenic and reprotoxic substances. They have been substituted by other structurally similar PFAS which were thought to be less harmful. However, after some years of use, these substitutions prove to be regrettable since they exhibit similar concerns and have therefore been targeted in recent regulatory activities.

According to the various uses of PFAS and PFAS-based materials, the substances and their degradation products are widely distributed in the environment. Residual monomers might either washed out or evaporate into the surrounding air during the use stage of the respective articles. Surfactants used e.g. in carpet- and textile-care products and are distributed continuously into the air when applied. Many PFAS are considered as potential precursors for stable perfluorocarboxylic acids – PFCAs.

At present it is only technically possible to quantify several dozen of PFAS. Monitoring data for these compounds show that PFAS concentrations and patterns vary widely between environmental compartments, species and matrices. It will be a huge challenge for research and regulation to understand and assess the environmental fate, behavior and effects of PFAS currently released into the environment. Recent data, which has been established with sum parameters e.g. TOP- and EOF assay demonstrate that the environmental exposure to PFAS is much higher than previously expected. Given the extreme persistence of PFAS as such, it is questionable whether we have the time to evaluate compound by compound, or whether the precautionary principle does not call for much more holistic approaches.

For our Environment

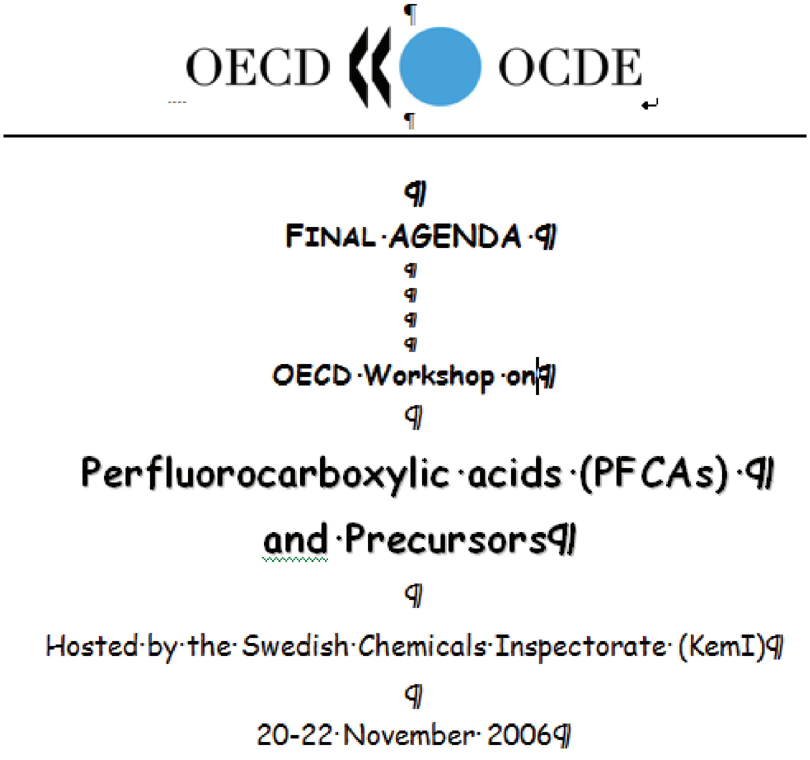
WORKSHOP ON PFAS MONITORING IN WATER AND OTHER MEDIA

PFAS – legacy contaminants or still emerging?

Christoph Schulte, Annegret Biegel-Engler, Jan Koschorreck

Department II 2 Water and Soil
Environment Agency (UBA)
Germany

Legacy contaminants?



OECD OCDE

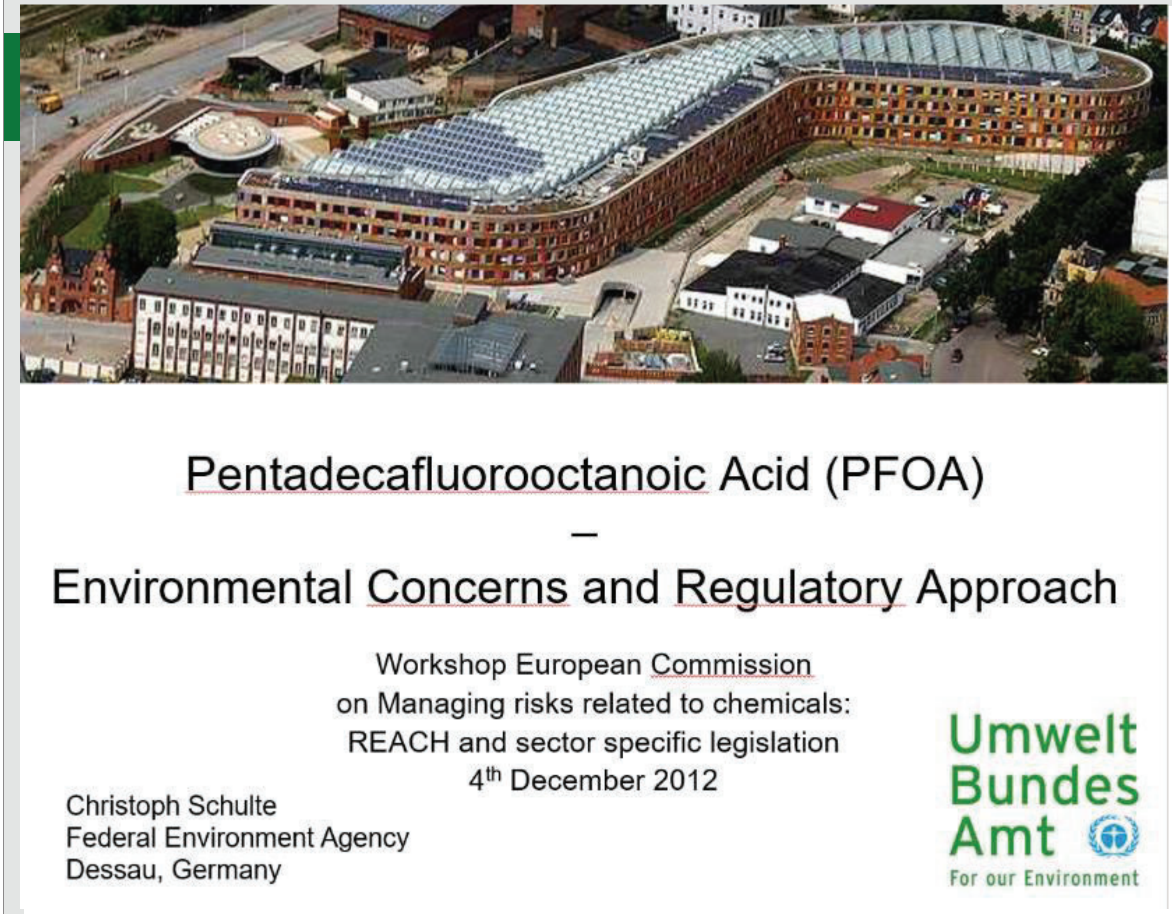
FINAL AGENDA

OECD Workshop on

Perfluorocarboxylic acids (PFCAs)
and Precursors

Hosted by the Swedish Chemicals Inspectorate (KemI)

20-22 November 2006

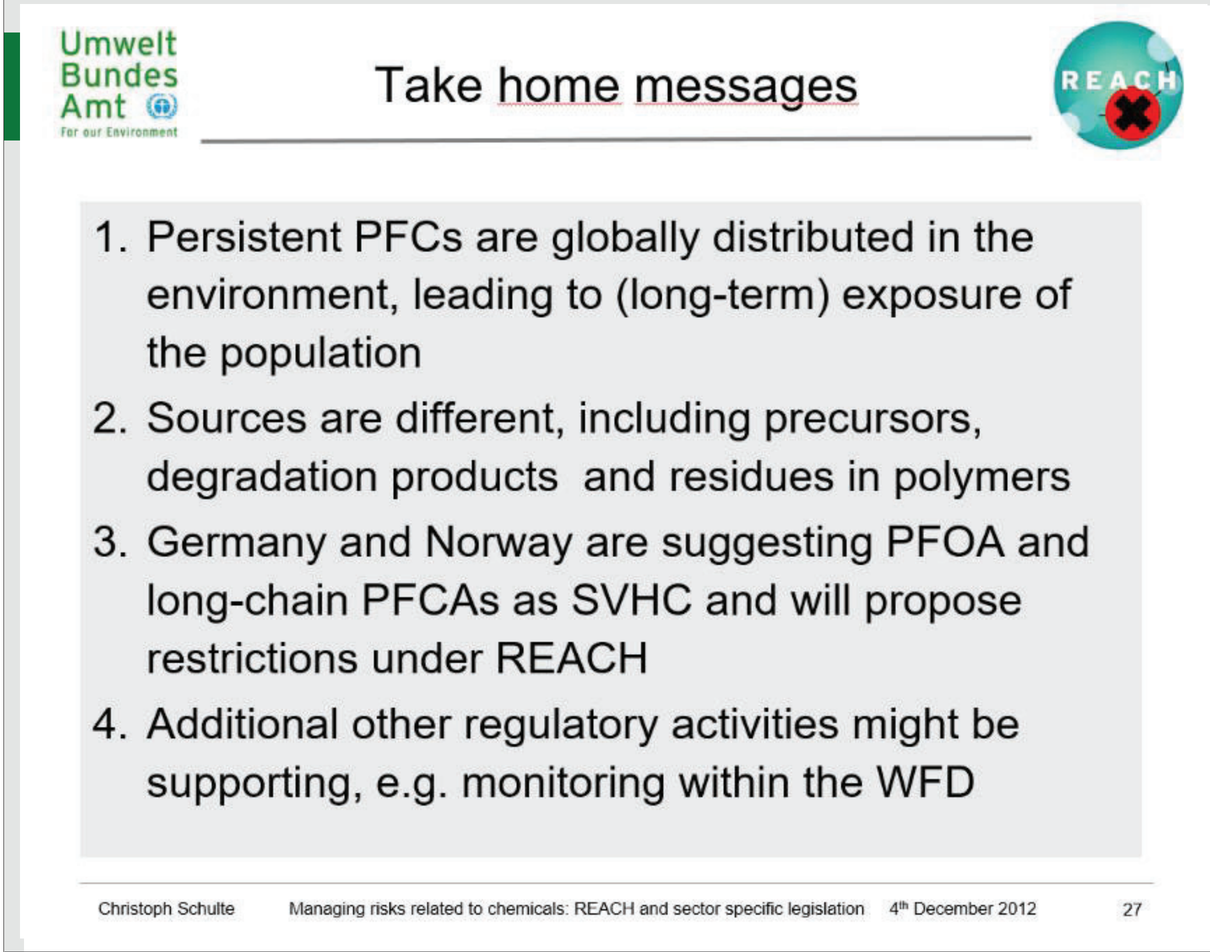


Pentadecafluorooctanoic Acid (PFOA)
–
Environmental Concerns and Regulatory Approach

Workshop European Commission
on Managing risks related to chemicals:
REACH and sector specific legislation
4th December 2012

Christoph Schulte
Federal Environment Agency
Dessau, Germany

Umwelt
Bundes
Amt
For our Environment



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Take home messages

REACH

1. Persistent PFCs are globally distributed in the environment, leading to (long-term) exposure of the population
2. Sources are different, including precursors, degradation products and residues in polymers
3. Germany and Norway are suggesting PFOA and long-chain PFCAs as SVHC and will propose restrictions under REACH
4. Additional other regulatory activities might be supporting, e.g. monitoring within the WFD

Christoph Schulte Managing risks related to chemicals: REACH and sector specific legislation 4th December 2012 27

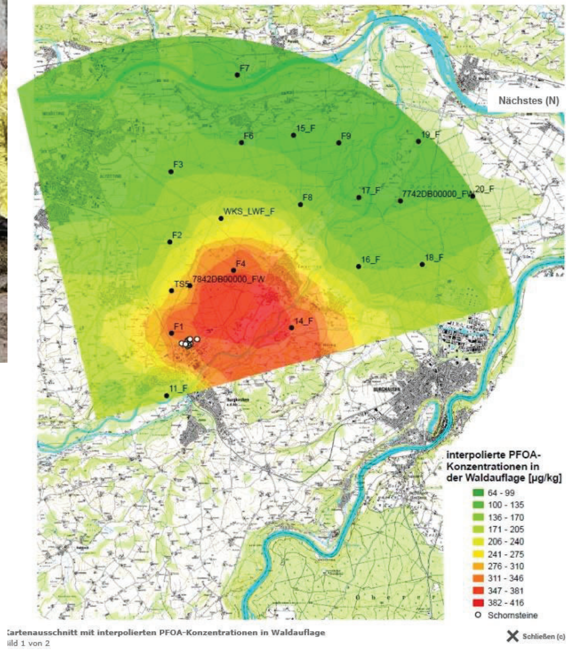
Perfluoroalkyl and polyfluoroalkyl substances - PFAS

- Perfluorocarboxylic acids (PFCAs), e.g. PFOA
- Perfluoroalkyl sulfonic acids (PFSAs), e.g. PFOS
- Long-chain PFAS:
  - PFCAs with eight carbons and greater
  - PFSAs with six carbons and greater
- Fluoropolymers: carbon only backbone polymer with fluorine directly attached; solid, chemical and thermic stable,
  e.g. PTFE (Polytetrafluoroethylene)
- Side-chain fluorinated polymers: polymers with non-fluorinated backbone with fluorinated side-chains

Buck et al. 2011

SOURCES

Fluoropolymer production



https://www.lfu.bayern.de/altlasten/pfoa_gendorf/bodenbelastungen/index.htm

SOURCES

Hot spots

Suspected and contaminated sites

- Unknown source
- Use of AFFF fire fighting foam
- Training with AFFF fire fighting foam
- B Soil application
- P Manufacturing site
- A other industrial sites

https://www.stadtwerke-rastatt.de/pfc-schadensfalluebersicht

SOURCES

Diffuse distribution

Footprints in the snow

Hazardous PFCs in remote locations around the globe

GREENPEACE

https://www.greenpeace.org/international/publication/6943/footprints-in-the-snow/

Products and uses

FluoroCouncil
Global Industry Council for FluoroTechnology

Uses and Benefits of FluoroTechnology

Welcome to the FluoroCouncil

Healthcare and Hospitals

Electronics

Chemicals and Pharmaceuticals

Auto

First Responder Safety

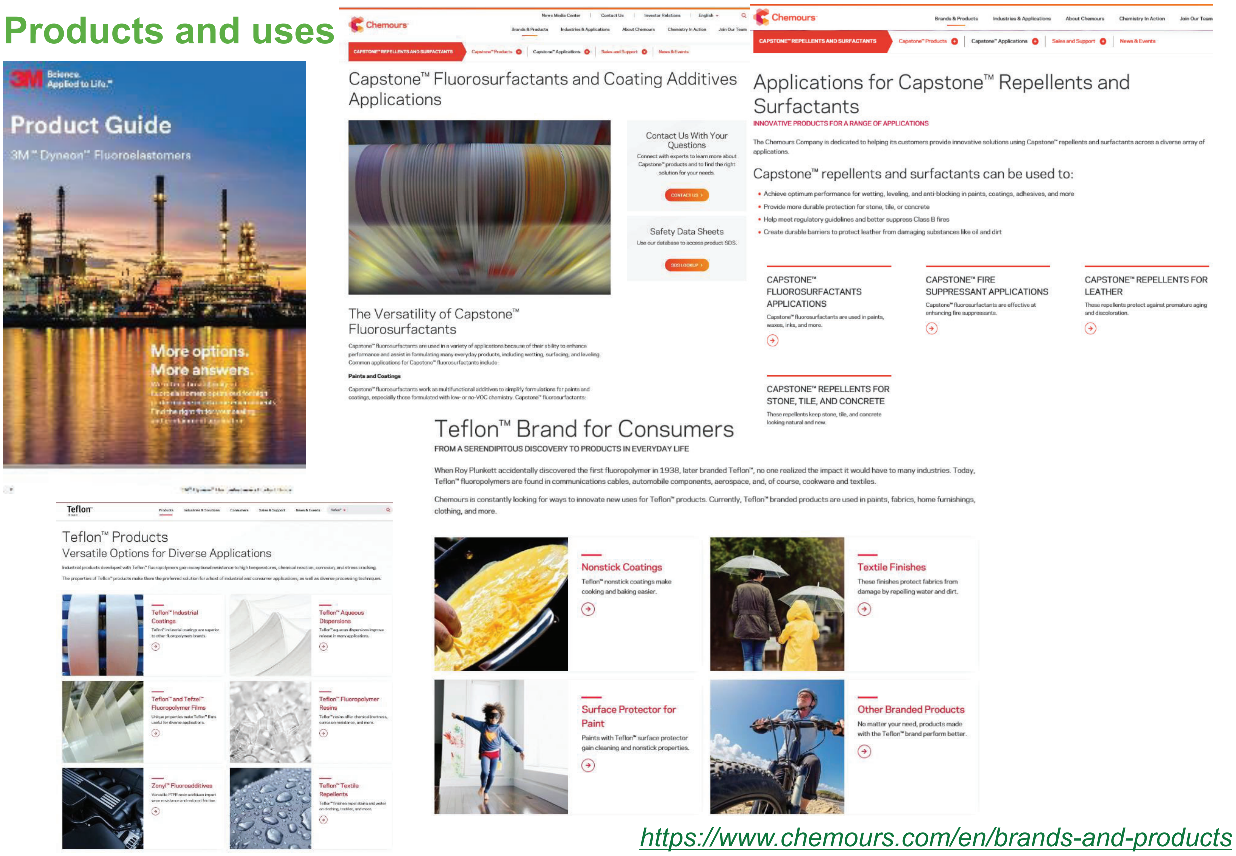
Aerospace

High Performance Benefits for Outdoor Apparel

Outdoor performance apparel and equipment enhanced with FluoroTechnology helps people stay warm, dry and safe. » Learn More

https://fluorocouncil.com/

Products and uses



3M Science. Applied to Life.™

Product Guide

3M™ Dyneon™ Fluoroelastomers

More options. More answers.

Chemours

CAPSTONE™ REPELLENTS AND SURFACTANTS | Capstone™ Products | Capstone™ Applications | Sales and Support | News & Events

Capstone™ Fluorosurfactants and Coating Additives Applications

Contact Us With Your Questions

Connect with experts to learn more about Capstone™ products and to find the right solution for your needs.

CONTACT US ›

Safety Data Sheets

Use our database to access product SDS.

SDS LOOKUP ›

The Versatility of Capstone™ Fluorosurfactants

Capstone™ fluorosurfactants are used in a variety of applications because of their ability to enhance performance and assist in formulating many everyday products, including wetting, surfacing, and leveling. Common applications for Capstone™ fluorosurfactants include:

Paints and Coatings

Capstone™ fluorosurfactants work as multifunctional additives to simplify formulations for paints and coatings, especially those formulated with low- or no-VOC chemistry. Capstone™ fluorosurfactants:

Applications for Capstone™ Repellents and Surfactants

INNOVATIVE PRODUCTS FOR A RANGE OF APPLICATIONS

The Chemours Company is dedicated to helping its customers provide innovative solutions using Capstone™ repellents and surfactants across a diverse array of applications.

Capstone™ repellents and surfactants can be used to:

- Achieve optimum performance for wetting, leveling, and anti-blocking in paints, coatings, adhesives, and more
- Provide more durable protection for stone, tile, or concrete
- Help meet regulatory guidelines and better suppress Class B fires
- Create durable barriers to protect leather from damaging substances like oil and dirt

CAPSTONE™ FLUOROSURFACTANTS APPLICATIONS

Capstone™ fluorosurfactants are used in paints, waxes, inks, and more.

CAPSTONE™ FIRE SUPPRESSANT APPLICATIONS

Capstone™ fluorosurfactants are effective at enhancing fire suppressants.

CAPSTONE™ REPELLENTS FOR LEATHER

These repellents protect against premature aging and discoloration.

CAPSTONE™ REPELLENTS FOR STONE, TILE, AND CONCRETE

These repellents keep stone, tile, and concrete looking natural and new.

Teflon™ Brand for Consumers

FROM A SERENDIPITOUS DISCOVERY TO PRODUCTS IN EVERYDAY LIFE

When Roy Plunkett accidentally discovered the first fluoropolymer in 1938, later branded Teflon™, no one realized the impact it would have to many industries. Today, Teflon™ fluoropolymers are found in communications cables, automobile components, aerospace, and, of course, cookware and textiles.

Chemours is constantly looking for ways to innovate new uses for Teflon™ products. Currently, Teflon™ branded products are used in paints, fabrics, home furnishings, clothing, and more.

Nonstick Coatings

Teflon™ nonstick coatings make cooking and baking easier.

Textile Finishes

These finishes protect fabrics from damage by repelling water and dirt.

Surface Protector for Paint

Paints with Teflon™ surface protector gain cleaning and nonstick properties.

Other Branded Products

No matter your need, products made with the Teflon™ brand perform better.

Teflon™ Products

Versatile Options for Diverse Applications

Industrial products developed with Teflon™ fluoropolymers gain exceptional resistance to high temperatures, chemical reaction, corrosion, and stress cracking.

The properties of Teflon™ products make them the preferred solution for a host of industrial and consumer applications, as well as diverse processing techniques.

Teflon™ Industrial Coatings

Teflon™ industrial coatings are superior to other fluoropolymers brands.

Teflon™ Aqueous Dispersions

Teflon™ aqueous dispersions improve release in many applications.

Teflon™ and Tefzel™ Fluoropolymer Films

Unique properties make Teflon™ films useful for diverse applications.

Teflon™ Fluoropolymer Resins

Teflon™ resins offer chemical inertness, corrosion resistance, and more.

Zonyl™ Fluoroadditives

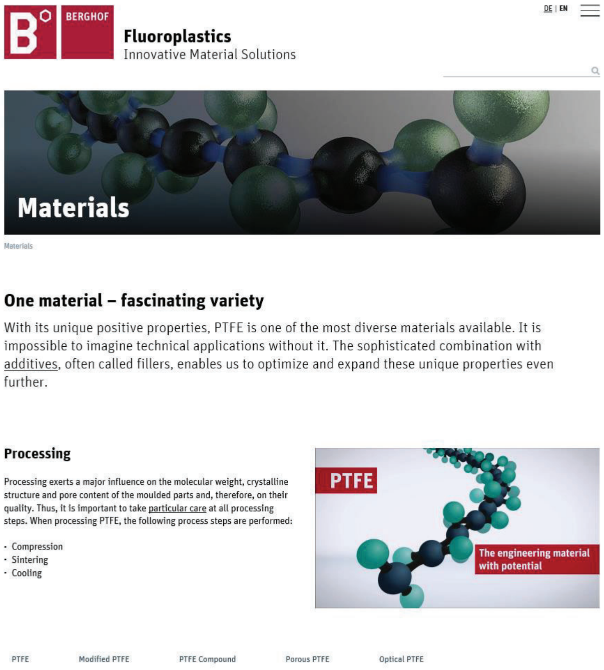
Versatile PTFE resin additives impart wear resistance and reduced friction.

Teflon™ Textile Repellents

Teflon™ Finishes repel stains and water on clothing, textiles, and more.

https://www.chemours.com/en/brands-and-products

Products and uses



BERGHOF Fluoroplastics
Innovative Material Solutions

Materials

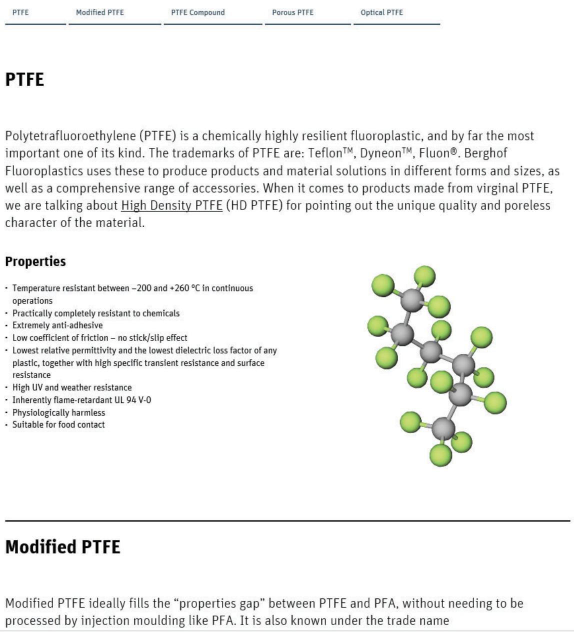
One material – fascinating variety

With its unique positive properties, PTFE is one of the most diverse materials available. It is impossible to imagine technical applications without it. The sophisticated combination with additives, often called fillers, enables us to optimize and expand these unique properties even further.

Processing

Processing exerts a major influence on the molecular weight, crystalline structure and pore content of the moulded parts and, therefore, on their quality. Thus, it is important to take particular care at all processing steps. When processing PTFE, the following process steps are performed:

- Compression
- Sintering
- Cooling



PTFE

Polytetrafluoroethylene (PTFE) is a chemically highly resilient fluoroplastic, and by far the most important one of its kind. The trademarks of PTFE are: Teflon™, Dyneon™, Fluon®. Berghof Fluoroplastics uses these to produce products and material solutions in different forms and sizes, as well as a comprehensive range of accessories. When it comes to products made from virginal PTFE, we are talking about High Density PTFE (HD PTFE) for pointing out the unique quality and poreless character of the material.

Properties

- Temperature resistant between –200 and +260 °C in continuous operations
- Practically completely resistant to chemicals
- Extremely anti-adhesive
- Low coefficient of friction – no stick/slip effect
- Lowest relative permittivity and the lowest dielectric loss factor of any plastic, together with high specific transient resistance and surface resistance
- High UV and weather resistance
- Inherently flame-retardant UL 94 V-0
- Physiologically harmless
- Suitable for food contact

Modified PTFE

Modified PTFE ideally fills the “properties gap” between PTFE and PFA, without needing to be processed by injection moulding like PFA. It is also known under the trade name

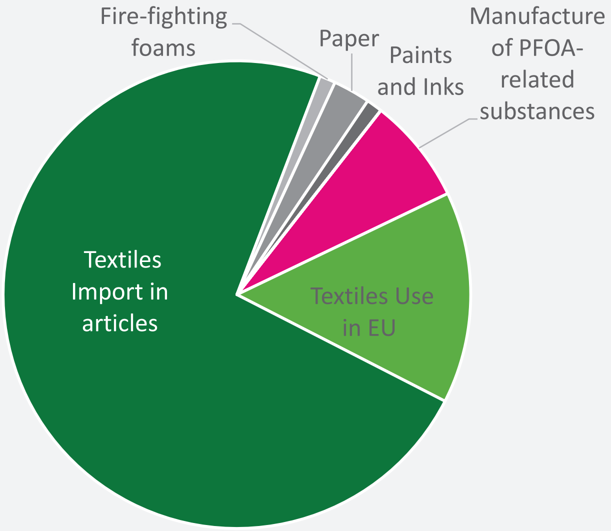
https://www.berghof-fluoroplastics.com/en/

Manufacturing, import and use of PFOA and precursors in the EU

PFOA
(≈ 40 t/a)

- 🟥 Import of PFOA
- 🟩 Import of PFOA in articles
- 🟩 Fluoropolymers import and use of PTFE mixtures

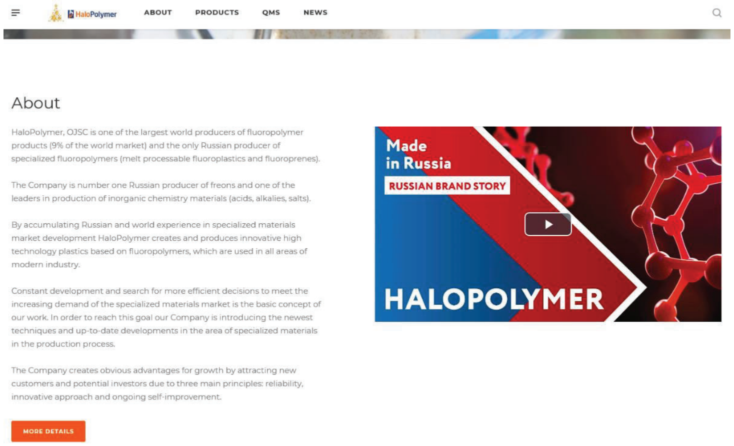
PFOA-Precursors
(2,250-11,400 t/a)



REACH Annex XV Dossier Restriction of PFOA

PRODUCTS AND USES

Products and uses



About

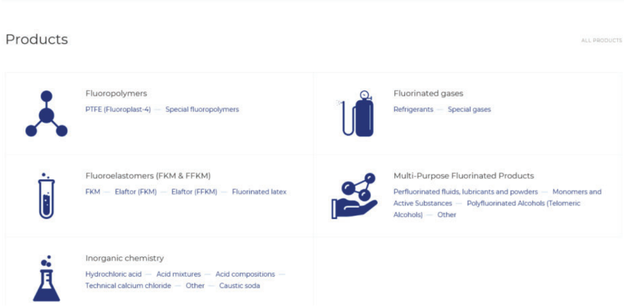
HaloPolymer, OJSC is one of the largest world producers of fluoropolymer products (9% of the world market) and the only Russian producer of specialized fluoropolymers (melt processable fluoroplastics and fluoroprenes).

The Company is number one Russian producer of freons and one of the leaders in production of inorganic chemistry materials (acids, alkalies, salts).

By accumulating Russian and world experience in specialized materials market development HaloPolymer creates and produces innovative high technology plastics based on fluoropolymers, which are used in all areas of modern industry.

Constant development and search for more efficient decisions to meet the increasing demand of the specialized materials market is the basic concept of our work. In order to reach this goal our Company is introducing the newest techniques and up-to-date developments in the area of specialized materials in the production process.

The Company creates obvious advantages for growth by attracting new customers and potential investors due to three main principles: reliability, innovative approach and ongoing self-improvement.



Products

Fluoropolymers
PTFE (Fluoroplast-4) — Special fluoropolymers

Fluorinated gases
Refrigerants — Special gases

Fluoroelastomers (FKM & FFKM)
FKM — Elaftor (FKM) — Elaftor (FFKM) — Fluorinated latex

Multi-Purpose Fluorinated Products
Perfluorinated fluids, lubricants and powders — Monomers and Active Substances — Polyfluorinated Alcohols (Telomeric Alcohols) — Other

Inorganic chemistry
Hydrochloric acid — Acid mixtures — Acid compositions — Technical calcium chloride — Other — Caustic soda

https://halopolymer.com/

MAIN CONCERNS

Sources of PFAS in the environment

- Emissions from production and processing
  - PFAS
  - Fluoropolymers and fluorinated polymers
- Emissions from use
  - Consumer products and professional products, e,g, fire fighting foams
  - Industrial applications and processes
- Disposal
  - Domestic and industrial waste
  - Landfill, waste, incineration, WWTPs
  - Inappropriate disposal (incidents)
- Metabolism and transformation in the environment

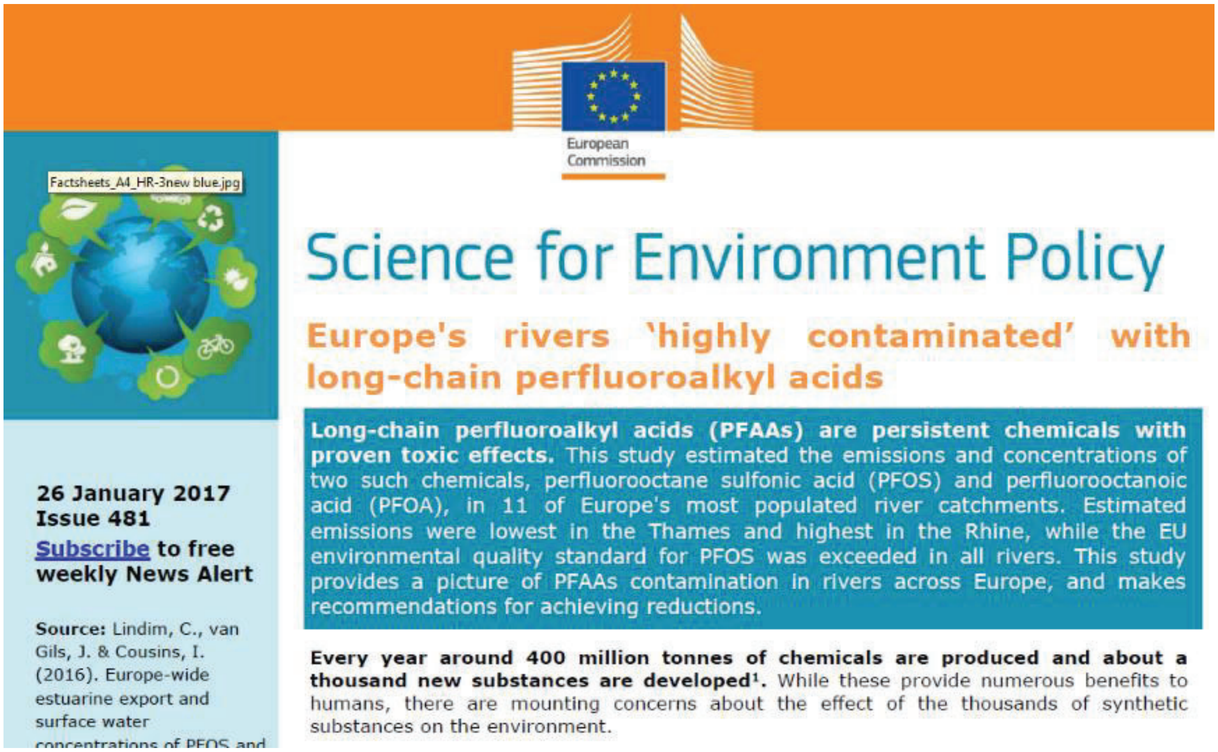
PFAS - Main concerns

- Environmental persistence
- Findings and distribution in surface water, soil and air
- Findings and accumulation in food webs, including top predators
- Long-range transport and findings in remote areas
- Occurrence in blood samples of the general population (& long elimination half lives)
- Occurrence in breast milk
- Findings in food and (increasingly) drinking water
- Toxicological profile (PFOS, PFNA, PFOA: Reprotoxic Cat. 1B)
- Remediation is extremely labour and cost effective

Short-chain PFAS

- Persistent chemicals with high mobility in the environment
- Potential for long-range transport
- Potential to reach remote regions
- Uptake in plants
- Accumulation in the environment
- High potential to reach ground water as a resource for drinking water
- Difficult to remediate (lower adsorption)

PFAS in rivers



Science for Environment Policy

Europe's rivers 'highly contaminated' with long-chain perfluoroalkyl acids

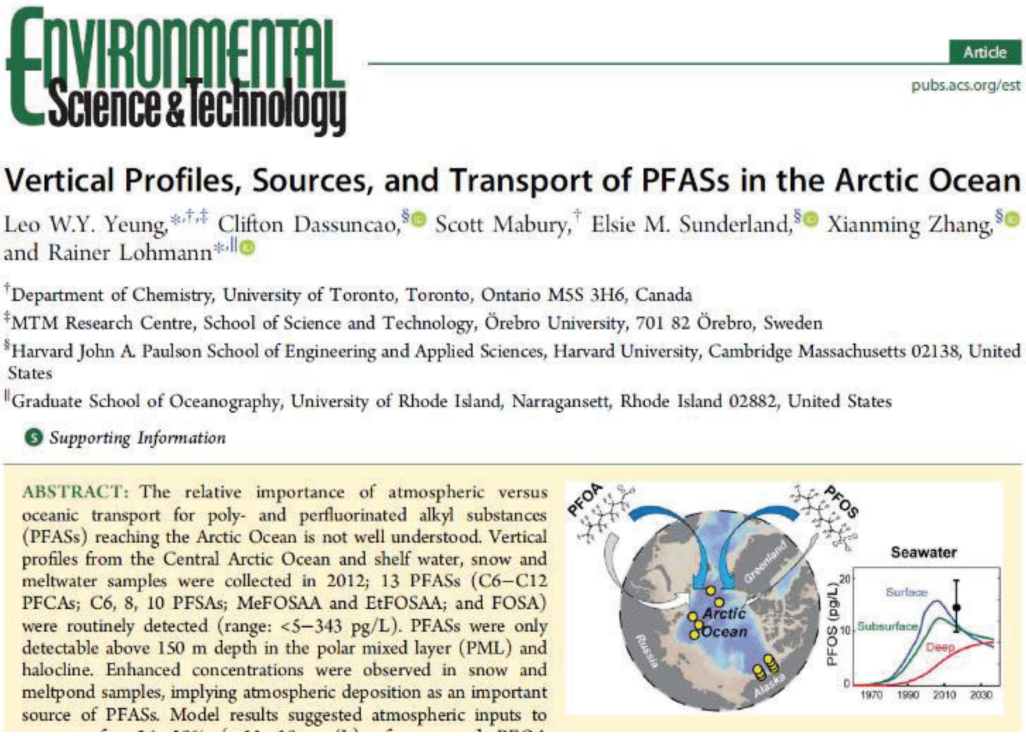
Long-chain perfluoroalkyl acids (PFAAs) are persistent chemicals with proven toxic effects. This study estimated the emissions and concentrations of two such chemicals, perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), in 11 of Europe's most populated river catchments. Estimated emissions were lowest in the Thames and highest in the Rhine, while the EU environmental quality standard for PFOS was exceeded in all rivers. This study provides a picture of PFAAs contamination in rivers across Europe, and makes recommendations for achieving reductions.

26 January 2017
Issue 481
Subscribe to free weekly News Alert

Source: Lindim, C., van Gils, J. & Cousins, I. (2016). Europe-wide estuarine export and surface water concentrations of PFOS and

Every year around 400 million tonnes of chemicals are produced and about a thousand new substances are developed[1]. While these provide numerous benefits to humans, there are mounting concerns about the effect of the thousands of synthetic substances on the environment.

PFAS in the Arctic



Environmental Science & Technology

Article

pubs.acs.org/est

Vertical Profiles, Sources, and Transport of PFASs in the Arctic Ocean

Leo W.Y. Yeung,[*,†,‡] Clifton Dassuncao,[§] Scott Mabury,[†] Elsie M. Sunderland,[§] Xianming Zhang,[§] and Rainer Lohmann[*,‖]

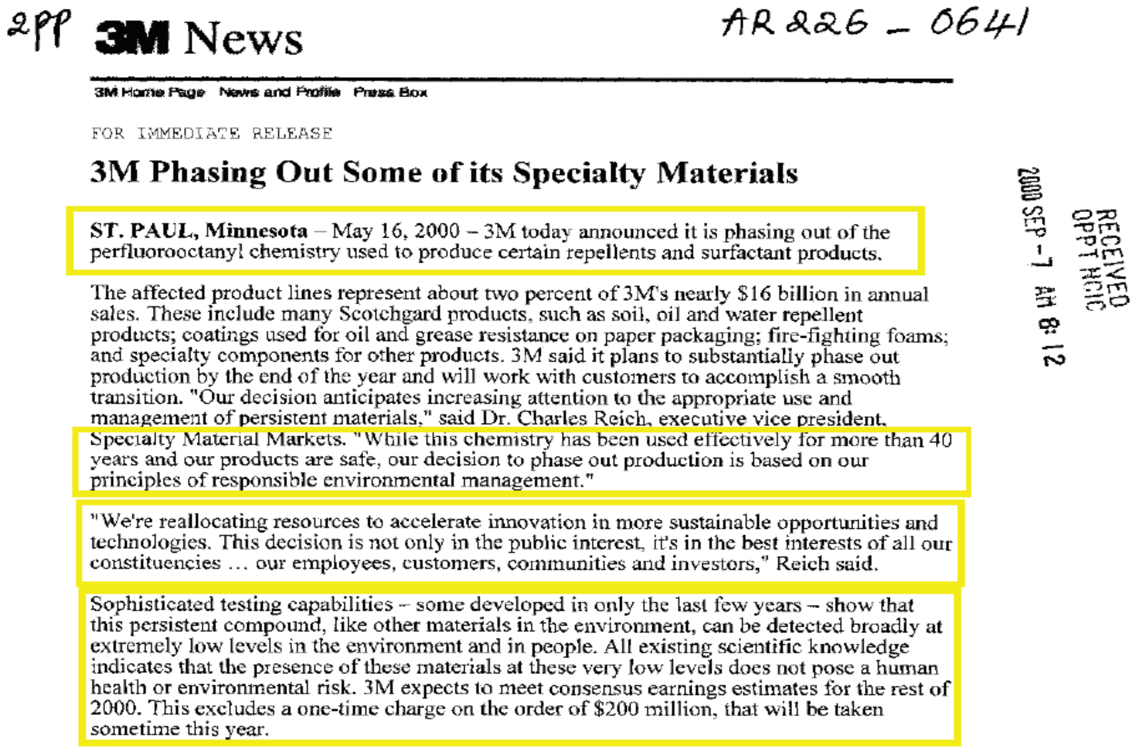
[†]Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada
[‡]MTM Research Centre, School of Science and Technology, Örebro University, 701 82 Örebro, Sweden
[§]Harvard John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge Massachusetts 02138, United States
[‖]Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island 02882, United States

Supporting Information

ABSTRACT: The relative importance of atmospheric versus oceanic transport for poly- and perfluorinated alkyl substances (PFASs) reaching the Arctic Ocean is not well understood. Vertical profiles from the Central Arctic Ocean and shelf water, snow and meltwater samples were collected in 2012; 13 PFASs (C6–C12 PFCAs; C6, 8, 10 PFSAs; MeFOSAA and EtFOSAA; and FOSA) were routinely detected (range: <5–343 pg/L). PFASs were only detectable above 150 m depth in the polar mixed layer (PML) and halocline. Enhanced concentrations were observed in snow and meltpond samples, implying atmospheric deposition as an important source of PFASs. Model results suggested atmospheric inputs to

MANAGEMENT

PFOS – May 2000



2pp **3M News** AR226 - 0641

3M Home Page News and Profile Press Box

FOR IMMEDIATE RELEASE

3M Phasing Out Some of its Specialty Materials

RECEIVED
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2000 SEP -7 AM 8:12

ST. PAUL, Minnesota – May 16, 2000 – 3M today announced it is phasing out of the perfluorooctanyl chemistry used to produce certain repellents and surfactant products.

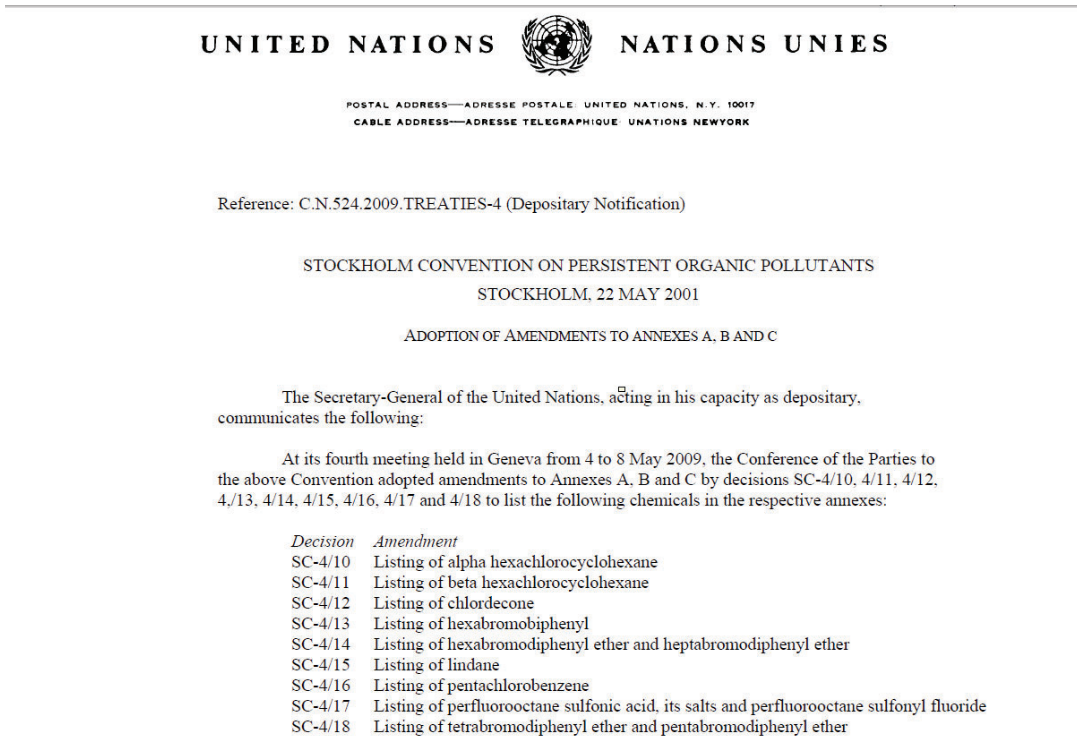
The affected product lines represent about two percent of 3M's nearly $16 billion in annual sales. These include many Scotchgard products, such as soil, oil and water repellent products; coatings used for oil and grease resistance on paper packaging; fire-fighting foams; and specialty components for other products. 3M said it plans to substantially phase out production by the end of the year and will work with customers to accomplish a smooth transition. "Our decision anticipates increasing attention to the appropriate use and management of persistent materials," said Dr. Charles Reich, executive vice president, Specialty Material Markets. "While this chemistry has been used effectively for more than 40 years and our products are safe, our decision to phase out production is based on our principles of responsible environmental management."

"We're reallocating resources to accelerate innovation in more sustainable opportunities and technologies. This decision is not only in the public interest, it's in the best interests of all our constituencies … our employees, customers, communities and investors," Reich said.

Sophisticated testing capabilities – some developed in only the last few years – show that this persistent compound, like other materials in the environment, can be detected broadly at extremely low levels in the environment and in people. All existing scientific knowledge indicates that the presence of these materials at these very low levels does not pose a human health or environmental risk. 3M expects to meet consensus earnings estimates for the rest of 2000. This excludes a one-time charge on the order of $200 million, that will be taken sometime this year.

MANAGEMENT

PFOS – August 2010



UNITED NATIONS NATIONS UNIES

POSTAL ADDRESS—ADRESSE POSTALE: UNITED NATIONS, N.Y. 10017
CABLE ADDRESS—ADRESSE TELEGRAPHIQUE: UNATIONS NEWYORK

Reference: C.N.524.2009.TREATIES-4 (Depositary Notification)

STOCKHOLM CONVENTION ON PERSISTENT ORGANIC POLLUTANTS
STOCKHOLM, 22 MAY 2001

ADOPTION OF AMENDMENTS TO ANNEXES A, B AND C

The Secretary-General of the United Nations, acting in his capacity as depositary, communicates the following:

At its fourth meeting held in Geneva from 4 to 8 May 2009, the Conference of the Parties to the above Convention adopted amendments to Annexes A, B and C by decisions SC-4/10, 4/11, 4/12, 4,/13, 4/14, 4/15, 4/16, 4/17 and 4/18 to list the following chemicals in the respective annexes:

Decision	*Amendment*
SC-4/10	Listing of alpha hexachlorocyclohexane
SC-4/11	Listing of beta hexachlorocyclohexane
SC-4/12	Listing of chlordecone
SC-4/13	Listing of hexabromobiphenyl
SC-4/14	Listing of hexabromodiphenyl ether and heptabromodiphenyl ether
SC-4/15	Listing of lindane
SC-4/16	Listing of pentachlorobenzene
SC-4/17	Listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride
SC-4/18	Listing of tetrabromodiphenyl ether and pentabromodiphenyl ether

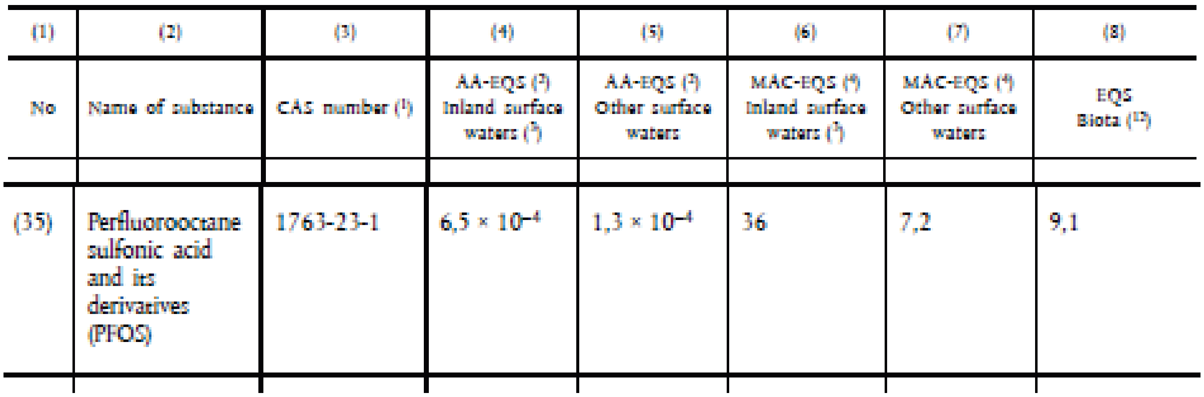
MANAGEMENT

Classification and labeling, REACH-SVHC, POP-Convention

PFAS	CLP (Annex VI)	REACH: Substance of very high concern (SVHC)	Restriction (REACH Annex XVII)	Stockholm Convention
PFOS	Carc. 2, Repr. 1B, STOT RE 1, Aquatic Chronic 2			POP (2009)
PFOA and APFO	Carc. 2, Repr. 1B, STOT RE 1	CMR, PBT (2013)	Manufacturing, import and use (with examptions - July 2020)	POP (2019)
PFNA and salts	Carc. 2., Repr. 1B, STOT RE 1	CMR, PBT (2014)	In preparation	
PFDA and salts	Carc. 2, Repr. 1B	CMR, PBT (2016)	In preparation	
PFTeDA; C11-PFCA		vPvB (2012)	In preparation	
PFUnDA; C12-PFCA		vPvB (2012)	In preparation	
PFTrDA; C13-PFCA		vPvB (2012)	In preparation	
PFTDA; C14-PFCA		vPvB (2012)	In preparation	
PFHxS , and Salts		vPvB (2017)	In preparation	Under discussion
GenX, HFPO-DA		vP, mobil, (2019)		
PFBS		vP, mobil, (2019)		
PFHxA			Proposal submitted	

MANAGEMENT

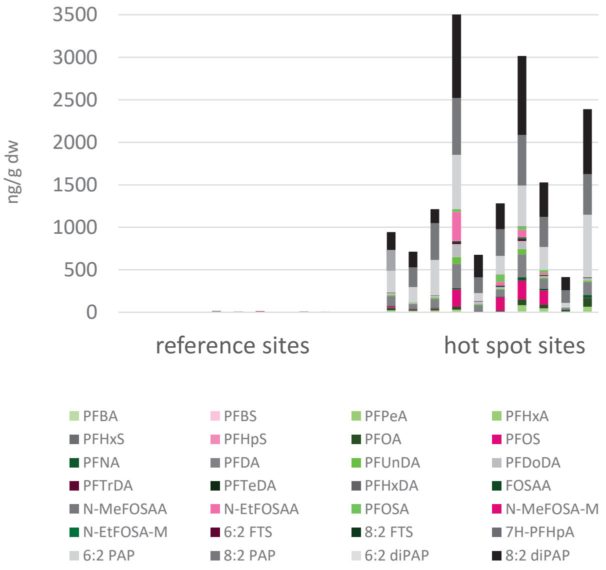
Environmental quality standards for PFOS under the WFD



(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
No	Name of substance	CAS number (1)	AA-EQS (2) Inland surface waters (3)	AA-EQS (2) Other surface waters	MAC-EQS (4) Inland surface waters (3)	MAC-EQS (4) Other surface waters	EQS Biota (12)
(35)	Perfluorooctane sulfonic acid and its derivatives (PFOS)	1763-23-1	$6,5 \times 10^{-4}$	$1,3 \times 10^{-4}$	36	7,2	9,1

Hot spot site in Rastatt, Southern Germany

Comparison of soil samples from the German environmental specimen bank
and from hot spot sites in Southern Germany, which are contaminated with PFAS from paper sludge.




Umweltskandal in Rastatt und Mannheim

Jetzt sind 747 Hektar mit PFC belastet

Von Thomas Faltin 12. Dezember 2017 - 14:43 Uhr

Im Norden Mannheims sind in diesem Jahr zahlreiche weitere Äcker entdeckt worden, auf die verunreinigte Papierschlämme ausgebracht worden sind. Die Stadtwerke Rastatt müssen Millionen von Euro investieren, um das Wasser zu schützen.

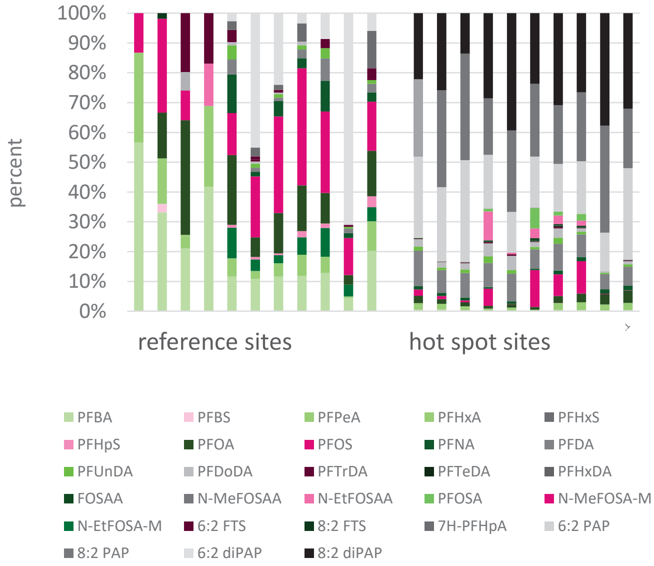
Rastatt/Mannheim - Es ist eine der größten Umweltverschmutzungen in der Geschichte Baden-Württembergs: Rund um Rastatt, Baden-Baden und Mannheim sind hunderte Hektar Fläche mit der Chemikalie PFC verseucht. Womöglich stammen die Stof-

Das Wasserwerk Rauental muss umgebaut und erweitert werden, um das belastete Trinkwasser reinigen zu können
Foto: Star Energiewerke

PFAS problem from
paper waste biosolids
in Southern Germany

Hot spot site in Rastatt, Southern Germany

Comparison of soil samples from the German environmental specimen bank
and from hot spot sites in Southern Germany, which are contaminated with PFAS from paper sludge.



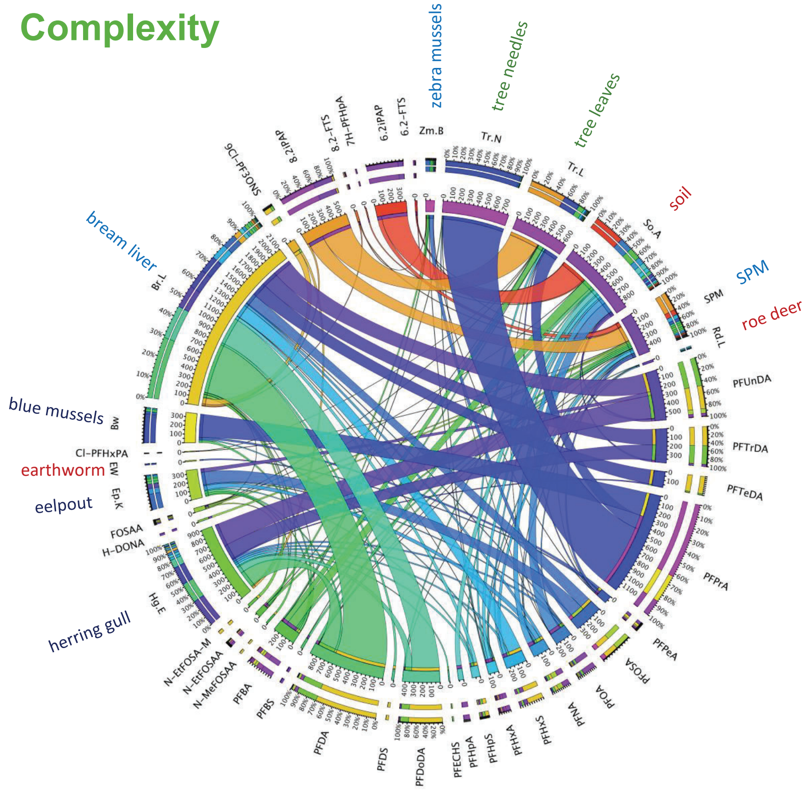
Representative spatial terrestrial data are needed to

- identify the yet unknown hot spots
- frame PFAS pattern and levels from hot spot sites into a larger picture

PFAS incidents may have different origins

- each type of PFAS incident has its own specific PFAS exposure pattern
- it is challenging to fully characterize the PFAS patterns at incident sites, including their transformation products

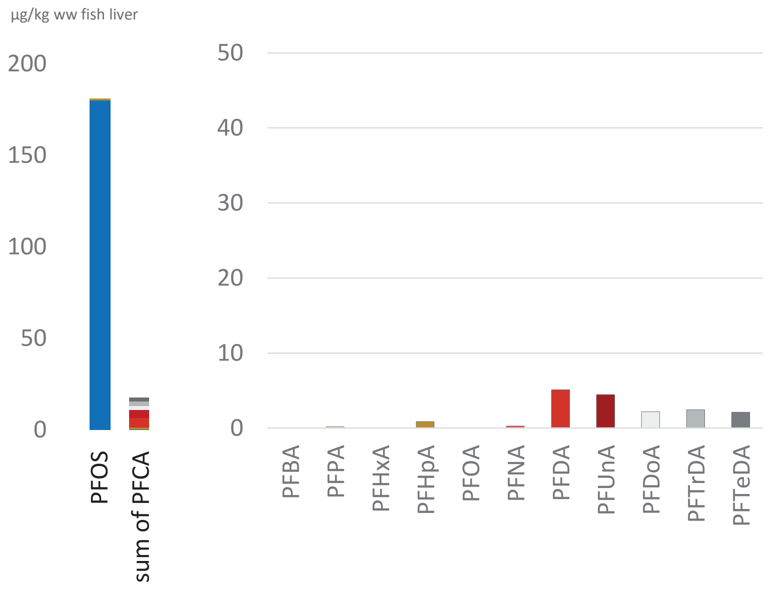
Complexity



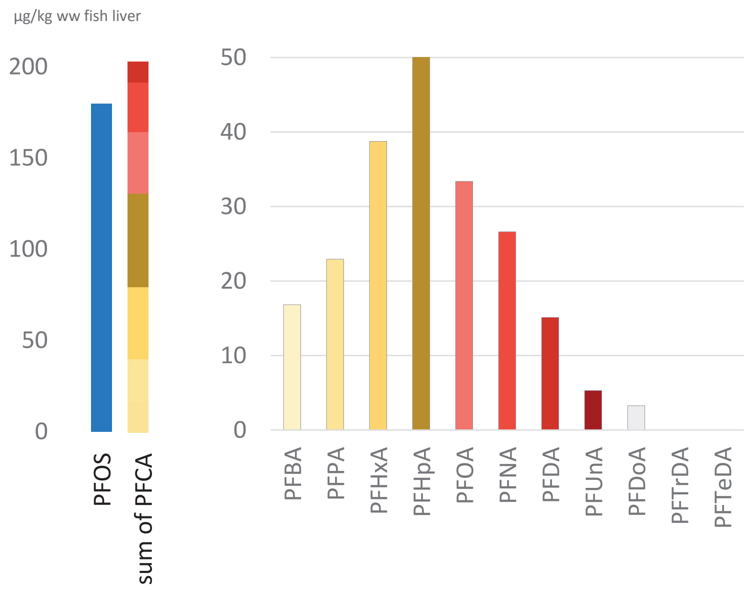
- Monitoring data show that PFAS concentrations and patterns vary widely between environmental compartments, species and matrices.
- It will be a huge challenge for research and regulation to understand and assess the environmental fate, behavior and effects of PFAS, which are currently released into the environment or have been in the past.

PFAS data (without PFOS) for coastal, freshwater and terrestrial German ecosystems; Kotthoff et al, 2020 (submitted)

PFCAs in fish liver, classical analysis



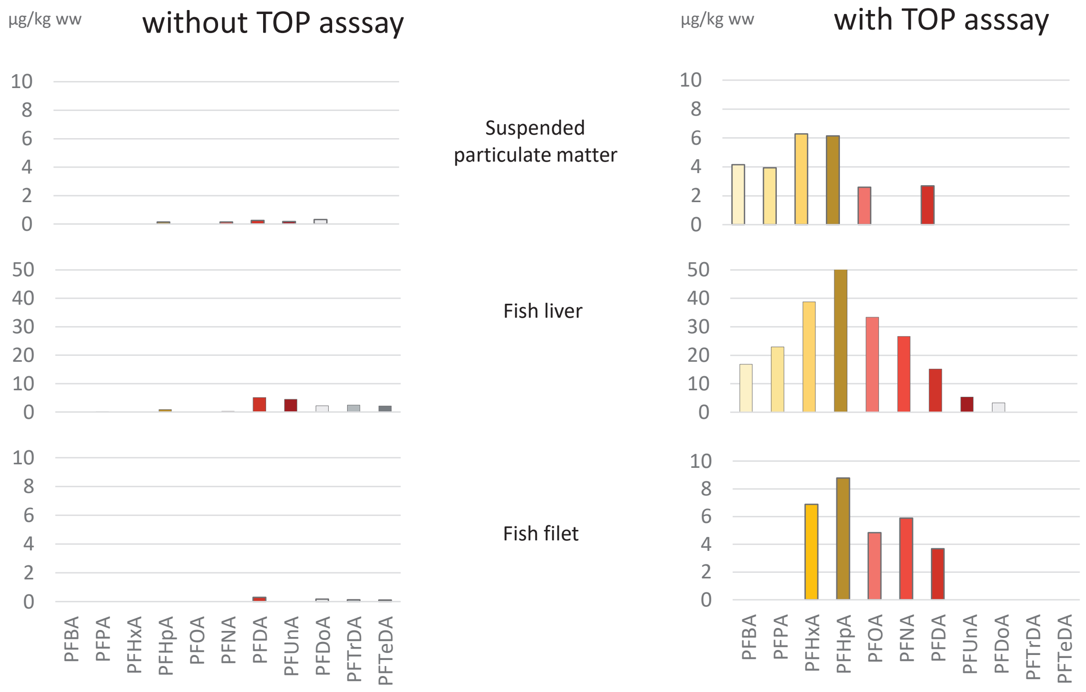
PFCAs in fish liver – after TOP assay



- The TOP assay oxidises polyfluorinated compounds in the samples to PFCAs, which are well known and can easily be analysed
- Regulatory monitoring labs are obliged to keep an eye on regulated PFAS,e.g. PFOS, PFOA, PFHxS
- However, without data on polyfluorinated precursors sources can not be sufficiently identified and controlled.
- PFAS sum parameters like the TOP and EOF assays need to be included in monitoring programmes.

Samples from river Rhine

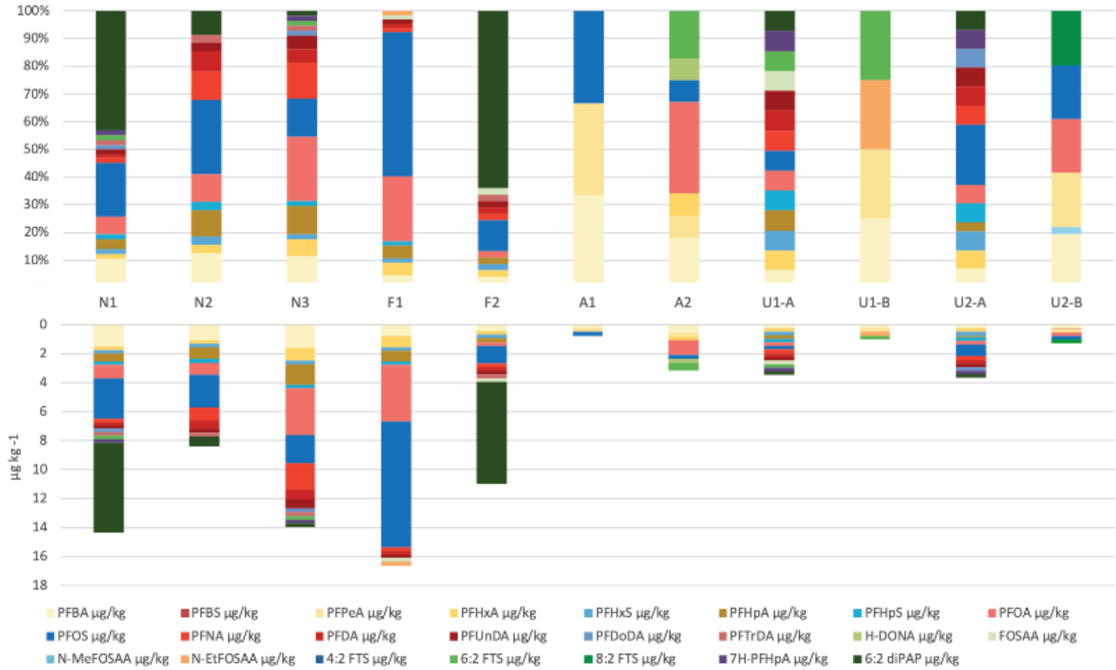
Consistent results for three sample types from rivers: liver, fillet, suspended particulate matter



(HOW) CAN WE FULLY CHARACTERISE THE EXPOSURE SITUATION FOR PFAS?

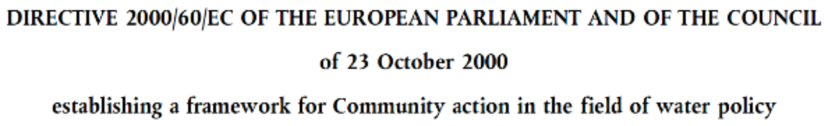
Soil PFAS data for terrestrial environments

Prisitine areas are higher contaminated than agrarian or urban regions



HOW TO PROCEED?

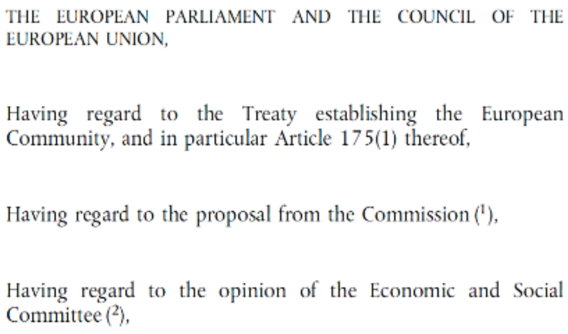
WFD – Art. 16 Strategies against pollution of water



DIRECTIVE 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 23 October 2000

establishing a framework for Community action in the field of water policy



THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION,

Having regard to the Treaty establishing the European Community, and in particular Article 175(1) thereof,

Having regard to the proposal from the Commission ([1]),

Having regard to the opinion of the Economic and Social Committee ([2]),

European Commission

Science for Environment Policy

Europe's rivers 'highly contaminated' with long-chain perfluoroalkyl acids

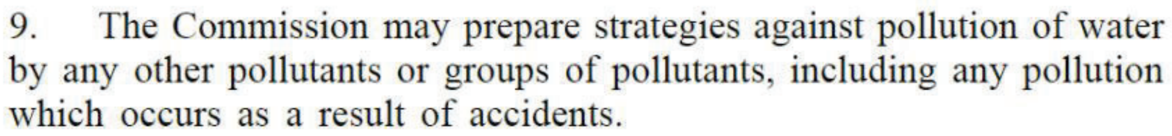
26 January 2017
Issue 481
Subscribe to free weekly News Alert

Source: Lindim, C., van Gils, J. & Cousins, I. (2016). Europe-wide estuarine export and surface water concentrations of PFOS and PFOA. *Water Research*, 103: 124–132. DOI: 10.1016/j.watres.2016.07.024.

Long-chain perfluoroalkyl acids (PFAAs) are persistent chemicals with proven toxic effects. This study estimated the emissions and concentrations of two such chemicals, perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), in 11 of Europe's most populated river catchments. Estimated emissions were lowest in the Thames and highest in the Rhine, while the EU environmental quality standard for PFOS was exceeded in all rivers. This study provides a picture of PFAAs contamination in rivers across Europe, and makes recommendations for achieving reductions.

Every year around 400 million tonnes of chemicals are produced and about a thousand new substances are developed[1]. While these provide numerous benefits to humans, there are mounting concerns about the effect of the thousands of synthetic substances on the environment.

This study focused on PFOS and PFOA — perfluoroalkyl acids used (or present as impurities) in industry and consumer items, such as textiles, food packaging and firefighting foams. These toxic, persistent and bioaccumulative substances have been linked to human health effects such as hormone disruption and cancer.



9. The Commission may prepare strategies against pollution of water by any other pollutants or groups of pollutants, including any pollution which occurs as a result of accidents.

Summary

1. The world-wide distribution of PFAS is leading to long-term and global exposure of ecosystems and the human population
2. Sources are complex and include precursors, polymers, degradation products and residues in articles
3. We need a Europe-wide overview about the environmental contamination in water, soil and air
4. Monitoring programmes need to include the potential precursors of stable PFCAs
5. We suggest that the Commission prepare a strategic action including the approaches of the Member States

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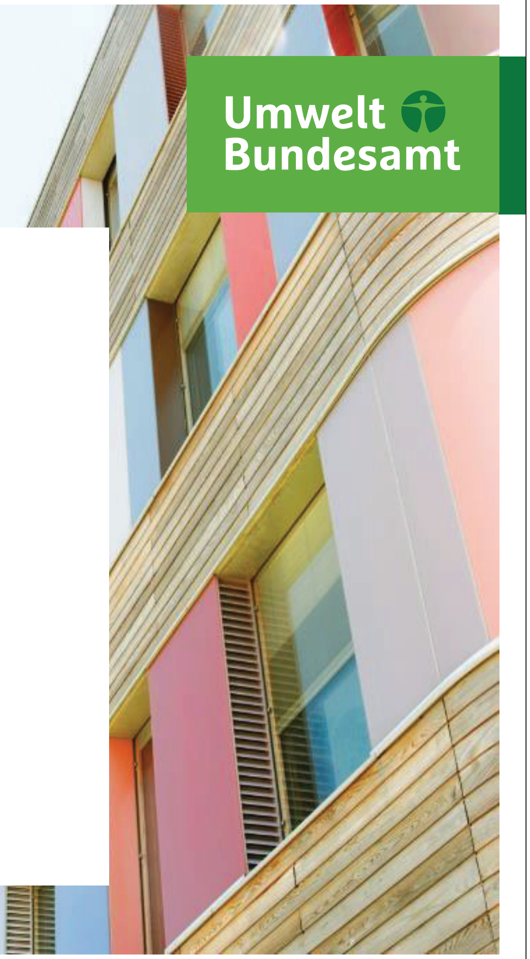


Umwelt Bundesamt

Thank you for your attention!

Dr. Christoph Schulte
Federal Environment Agency - Umweltbundesamt (UBA)
Department II 2 Water and Soil
Wörlitzer Platz 1, 06844 Dessau, Germany
+49-340-2103-3162
Email: christoph.schulte@uba.de

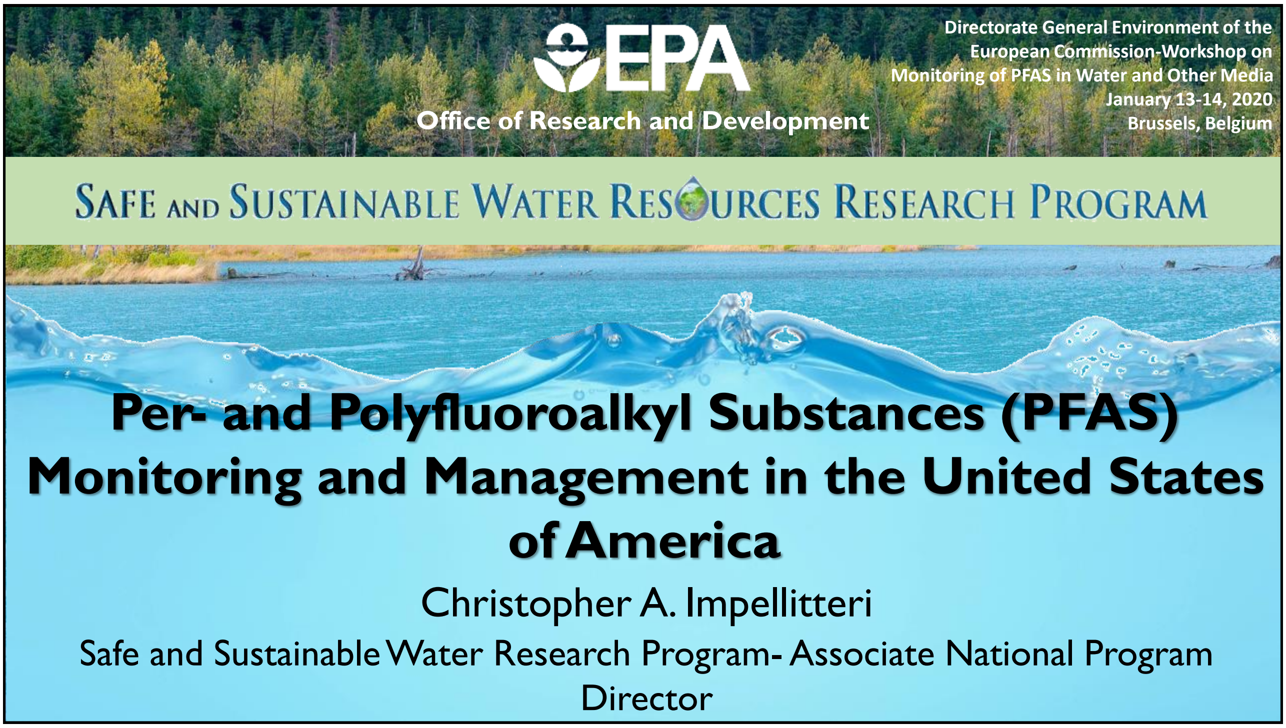
www.uba.de

Acknowledgement:
PFAS data elaborated by Mark Büking, Bernd Göckener, Matthias Kotthoff; Fraunhofer IME

II.5.3 PFAS Monitoring and Management in the United States of America

Christopher A. Impellitteri, Andrew J. Gillespie, Tom Speth and Marc Mills
United States Environmental Protection Agency (USEPA), Office of Research and Development

Per- and polyfluoroalkyl substances (PFAS) are a large class of man-made chemicals generally consisting of chains of carbon atoms surrounded by varying numbers fluorine atoms. PFAS are widely used throughout the world in industrial processes and consumer products. Some PFAS are known to be persistent in the environment, bioaccumulative, and toxic. This presentation will cover an overview of the USEPA action plans for PFAS including toxicity, exposure, risk assessment, treatment and remediation options, and analytical method development. The USEPA is addressing knowledge gaps in human toxicity information for many PFAS through standard toxicity assessments where data are available and in vitro high throughput screening approaches to fill in data gaps. Ecotoxicity research plans include the identification of sensitive taxa and bioaccumulation patterns using adverse outcome pathways (AOP) as an organizational framework. Analytical methods target specific PFAS in drinking, ground, surface, and wastewaters in addition to solid samples such as soils, sediments, biosolids, and tissues. Protocols for sampling and analysis of air emissions are being developed. The USEPA is also developing and evaluating methods for total organic fluorine, total oxidizable precursors, and non-targeted analyses. We must also improve our knowledge on exposure routes for PFAS through developing and evaluating methods, models and databases to characterize PFAS sources and exposures. Results from toxicity and exposure research will allow the identification and assessment of risk from various PFAS sources and help to prioritize and address actions for risk management. The USEPA conducts research on effective treatment methods for water and wastewater including residuals management issues (e.g. biosolids and spent treatment media). Treatment technologies to be discussed include sorptive (e.g. granular activated carbon, ion exchange) and destructive technologies (e.g. electron beam, thermal treatment). Contaminated site remediation will be addressed through the characterization of PFAS sources and the evaluation of technologies for remediating PFAS-impacted soils, waters, and sediments. Materials management issues will be examined through evaluating end-of-life disposal pathways for PFAS-containing materials and the efficacy of materials management strategies, such as landfill disposal and incineration, for minimizing, or eliminating, PFAS releases to the environment.



EPA
Office of Research and Development

Directorate General Environment of the
European Commission-Workshop on
Monitoring of PFAS in Water and Other Media
January 13-14, 2020
Brussels, Belgium

SAFE AND SUSTAINABLE WATER RESOURCES RESEARCH PROGRAM

Per- and Polyfluoroalkyl Substances (PFAS) Monitoring and Management in the United States of America

Christopher A. Impellitteri

Safe and Sustainable Water Research Program- Associate National Program Director

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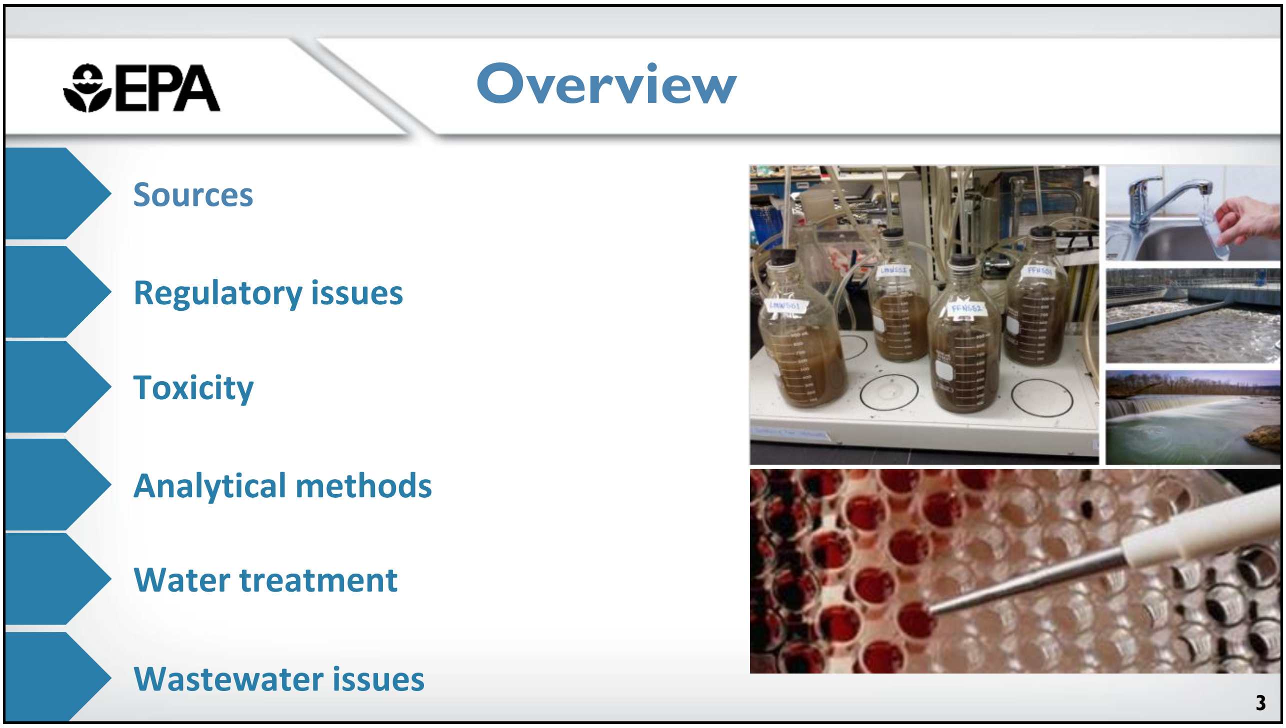
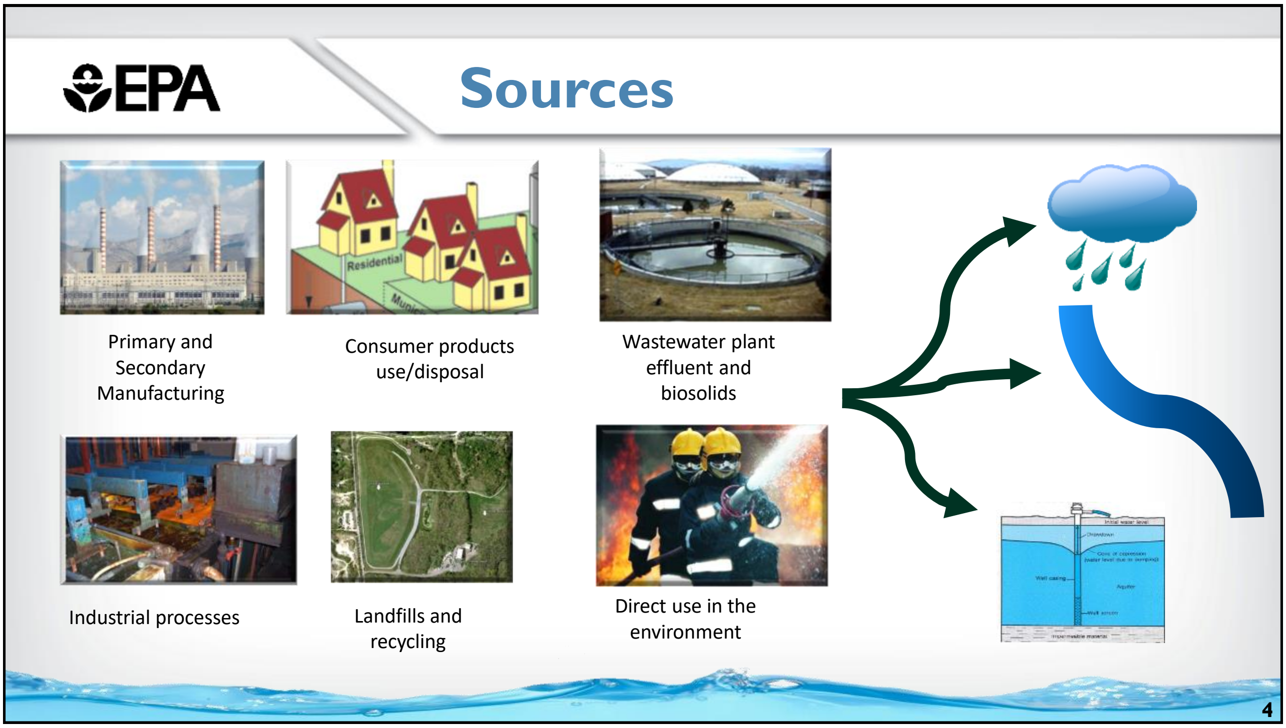
Disclaimer

The information in the EPA presentation has been reviewed and approved for public dissemination in accordance with U.S. Environmental Protection Agency (EPA) policy. The views expressed in this presentation are those of the author(s) and do not necessarily represent the views or policies of the Agency. Any mention of trade names or commercial products does not constitute EPA endorsement or recommendation for use.



Overview

- Sources
- Regulatory issues
- Toxicity
- Analytical methods
- Water treatment
- Wastewater issues



Sources

Primary and Secondary Manufacturing

Consumer products use/disposal

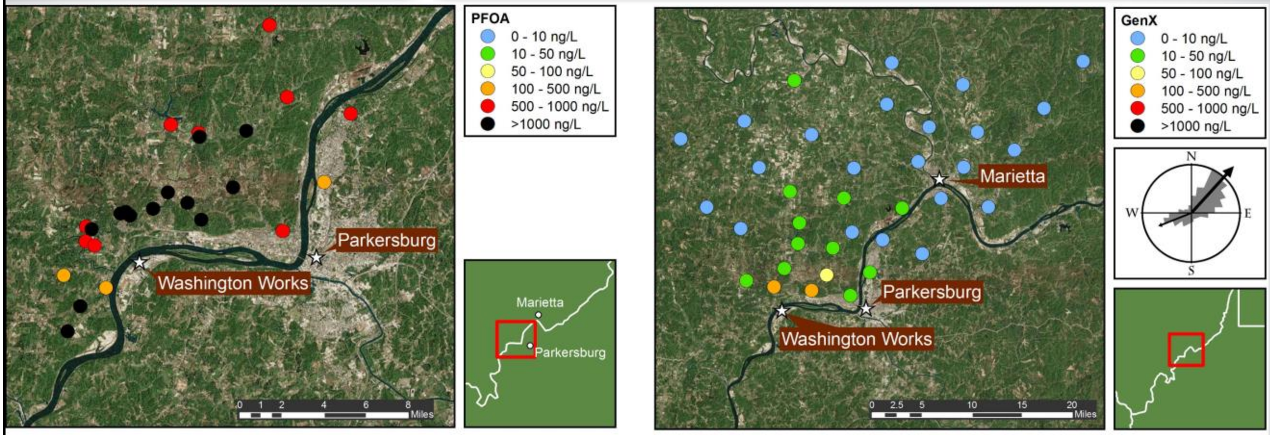
Wastewater plant effluent and biosolids

Industrial processes

Landfills and recycling

Direct use in the environment

Sources-Air



Three rounds of field sampling (2016) for PFAS in groundwater wells

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Sources-Land

Landfills

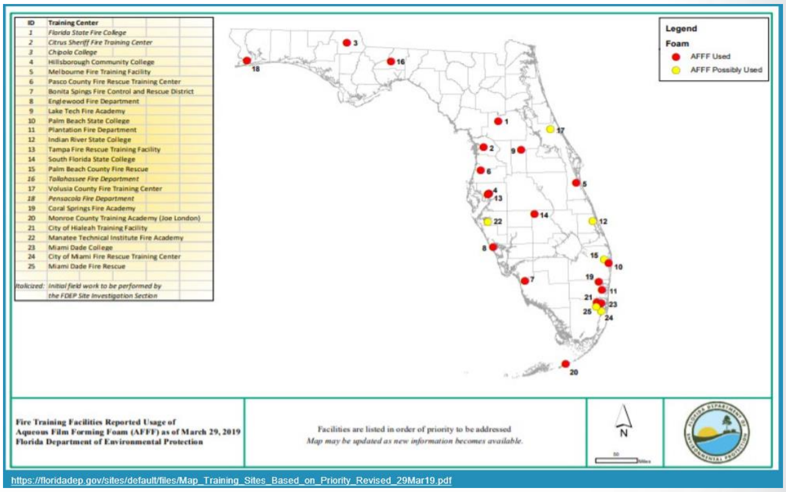
- Food contact surfaces such as cookware[1], pizza boxes, fast food wrappers, popcorn bags, etc.
- Polishes, waxes, and paints
- Stain repellants for carpets, clothing, upholstered furniture, etc.
- Cleaning products

Landfill leachate → Wastewater Treatment Plant

[1] PFOA has been phased out, however research needed to demonstrate safety of replacements

Sources-Land

Aqueous film forming film-AFFF



ID	Training Center
1	*Florida State Fire College*
2	*Citrus Sheriff Fire Training Center*
3	*Chipola College*
4	Hillsborough Community College
5	Melbourne Fire Training Facility
6	Pasco County Fire Rescue Training Center
7	Bonita Spings Fire Control and Rescue District
8	Englewood Fire Department
9	Lake Tech Fire Academy
10	Palm Beach State College
11	Plantation Fire Department
12	Indian River State College
13	Tampa Fire Rescue Training Facility
14	South Florida State College
15	Palm Beach County Fire Rescue
16	*Tallahassee Fire Department*
17	Volusia County Fire Training Center
18	*Pensacola Fire Department*
19	Coral Springs Fire Academy
20	Monroe County Training Academy (Joe London)
21	City of Hialeah Training Facility
22	Manatee Technical Institute Fire Academy
23	Miami Dade College
24	City of Miami Fire Rescue Training Center
25	Miami Dade Fire Rescue
Italicized:	*Initial field work to be performed by the FDEP Site Investigation Section*

Fire Training Facilities Reported Usage of Aqueous Film Forming Foam (AFFF) as of March 29, 2019
Florida Department of Environmental Protection

Facilities are listed in order of priority to be addressed
Map may be updated as new information becomes available.

https://floridadep.gov/sites/default/files/Map_Training_Sites_Based_on_Priority_Revised_29Mar19.pdf

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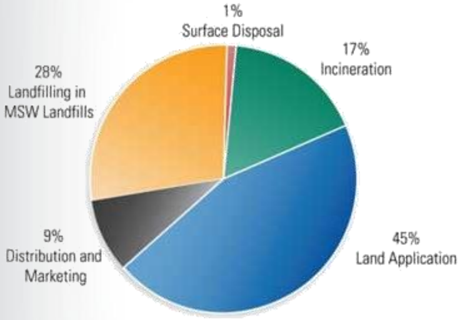
Sources-Land

U.S. Biosolids Management Practices



"Biosolids Management: Options, Opportunities & Challenges", NACWA

~55 % of residuals are land applied
~30% Landfilled
~15 % Incinerated @ low temp

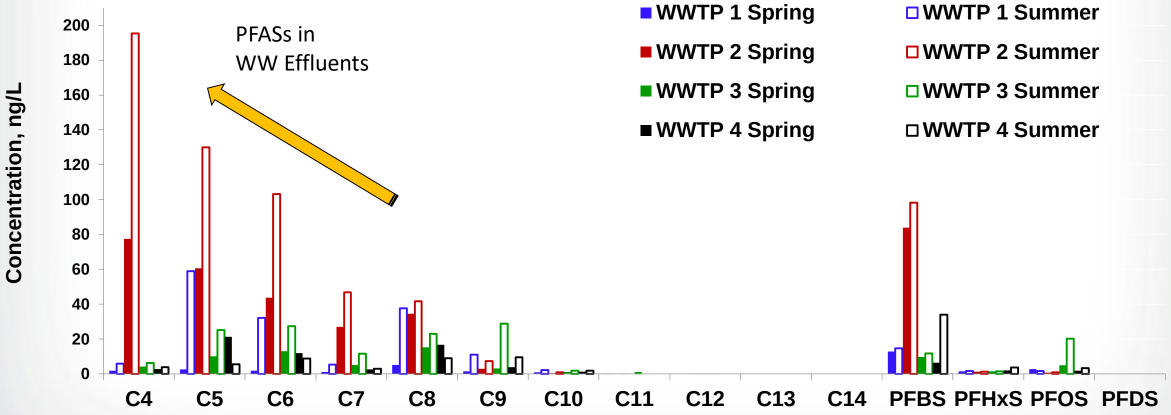
Year	Dry tons generated	% Beneficial Use	Dry tons used	Acres covered
1976	3,970,000	25	992,500	330,833
1984	6,500,000	25	1,625,000	541,667
1988	5,328,429	36	1,918,234	639,411
1993	5,357,200	44	2,357,168	785,723
1998	6,900,000	60	4,140,000	1,380,000
2004	7,188,070	55	3,953,439	1,317,813
2010	7,188,070	55	3,953,439	1,317,813

- Sewage sludges applied pre-Regs (80s)
- Many fields have 20+ years of biosolids land application
- **Other wastes are also land applied – pulp/paper sludge, CAFO wastes, refinery/industrial wastes, DW residuals, etc.**

EPA

Sources-Water

Wastewater discharge



EPA

Regulations/Guidance

State/Organization	Year First Listed	Standard/Guidance	Promulgated Rule?	PFOA (ng/L or ppt)	PFOS (ng/L or ppt)	Footnote
USEPA	2016	Health advisory-DW	No	70	70	a
Alaska	2018	Action level-DW/GW/SW	No	70	70	a
California	2019	Notification level-DW	No	5.1	6.5	
Connecticut	2016	Action level-DW/GW	No	70	70	b
New Jersey	2017/2018	MCL-DW	Pending	14	13	c
New York	2019	MCL-DW	Pending	10	10	
Nevada	2015	Basic Comparison Levels-DW	No	667	667	d
Vermont	2018	Health Advisory-DW/GW	Yes	20	20	b

a Applies to the individual results for PFOA and PFOS, as well as the sum of PFOA + PFOS

b Applies to the individual results for PFOA, PFOS, PFHpA, PFNA, and PFHxS as well as the sum of all 5

c New Jersey set an MCL for PFNA (13 ng/L) in drinking water in September 2018

d Basic comparison levels-technical screening tool. Not generated to represent action or final cleanup levels.

Source: ITRC Fact Sheet (June 2019) https://www.itrcweb.org/Guidance/ListDocuments?TopicID=56&SubTopicID=58

Regulations/Guidance

State/Organization	Year First Listed	Standard/Guidance	Promulgated Rule?	PFOA (ng/L)	PFOS (ng/L)	PFHxS (ng/L)	PFNA (ng/L)	PFBS (ng/L)	HFPO-DA (GenX chemical-ng/L)	PFHxA (ng/L)	Foot note
Michigan	2019	Health-based value-DW	Pending	8	16	51	6	420	370	400,000	a
Washington	2019	State Action Level-DW	Pending	10	15	70	14	1300	N/A	N/A	b
New Hampshire	2019	MCL-DW	Pending	12	15	18	11	N/A	N/A	N/A	c

a Health-based values are a starting point for MCL development. Source: https://www.michigan.gov/documents/pfasresponse/MPART_MCL_Frequently_Asked_Questions_659792_7.pdf

b State Action Level is concentration in water expected to be without appreciable health effects over a lifetime of exposure. Includes testing and monitoring requirements. State and local health officers have authority to require mitigation.

c Source: https://www.des.nh.gov/media/pr/2019/20190628-pfas-standards.htm

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Research – Human Health

- **Problem**: Lack of human toxicity information for many PFAS of interest
- **Action**: 2-prong strategy
    - Develop standard toxicity assessments (e.g. IRIS) where data are available
    - Use in vitro, high throughput screening approaches to fill in gaps
- **Results**:
    - Initial search of published toxicity data for 31 PFAS of interest, ~21 have data
    - Draft toxicity assessments available for HFPO-DA (GenX) and PFBS
    - Draft IRIS assessments underway for PFBA, PFHxS, PFHxA, PFNA and PFDA
    - Seven sets of high throughput assays underway for 150 PFAS representative of chemical space to support prioritization for further tox testing, chemical grouping, read across, relative toxicity and mixtures assessment
- **Impact**: Stakeholders will have PFAS toxicity information to inform risk management decisions and risk communication

Research – Ecological Toxicity

- **Problem**: Lack of ecological toxicity information for PFAS of concern
- **Action**:
  - Systematic review of literature, assembled in the ECOTOX database
  - Developing research plan including identification of sensitive taxa, bioaccumulation, benchmarks, and thresholds
  - Use Adverse Outcome Pathways (AOP) as organizational framework
- **Results**:
  - 437 references, 96 PFAS, 264 species, 889 effect measurements in ECOTOX
  - AOP development, verification getting underway
- **Impact**: Stakeholders will have PFAS ecotoxicity information to support risk management decisions and risk communication

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Methods

Three broad categories of EPA Methods:

- Safe Drinking Water Act Methods
  - https://www.epa.gov/dwanalyticalmethods

- Clean Water Act Methods
  - https://www.epa.gov/cwa-methods

- SW846 Methods
  - https://www.epa.gov/hw-sw846/guidance-methods-development-and-methods-validation-resource-conservation-and-recovery-act

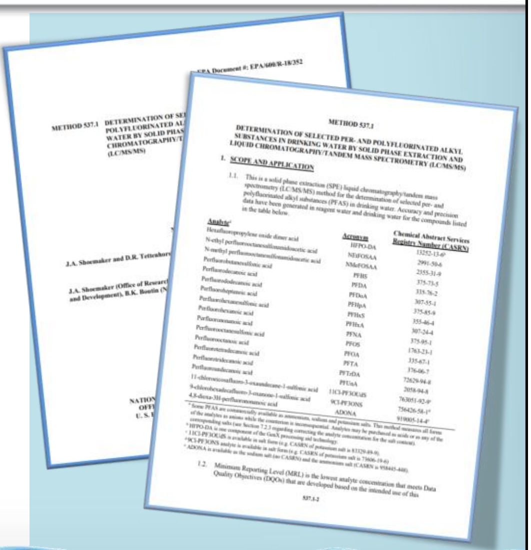
Methods

Sampling

- No teflon
- Avoid contact with clothes, materials containing PFAS (e.g. some food wrappers)
- See Interstate Technology and Regulatory Council Fact Sheet: *Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for PFAS* pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_site_characterization_3_15_18.pdf
- PFAS Quality Assurance Plan and Data Review issues epa.gov/fedfac/technical-fact-sheet-perfluorooctane-sulfonate-pfos-and-perfluorooctanoic-acid-pfoa-0

Drinking Water Method 537: Revision 1

- **Update: External lab validation for additional analytes by 537**
  - Perfluoro-2-propoxypropanoic acid (GenX chemical HFPO-DA, CAS 13252-13-6)
  - Potassium 9-chlorohexadecafluoro-3-oxanone-1-sulfonate (9Cl-PF3ONS, CAS 73606-19-6)
  - Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS, CAS 83329-89-9)
  - Sodium dodecafluoro-3H-4,8-dioxanonate (ADONA, CAS 958445-44-8)
- **Incorporated clarifications issued in EPA Technical Advisory** epa.gov/sites/production/files/2016-09/documents/pfoa-technical-advisory.pdf
- **Final published method (November, 2018)** epa.gov/water-research/epa-drinking-water-research-methods



EPA Document #: EPA/600/R-18/352

METHOD 537.1

DETERMINATION OF SELECTED PER- AND POLYFLUORINATED ALKYL SUBSTANCES IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC/MS/MS)

1. SCOPE AND APPLICATION

1.1. This is a solid phase extraction (SPE) liquid chromatography/tandem mass spectrometry (LC/MS/MS) method for the determination of selected per- and polyfluorinated alkyl substances (PFAS) in drinking water. Accuracy and precision data have been generated in reagent water and drinking water for the compounds listed in the table below.

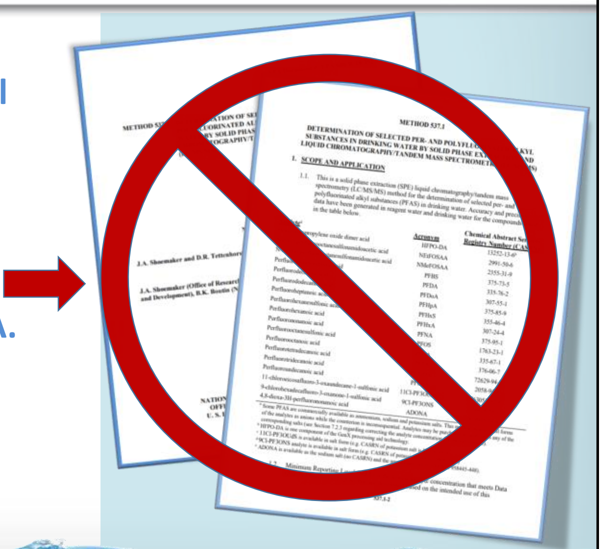
Analyte	Acronym	Chemical Abstract Services Registry Number (CASRN)
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluorononanoic acid	PFNA	375-95-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorotetradecanoic acid	PFTA	376-06-7
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluoroundecanoic acid	PFUnA	2058-94-8
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS	756426-58-1
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4

1.2. Minimum Reporting Level (MRL) is the lowest analyte concentration that meets Data Quality Objectives (DQOs) that are developed based on the intended use of this

537.1-2

Drinking Water Method 537: "Modified"

- Method 537 often modified by analytical laboratories for use on non-drinking water samples.
- If modifications are made that are not explicitly listed in 537 or 537 Revision 1, the method is not considered 537 by EPA.
- The most common modification is inclusion of isotope dilution.



Drinking Water Method 533

Solid phase extraction/isotope dilution method targeting PFAS <C12

- Method 537 generally performs poorly for C4 compounds (e.g. PFBA, PFBS)
- Method contains options for using isotope dilution or external standard calibration (or, possibly, two separate methods will be posted)
- Will support the fifth Unregulated Contaminant Monitoring Rule
- Released December 2019
  - https://www.epa.gov/dwanalyticalmethods/analytical-methods-developed-epa-analysis-unregulated-contaminants

Non-Drinking Water Sample Methods:
SW-846 Draft Method 8327—Direct Injection

Non-drinking water aqueous matrices:

- Groundwater
- Surface water
- Wastewater

Find a balance among sensitivity, ease of implementation, and monitoring requirements

- Simplicity
- Robustness
- Maximizing throughput for production lab use
- Minimizing sample transfers, extractions, filter steps, chemical additions (e.g., pH adjustments)

https://www.epa.gov/hw-sw846/validated-test-method-8327-and-polyfluoroalkyl-substances-pfas-using-external-standard

Non-Drinking Water Sample Methods:
SW-846 Draft Method 8327—Direct Injection

24 PFAS (including all target analytes in EPA Method 537)

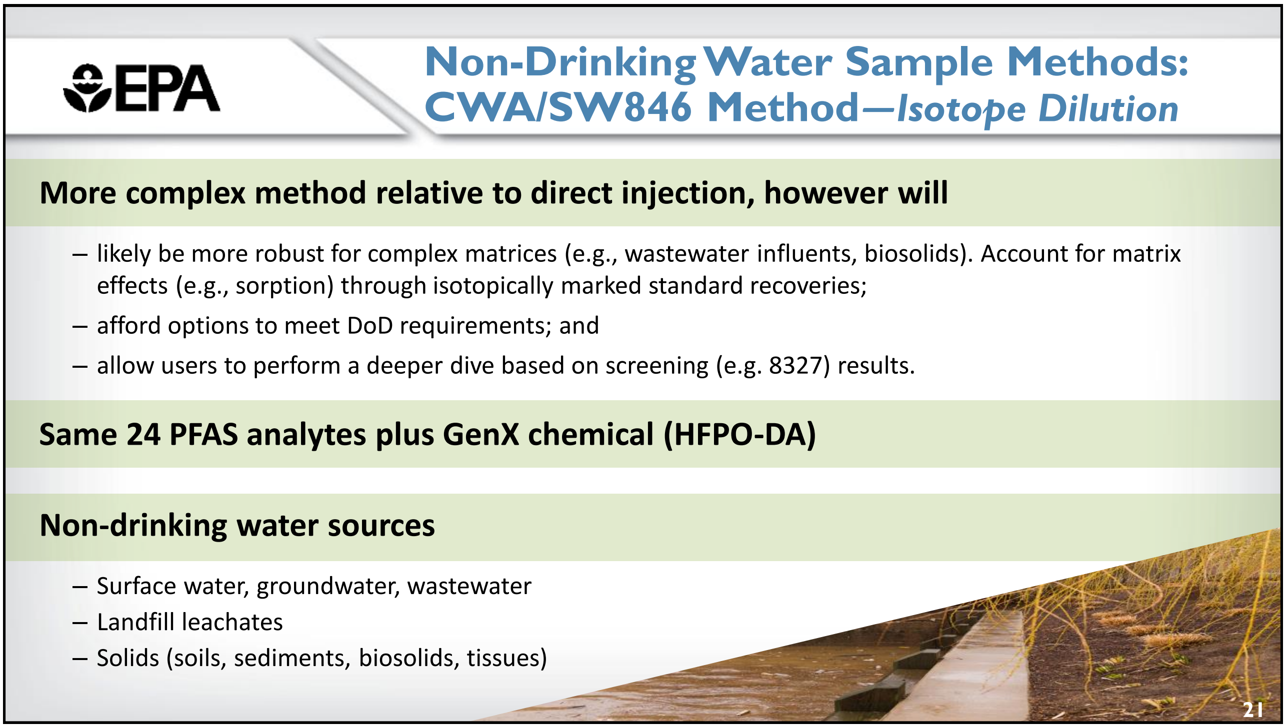
- Commercially available standards (“neat” and isotopically labeled)

Direct injection based on EPA Region 5/Chicago Lab Method

- Similar to draft American Society for Testing and Materials (ASTM) Method D7979
- Multi-laboratory validation study completed in 2018
- Currently reviewing full data packages and conducting statistical analysis
- Currently Revising final draft

Public comment period closed August 26, 2019

Target Quantitation Limits: 10 nanogram/L



Non-Drinking Water Sample Methods: CWA/SW846 Method—*Isotope Dilution*

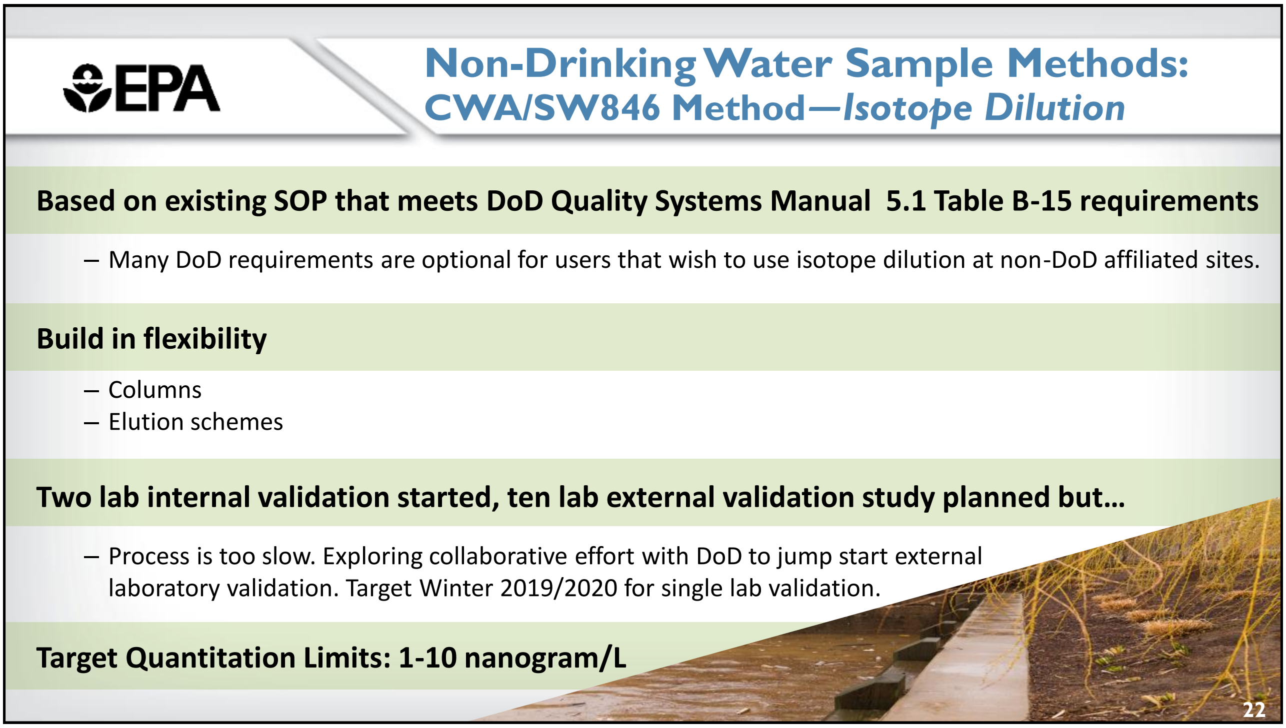
More complex method relative to direct injection, however will

- likely be more robust for complex matrices (e.g., wastewater influents, biosolids). Account for matrix effects (e.g., sorption) through isotopically marked standard recoveries;
- afford options to meet DoD requirements; and
- allow users to perform a deeper dive based on screening (e.g. 8327) results.

Same 24 PFAS analytes plus GenX chemical (HFPO-DA)

Non-drinking water sources

- Surface water, groundwater, wastewater
- Landfill leachates
- Solids (soils, sediments, biosolids, tissues)



Non-Drinking Water Sample Methods: CWA/SW846 Method—*Isotope Dilution*

Based on existing SOP that meets DoD Quality Systems Manual 5.1 Table B-15 requirements

- Many DoD requirements are optional for users that wish to use isotope dilution at non-DoD affiliated sites.

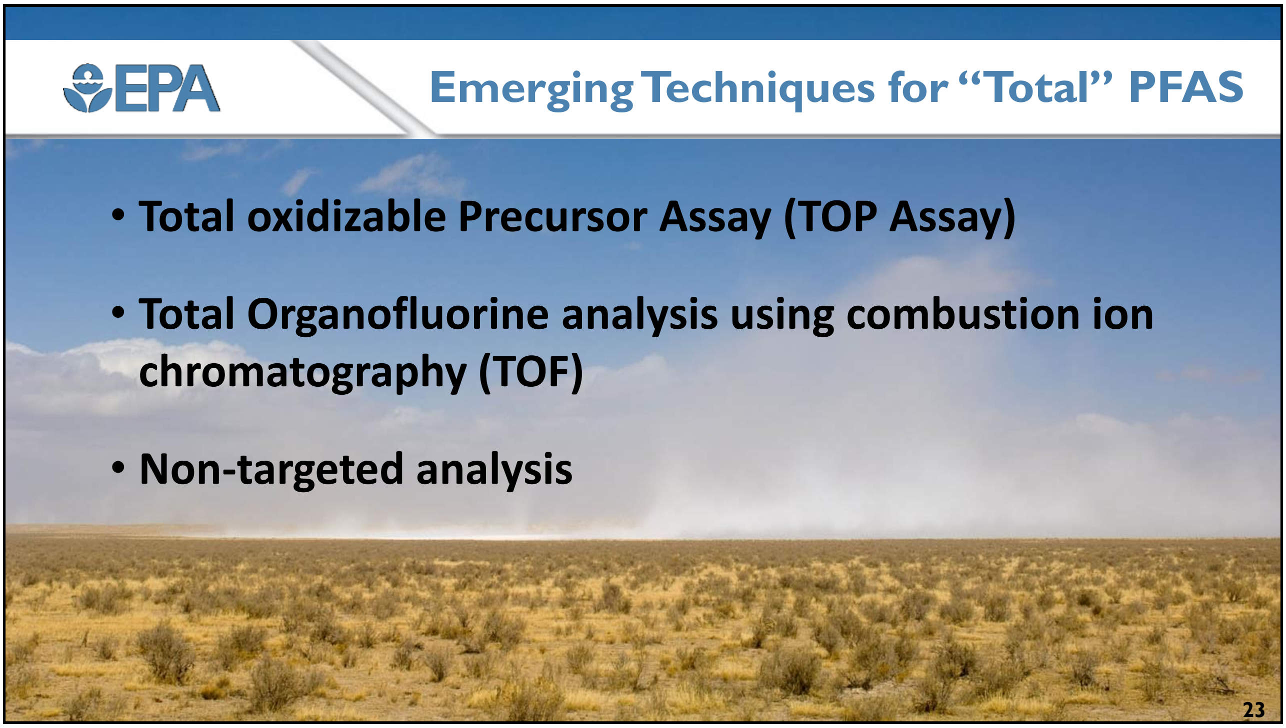
Build in flexibility

- Columns
- Elution schemes

Two lab internal validation started, ten lab external validation study planned but…

- Process is too slow. Exploring collaborative effort with DoD to jump start external laboratory validation. Target Winter 2019/2020 for single lab validation.

Target Quantitation Limits: 1-10 nanogram/L



Emerging Techniques for "Total" PFAS

- Total oxidizable Precursor Assay (TOP Assay)
- Total Organofluorine analysis using combustion ion chromatography (TOF)
- Non-targeted analysis

Total Organofluorine Analysis using Combustion Ion Chromatography (TOF)

Adsorption of PFAS on to activated carbon / other sorbents

Combustion

Release of F

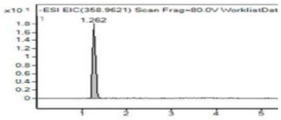
Ion Chromatography

- No specialized or costly instrumentation required
- Applied for aqueous matrices and blood samples
- Removing the background inorganic F^- from the sample is important to make sure that the reported F^- is organic
- Can be developed on a wide commercial scale

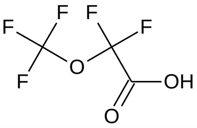
Non-Targeted Analysis

Explore Unknown compounds using High resolution mass spectrometry. Identify a peak in a chromatogram and to ultimately predict the identity of this unknown

- **Mass spectrometer assigns a high resolution mass for peaks observed in the chromatogram**



- **Software calculates the exact number and type of atoms needed to achieve the measured mass.**
- **Fragmentation experiments allow determination of most likely structure:**



Molecular Formula: $C_3HF_5O_3$
Monoisotopic Mass: 179.984585 Da
[M-H]-: 178.977308 Da

- **Using mass, formula, and structure, identity can be assigned by searching against databases of known compounds**
- **Compare peak to commercial to confirm identification if possible**

Overview: EPA Drinking Water Research

- **Problem**: Utilities lack treatment technology cost data for PFAS removal
- **Action**:
  - Gather performance and cost data from available sources (DOD, utilities, industry, etc.)
  - Conduct EPA research on performance of treatment technologies including home treatment systems
  - Update EPA’s Treatability Database and Unit Cost Models
  - Connect EPA’s Treatability Database to EPA’s Unit Cost Models for ease of operation
  - Model performance and cost, and then extrapolate to other scenarios
    - Variable source waters
    - Variable PFAS concentrations in source water
    - Different reactivation/disposal options
    - Document secondary benefits
    - Address treatment impact on corrosion
  - Evaluate reactivation of granular activated carbon
- **Impact**: Enable utilities to make informed decisions about cost-effective treatment strategies for removing PFAS from drinking water

Drinking Water Treatment for PFOS

Ineffective Treatments

Conventional Treatment
Low Pressure Membranes
Biological Treatment (including slow sand filtration)
Disinfection
Oxidation
Advanced oxidation

<u>PAC Dose to Achieve</u>	
50% Removal	16 mg/l
90% Removal	>50 mg/L

Dudley et al., 2015

Effective Treatments

	Percent Removal	
Anion Exchange Resin (IEX)	90 to 99	- **Effective**
High Pressure Membranes	93 to 99	- **Effective**
Powdered Activated Carbon (PAC)	10 to 97	- **Effective for only select applications**
Granular Activated Carbon (GAC)		
Extended Run Time	0 to 26	- **Ineffective**
Designed for PFAS Removal	> 89 to > 98	- **Effective**

Advantages of Select Treatments

Granular Activated Carbon (GAC)	**Most studied technology** **Will remove 100% of the contaminants, for a time** **Good capacity for some PFAS** Will remove a significant number of disinfection byproduct precursors Will help with maintaining disinfectant residuals Will remove many co-contaminants Likely positive impact on corrosion (lead, copper, iron)
Anion Exchange Resin (PFAS selective)	**Will remove 100% of the contaminants, for a time** **High capacity for some PFAS** **Smaller beds compared to GAC** Can remove select co-contaminants
High Pressure Membranes	**High PFAS rejection** Will remove many co-contaminants Will remove a significant number of disinfection byproduct precursors Will help with maintaining disinfectant residuals

Issues to Consider

EPA is evaluating these issues to document where and when they will be an issue

Granular Activated Carbon (GAC)	**GAC run time for short-chained PFAS (shorter run time)** **Potential overshoot of poor adsorbing PFAS if not designed correctly** **Reactivation/removal frequency** Disposal or reactivation of spent carbon
Anion Exchange Resin (PFAS selective)	**Run time for select PFAS (shorter run time)** **Overshoot of poor adsorbing PFAS if not designed correctly** Unclear secondary benefits Disposal of resin
High Pressure Membranes	**Capital and operations costs** Membrane fouling Corrosion control Lack of options for concentrate stream treatment or disposal

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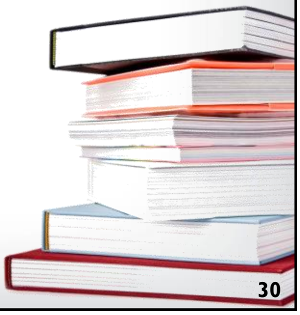
Research: Treatment

Drinking Water Treatability Database

Publicly available interactive literature review database that contains over 65 regulated and unregulated contaminants and covers 34 treatment processes commonly employed or known to be effective (thousands of sources assembled on one site).

Currently available:

- **Nitrate**
- **Perchlorate**
- **Microcystins**
- **PFOA, PFOS, group of 20 PFAS**

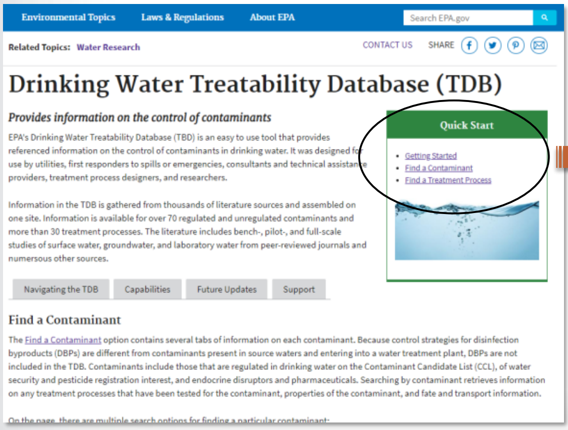


epa.gov/water-research/drinking-water-treatability-database-tdb

Search: EPA TDB

Treatability Database

Agency Landing Page



Related Topics: Water Research

Drinking Water Treatability Database (TDB)

Provides information on the control of contaminants

EPA's Drinking Water Treatability Database (TBD) is an easy to use tool that provides referenced information on the control of contaminants in drinking water. It was designed for use by utilities, first responders to spills or emergencies, consultants and technical assistance providers, treatment process designers, and researchers.

Information in the TDB is gathered from thousands of literature sources and assembled on one site. Information is available for over 70 regulated and unregulated contaminants and more than 30 treatment processes. The literature includes bench-, pilot-, and full-scale studies of surface water, groundwater, and laboratory water from peer-reviewed journals and numersous other sources.

Quick Start

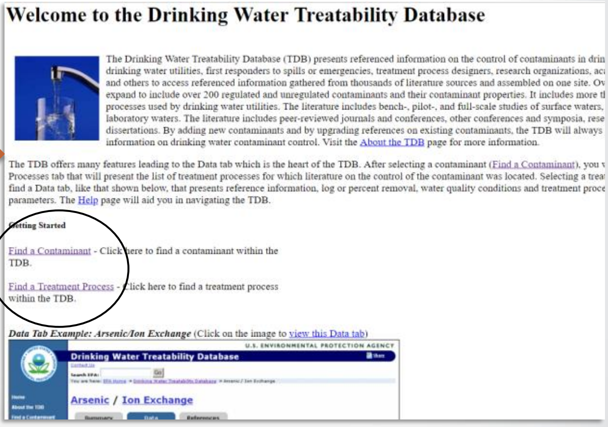
- Getting Started
- Find a Contaminant
- Find a Treatment Process

Find a Contaminant

The Find a Contaminant option contains several tabs of information on each contaminant. Because control strategies for disinfection byproducts (DBPs) are different from contaminants present in source waters and entering into a water treatment plant, DBPs are not included in the TDB. Contaminants include those that are regulated in drinking water on the Contaminant Candidate List (CCL), of water security and pesticide registration interest, and endocrine disruptors and pharmaceuticals. Searching by contaminant retrieves information on any treatment processes that have been tested for the contaminant, properties of the contaminant, and fate and transport information.

On the page, there are multiple search options for finding a particular contaminant:

Database Homepage



Welcome to the Drinking Water Treatability Database

The Drinking Water Treatability Database (TDB) presents referenced information on the control of contaminants in drin
drinking water utilities, first responders to spills or emergencies, treatment process designers, research organizations, ac
and others to access referenced information gathered from thousands of literature sources and assembled on one site. Ov
expand to include over 200 regulated and unregulated contaminants and their contaminant properties. It includes more t
processes used by drinking water utilities. The literature includes bench-, pilot-, and full-scale studies of surface waters,
laboratory waters. The literature includes peer-reviewed journals and conferences, other conferences and symposia, rese
dissertations. By adding new contaminants and by upgrading references on existing contaminants, the TDB will always
information on drinking water contaminant control. Visit the About the TDB page for more information.

The TDB offers many features leading to the Data tab which is the heart of the TDB. After selecting a contaminant (Find a Contaminant), you v
Processes tab that will present the list of treatment processes for which literature on the control of the contaminant was located. Selecting a trea
find a Data tab, like that shown below, that presents reference information, log or percent removal, water quality conditions and treatment proce
parameters. The Help page will aid you in navigating the TDB.

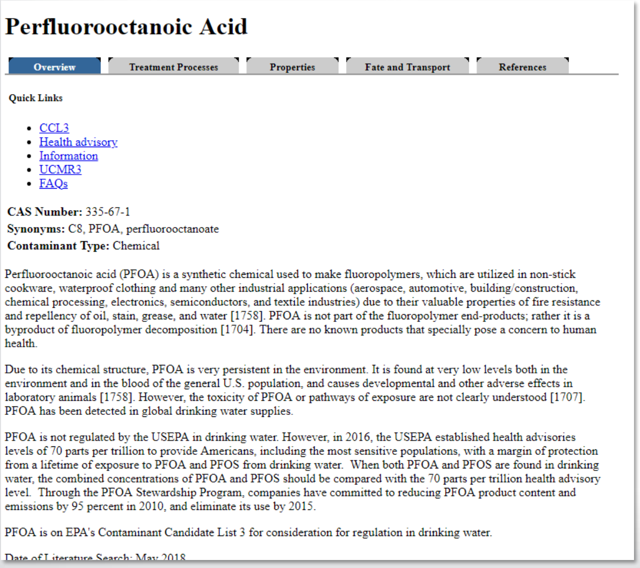
Getting Started

Find a Contaminant - Click here to find a contaminant within the TDB.

Find a Treatment Process - Click here to find a treatment process within the TDB.

Data Tab Example: Arsenic/Ion Exchange (Click on the image to view this Data tab)

Treatability Database



Perfluorooctanoic Acid

Quick Links

- CCL3
- Health advisory
- Information
- UCMR3
- FAQs

CAS Number: 335-67-1
Synonyms: C8, PFOA, perfluorooctanoate
Contaminant Type: Chemical

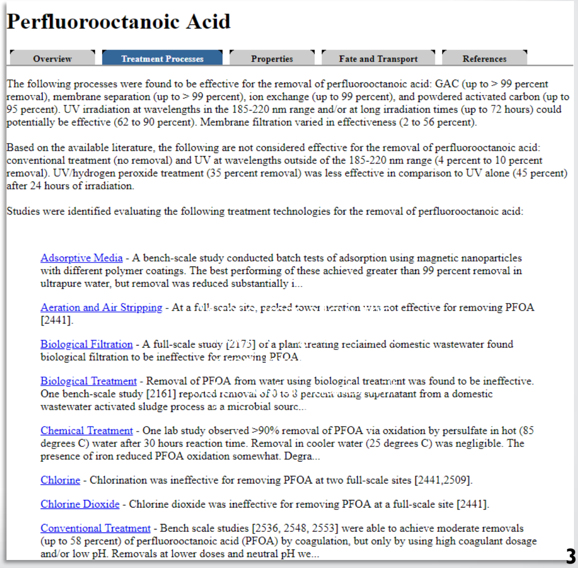
Perfluorooctanoic acid (PFOA) is a synthetic chemical used to make fluoropolymers, which are utilized in non-stick cookware, waterproof clothing and many other industrial applications (aerospace, automotive, building/construction, chemical processing, electronics, semiconductors, and textile industries) due to their valuable properties of fire resistance and repellency of oil, stain, grease, and water [1758]. PFOA is not part of the fluoropolymer end-products; rather it is a byproduct of fluoropolymer decomposition [1704]. There are no known products that specially pose a concern to human health.

Due to its chemical structure, PFOA is very persistent in the environment. It is found at very low levels both in the environment and in the blood of the general U.S. population, and causes developmental and other adverse effects in laboratory animals [1758]. However, the toxicity of PFOA or pathways of exposure are not clearly understood [1707]. PFOA has been detected in global drinking water supplies.

PFOA is not regulated by the USEPA in drinking water. However, in 2016, the USEPA established health advisories levels of 70 parts per trillion to provide Americans, including the most sensitive populations, with a margin of protection from a lifetime of exposure to PFOA and PFOS from drinking water. When both PFOA and PFOS are found in drinking water, the combined concentrations of PFOA and PFOS should be compared with the 70 parts per trillion health advisory level. Through the PFOA Stewardship Program, companies have committed to reducing PFOA product content and emissions by 95 percent in 2010, and eliminate its use by 2015.

PFOA is on EPA's Contaminant Candidate List 3 for consideration for regulation in drinking water.

Date of Literature Search: May 2018



Perfluorooctanoic Acid

The following processes were found to be effective for the removal of perfluorooctanoic acid: GAC (up to > 99 percent removal), membrane separation (up to > 99 percent), ion exchange (up to 99 percent), and powdered activated carbon (up to 95 percent). UV irradiation at wavelengths in the 185-220 nm range and/or at long irradiation times (up to 72 hours) could potentially be effective (62 to 90 percent). Membrane filtration varied in effectiveness (2 to 56 percent).

Based on the available literature, the following are not considered effective for the removal of perfluorooctanoic acid: conventional treatment (no removal) and UV at wavelengths outside of the 185-220 nm range (4 percent to 10 percent removal). UV/hydrogen peroxide treatment (35 percent removal) was less effective in comparison to UV alone (45 percent) after 24 hours of irradiation.

Studies were identified evaluating the following treatment technologies for the removal of perfluorooctanoic acid:

Adsorptive Media - A bench-scale study conducted batch tests of adsorption using magnetic nanoparticles with different polymer coatings. The best performing of these achieved greater than 99 percent removal in ultrapure water, but removal was reduced substantially i...

Aeration and Air Stripping - At a full-scale site, packed tower aeration was not effective for removing PFOA [2441].

Biological Filtration - A full-scale study [2175] of a plant treating reclaimed domestic wastewater found biological filtration to be ineffective for removing PFOA.

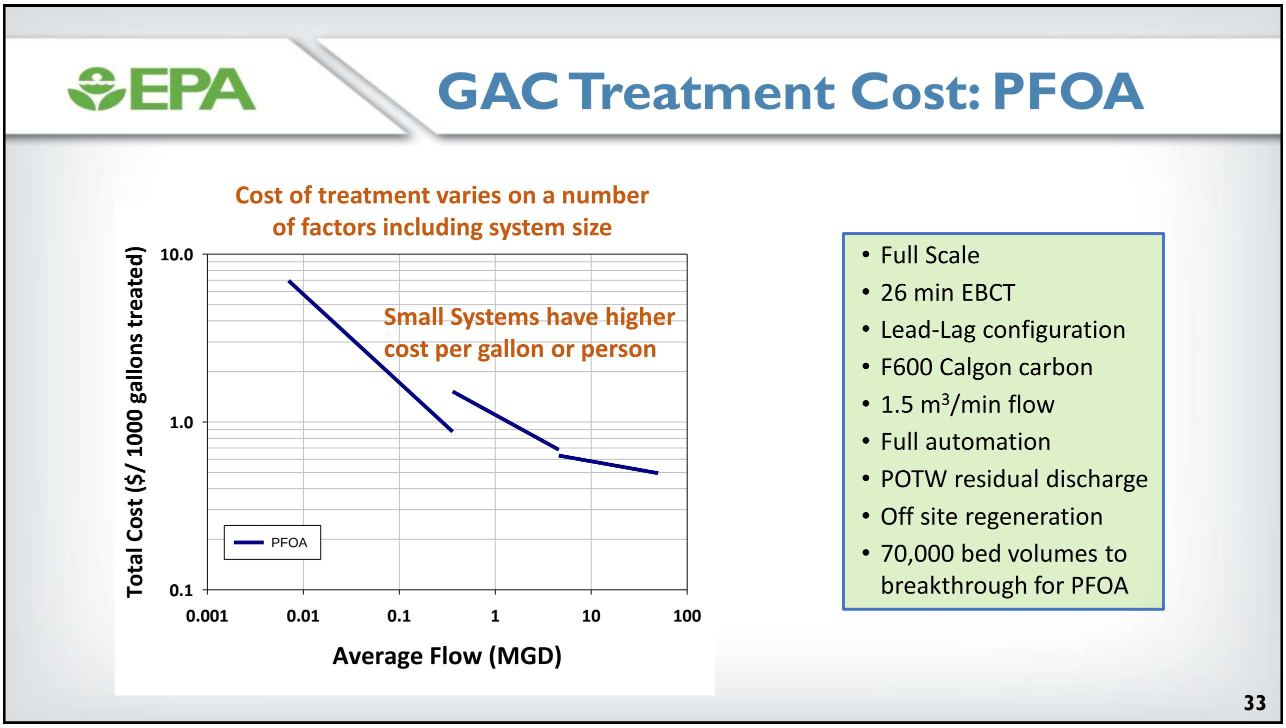
Biological Treatment - Removal of PFOA from water using biological treatment was found to be ineffective. One bench-scale study [2161] reported removal of 0 to 8 percent using supernatant from a domestic wastewater activated sludge process as a microbial sourc...

Chemical Treatment - One lab study observed >90% removal of PFOA via oxidation by persulfate in hot (85 degrees C) water after 30 hours reaction time. Removal in cooler water (25 degrees C) was negligible. The presence of iron reduced PFOA oxidation somewhat. Degra...

Chlorine - Chlorination was ineffective for removing PFOA at two full-scale sites [2441,2509].

Chlorine Dioxide - Chlorine dioxide was ineffective for removing PFOA at a full-scale site [2441].

Conventional Treatment - Bench scale studies [2536, 2548, 2553] were able to achieve moderate removals (up to 58 percent) of perfluorooctanoic acid (PFOA) by coagulation, but only by using high coagulant dosage and/or low pH. Removals at lower doses and neutral pH we...

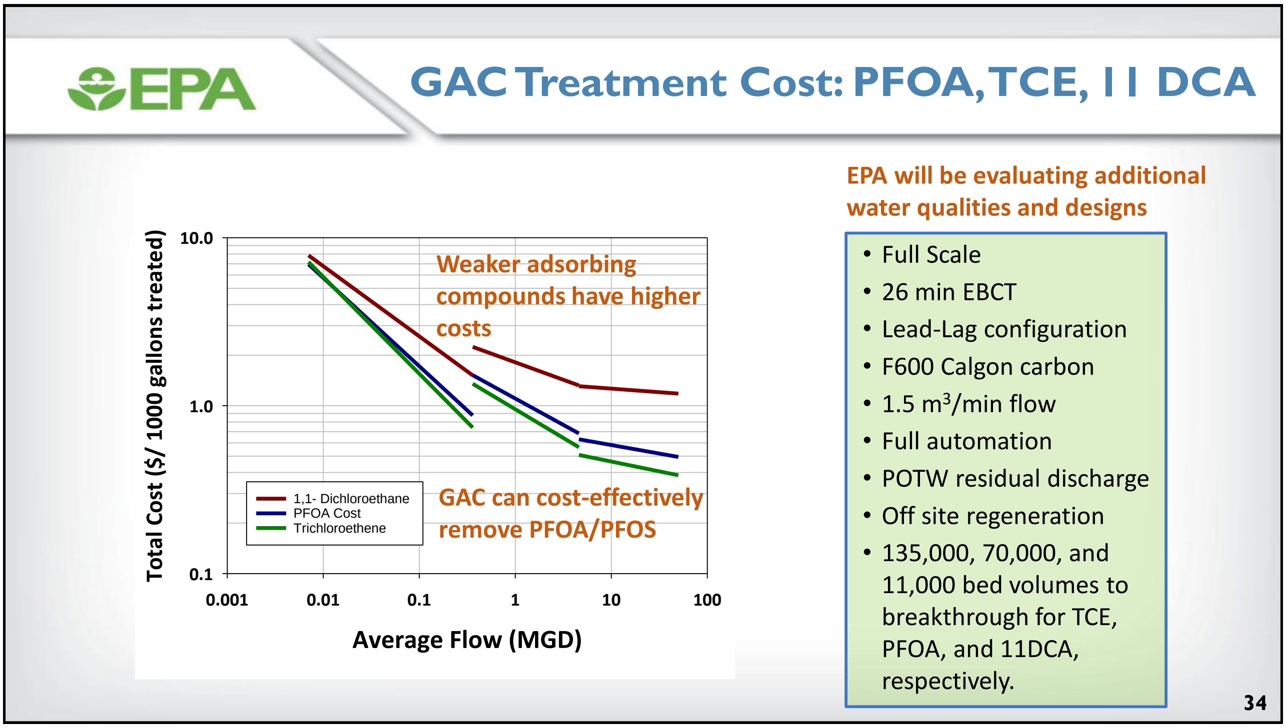


GAC Treatment Cost: PFOA

Cost of treatment varies on a number of factors including system size

Small Systems have higher cost per gallon or person

- Full Scale
- 26 min EBCT
- Lead-Lag configuration
- F600 Calgon carbon
- 1.5 m^3/min flow
- Full automation
- POTW residual discharge
- Off site regeneration
- 70,000 bed volumes to breakthrough for PFOA



GAC Treatment Cost: PFOA, TCE, 11 DCA

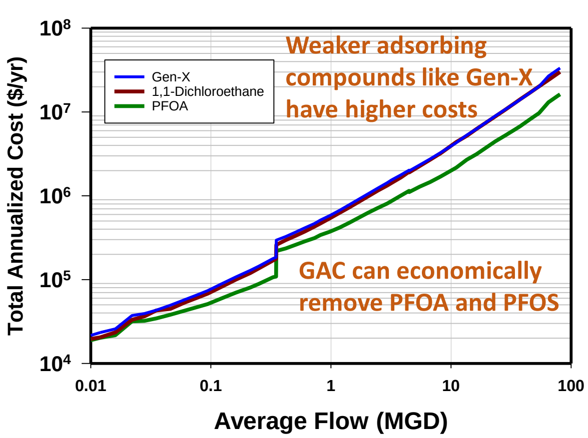
EPA will be evaluating additional water qualities and designs

Weaker adsorbing compounds have higher costs

GAC can cost-effectively remove PFOA/PFOS

- Full Scale
- 26 min EBCT
- Lead-Lag configuration
- F600 Calgon carbon
- 1.5 m^3/min flow
- Full automation
- POTW residual discharge
- Off site regeneration
- 135,000, 70,000, and 11,000 bed volumes to breakthrough for TCE, PFOA, and 11DCA, respectively.

Cost for Additional PFAS



Weaker adsorbing compounds like Gen-X have higher costs

GAC can economically remove PFOA and PFOS

- Pilot Scale Performance Data
- 20 min EBCT
- F400 Calgon carbon
- Full automation
- POTW residual discharge
- Off site regeneration
- 31,000, 7,100, and 5,560 bed volumes to breakthrough for PFOA, Gen-X, and 11-DCA, respectively.

EPA's Drinking Water Cost Models

- Adsorptive media
- **Anion exchange***
- Biological treatment*
- Cation exchange
- **GAC***
- Greensand filtration
- Microfiltration / ultrafiltration
- Multi-stage bubble aeration*

- Non-treatment
- Packed tower aeration
- **POU/POE#**
- **Reverse Osmosis / Nanofiltration**
- UV disinfection
- UV Advanced Oxidation

*** Search: EPA WBS** epa.gov/dwregdev/drinking-water-treatment-technology-unit-cost-models-and-overview-technologies

 # For POU/POE search: EPA small system compliance help
water.epa.gov/type/drink/pws/smallsystems/compliancehelp.cfm

Wastewater Treatment and Land Application of Biosolids/Wastes

- **Problem**: Lack of knowledge regarding end-of-life management of PFAS-containing consumer and industrial products in wastewater.
- **Action:**
  - Characterize wastewater and relate discharge streams (e.g. municipal and industrial wastewater, land applied waste streams).
  - Evaluate efficacy of existing management technologies to manage end-of-life disposal (e.g., land application of biosolids).
  - Evaluate performance and cost data to manage these waste streams and environmental PFAS releases.
- **Results**: Provide technologies, data, and tools to manage wastewater streams.
- **Impact**: Responsible officials will be able to manage PFAS-containing waste streams.

PFAS in Biosolids

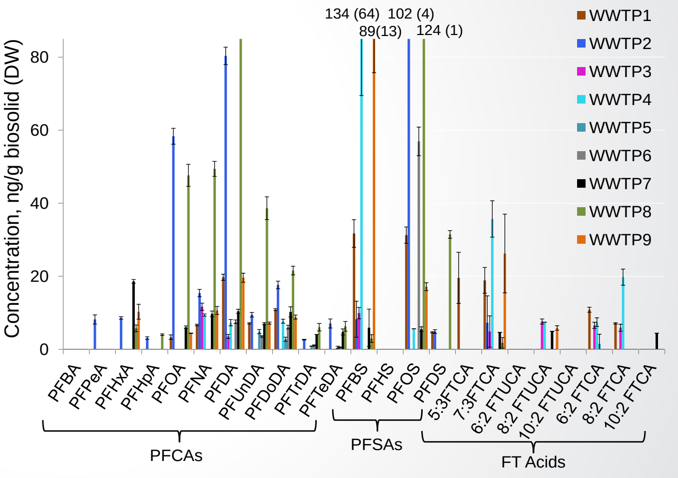
	PFOA (ng/g dry wt)	PFOS (ng/g dry wt)
Navarro, 2016	1 - 14	4 - 84
Sepulvado, 2011	8-68	80-219
Venkatesan, 2013	12-70	308-618
Washington et al, 2010, 2011	50-320	30-410
Mills, Dasu (in prep)	10-60	30-102

- Does not include other PFAS and precursors that can be degraded over time to more stable PFAAs.
- PFAAs end products do not degrade and do bioaccumulate.
- Many more PFAS compounds present and more being introduced.
- Lindstrom et al, 2011 found there may be a relationship between land applied biosolids and contamination in wells in Decatur, AL.

PFAS in wastewater residuals

In conjunction with Region 6

- **Action:** Nine wastewater treatment plants were sampled seasonally.
  - The solids treatment included anaerobic digestion and aerobic digestion.
  - Solid residuals and effluent were analyzed for PFAAs, precursors, and transformation products.
- **Results:** PFAS and PFAS precursors of varying distributions were found.



PFAAs concentrations in biosolids collected during Fall sampling

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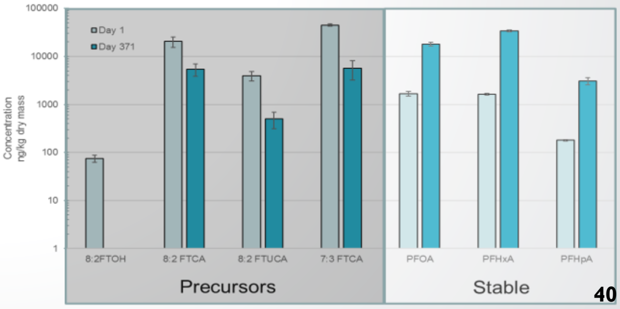
Land Application of Biosolids

Action: Evaluate application methods for liquid and solid biosolids and measure the natural attenuation for various analytes including PFAS.

Results

- Precursor concentrations were similar to PFAA concentrations.
- Precursor concentrations decreased with time.
- Stable PFAAs increased over 371 days commensurate to the expected metabolic pathways from precursor material.

PFAS Precursors in Biosolids Controls



Land Application of Biosolids: PFAS uptake into edible plants

In Conjunction with Region 5

Action: A variety of food crops were grown in soil amended with biosolids.

- The biosolids contained PFAAs.
- PFAA concentrations in edible portion of the plant were measured.

Results

- The edible portion had measurable levels of PFOA, among other PFAS.
- Further research needed to characterize uptake in more crops under varying conditions.
- Research needed to assess plant uptake as a route of human and ecological exposure.

- Blaine, et al (2013). ES&T 47(24): 14062-14069
- Blaine, et al (2014). ES&T 48(14): 7858-7865.

Incineration of PFAS

The strength of the C-F bonds require temperatures above 1,000 °C for >1 second.

- For example, CF_4 requires 1400 °C.
- Information is lacking in the literature and in practice.
- Its decomposition product, HF, is easily monitored.

Products of Incomplete Combustion (PICs) are more likely formed with F radicals than other halogens such as Cl

- Sufficient temperatures, times, and turbulence are necessary to ensure destruction.
- PIC data from incineration studies are lacking.
- The effect of mixed halogens in the waste stream introduces more unknowns.
- Measurement methods for PICs are under development at ORD.

Initiating collaborative projects with DoD and industry partners to evaluate existing technologies:

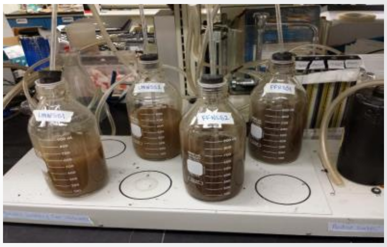
- Thermal treatment system for PFAS-contaminated soils in Alaska.
- GAC reactivation from PFAS treatment systems.

Future research: Wastewater Treatment

Problem: Wastewater Treatment Plants are a source of PFAS.

Action: Develop research to support

- more robust and expanded analytical methods,
- bioassays to better understand if treatments are effective and to identify risks;
- evaluation of WWTP conventional and advanced unit operations to manage PFAS;
- evaluation of air emissions from unit operations (e.g. activated sludge, biosolids drying, sewage sludge incineration;
- evaluations of biosolids treatment (e.g land application under wide range of soil types, biosolids, and management strategies; and
- Evaluations of pretreatment technologies to address "sources" to wastewater.

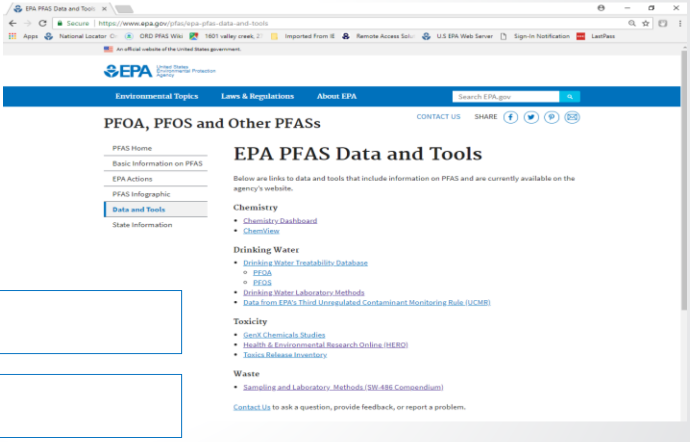


EPA PFAS Data and Tools

Links to data and tools that include information related to PFAS and are available on EPA's website:

epa.gov/pfas

epa.gov/pfas/epa-pfas-data-and-tools



PFOA, PFOS and Other PFASs

EPA PFAS Data and Tools

Below are links to data and tools that include information on PFAS and are currently available on the agency's website.

Chemistry

- Chemistry Dashboard
- ChemView

Drinking Water

- Drinking Water Treatability Database
  - PFOA
  - PFOS
- Drinking Water Laboratory Methods
- Data from EPA's Third Unregulated Contaminant Monitoring Rule (UCMR)

Toxicity

- GenX Chemicals Studies
- Health & Environmental Research Online (HERO)
- Toxics Release Inventory

Waste

- Sampling and Laboratory Methods (SW-486 Compendium)

Contact Us to ask a question, provide feedback, or report a problem.

Contacts for Questions or Comments

- Chris Impellitteri, Analytical Methods: Impellitteri.Christopher@epa.gov
- Michelle Latham, Communications: latham.michelle@epa.gov
- Jonathan Burkhardt, Cost Modeling/DW Treatment: burkhardt.jonathan@epa.gov
- Thomas Speth, Cost Modeling/DW Treatment: speth.thomas@epa.gov
- Marc Mills, Wastewater: mills.marc@epa.gov

EPA

Office of Research and Development

Questions?

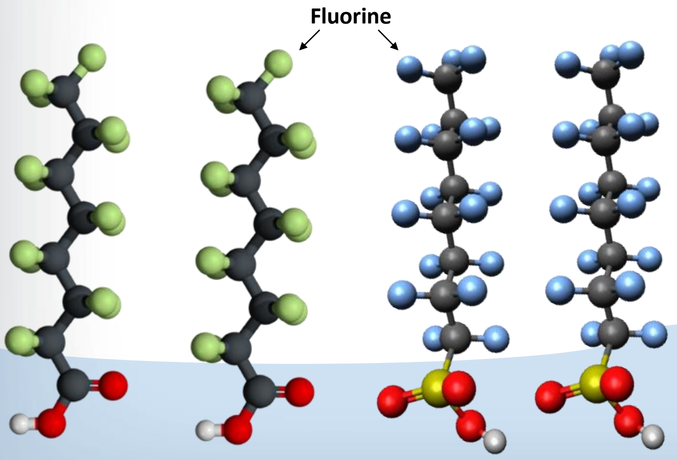
Dank je

Merci

Thank you

Additional Slides

Per- and Polyfluoroalkyl Substances (PFAS)



Perfluorooctanoic acid (PFOA) *Perfluorooctanesulfonic acid (PFOS)*

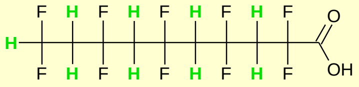
A class of chemicals

- Chains of carbon (C) atoms surrounded by fluorine (F) atoms.
  - ➢ Water-repellent (hydrophobic body)
  - ➢ Stable C-F bond
- Some PFAS include oxygen, hydrogen, sulfur and/or nitrogen atoms, creating a polar end.

Per- and Polyfluoroalkyl Substances (PFAS) Chemistry 101

Thousands of PFAS in production of industrial and consumer products.

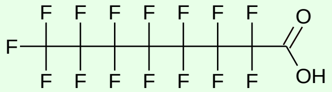
Poly fluorinated = many fluorines



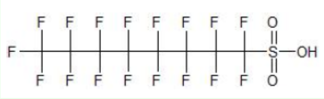
Polyfluorinated carboxylic acid from the production of polyvinylidene fluoride (PVDF) plastic

Newton et al., 2017. Novel polyfluorinated compounds identified downstream of manufacturing facilities near Decatur, AL using high resolution mass spectrometry

Per fluorinated = fully fluorinated



Perfluorooctanoic acid (PFOA ,C-8)



Perfluorooctanesulfonate (PFOS)

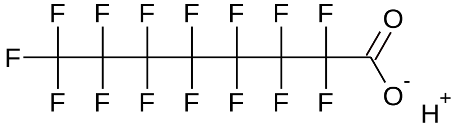
Very stable (C-F bond energy 485 kJ/mol)
(C-C 346, C-N 305, C-O 358, C-Cl 327 kJ/mol)

Chemical and Physical Properties

- Properties of PFAS range depending on carbon chain lengths and functional groups.
- PFAS generally occur as mixtures and are not well characterized.
- PFAS provide desirable performance because they repel both oil and water:
  - The fluorinated carbon tail is both lipophobic/oleophobic (repelled by fats and oils) and hydrophobic (repelled by water).
  - The functional group head can vary but is often hydrophilic (attracted to water).
- As a result of these unique surfactant properties and their stability, they are common surfactants and stain preventers.

Long-Chain PFAS

Long-chain = have longer carbon chain lengths and include perfluorinated carboxylic acids $\geq C_7$ and sulfonic acids $\geq C_6$.



Long-chain includes all salts and precursors that can degrade to $C_7 \geq$ carboxylic and $C_6 \geq$ sulfonic acid.

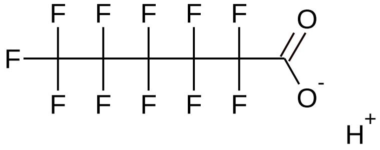
Long-chain compounds are a concern:

- They bioaccumulate, have long half lives in blood, and are thought to be more toxic
- But, less mobile compared to short chain PFAS.

PFOA human half life ($t_{½}$) = 3.8 years

Short-Chain PFAS

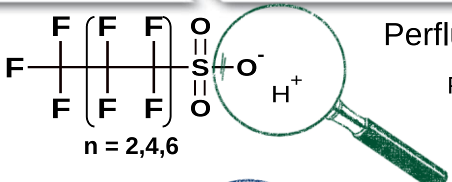
Short-chain = shorter carbon chain lengths and includes carboxylic acids $\leq C_6$ and sulfonic acids $\leq C_5$.



Short-chain compounds tend have shorter half-lives in blood, but they are more mobile and not easily removed during drinking water treatment.

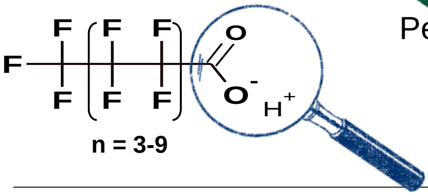
Perfluorohexanoic acid (PFHxA) human half life ($t_{½}$) = 32 days.

Common PFAS Structures



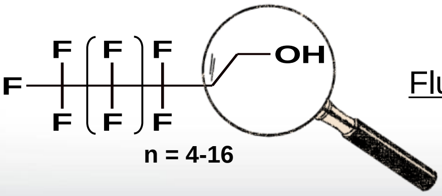
Perfluorosulfonic Acids

PFBS, PFHS, PFOS



Perfluorocarboxylic Acids

C_6 acid – C_{12} acid
PFOA C8 acid



Fluorotelomer Alcohols

6:2, 8:2 and 10:2

Anionic at environmental pH, water soluble

More volatile

Production of PFAS

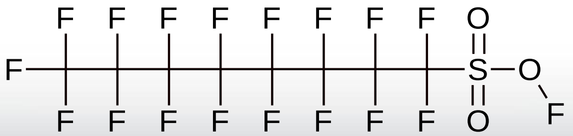
Electrochemical fluorination (ECF) method

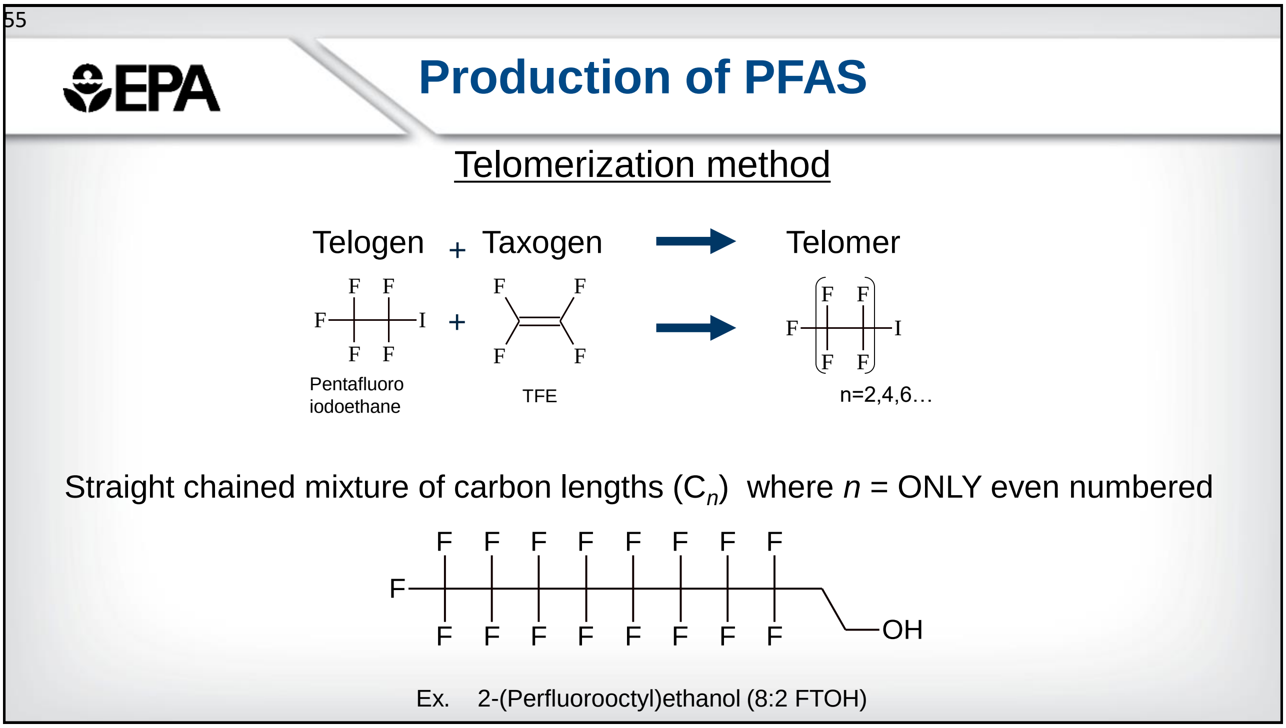
Alkanes $\xrightarrow{\text{HF + Electricity}}$ Perfluorinated Alkanes

Relatively crude process, inexpensive, yields branched isomers, distribution of chain lengths around target (e.g., C_8), but wide range of C_n (n = 2-12), even and odd numbered.

(Moody and Field, 2000, ES&T)

Ex. Perfluorooctane Sulfonyl Fluoride (POSF)


$CF_3(CF_2)_7SO_2F$



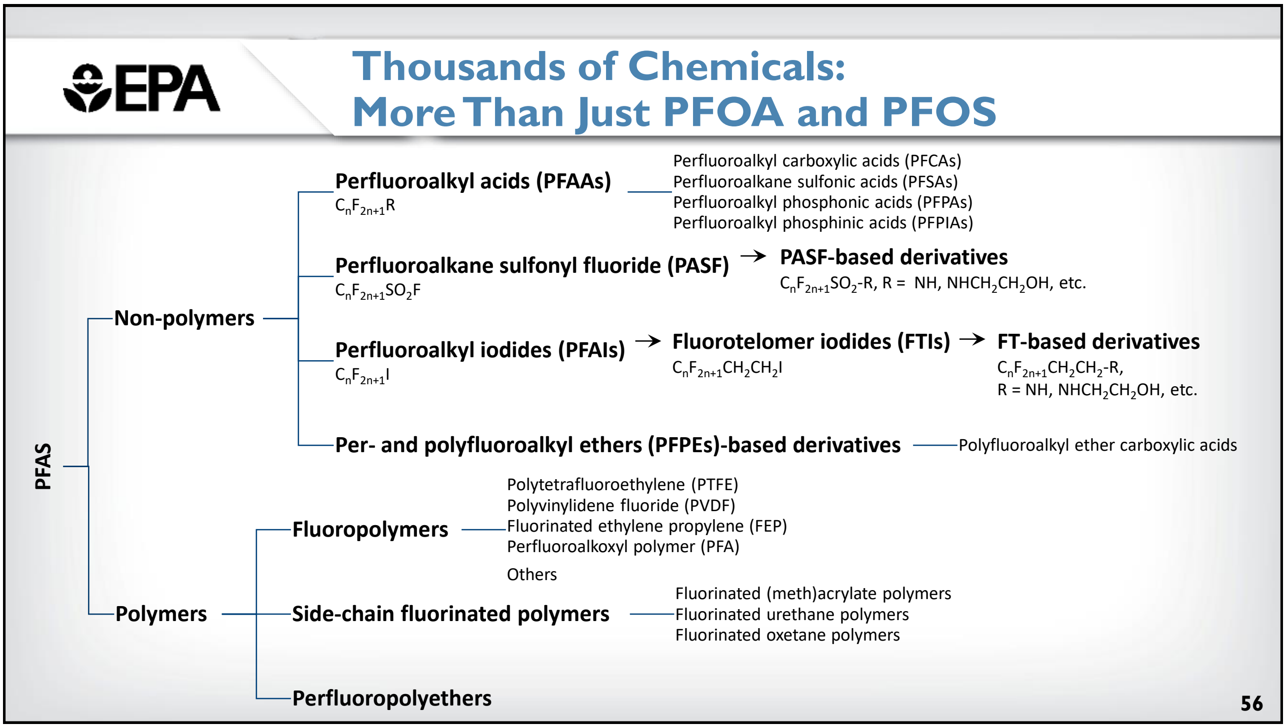
Production of PFAS

Telomerization method

Telogen + Taxogen → Telomer

Straight chained mixture of carbon lengths (C_n) where *n* = ONLY even numbered

Ex. 2-(Perfluorooctyl)ethanol (8:2 FTOH)



Thousands of Chemicals: More Than Just PFOA and PFOS

- PFAS
  - **Non-polymers**
    - **Perfluoroalkyl acids (PFAAs)** $C_nF_{2n+1}R$
      - Perfluoroalkyl carboxylic acids (PFCAs)
      - Perfluoroalkane sulfonic acids (PFSAs)
      - Perfluoroalkyl phosphonic acids (PFPAs)
      - Perfluoroalkyl phosphinic acids (PFPIAs)
    - **Perfluoroalkane sulfonyl fluoride (PASF)** $C_nF_{2n+1}SO_2F$ → **PASF-based derivatives** $C_nF_{2n+1}SO_2$-R, R = NH, $NHCH_2CH_2OH$, etc.
    - **Perfluoroalkyl iodides (PFAIs)** $C_nF_{2n+1}I$ → **Fluorotelomer iodides (FTIs)** $C_nF_{2n+1}CH_2CH_2I$ → **FT-based derivatives** $C_nF_{2n+1}CH_2CH_2$-R, R = NH, $NHCH_2CH_2OH$, etc.
    - **Per- and polyfluoroalkyl ethers (PFPEs)-based derivatives**
      - Polyfluoroalkyl ether carboxylic acids
  - **Polymers**
    - **Fluoropolymers**
      - Polytetrafluoroethylene (PTFE)
      - Polyvinylidene fluoride (PVDF)
      - Fluorinated ethylene propylene (FEP)
      - Perfluoroalkoxyl polymer (PFA)
      - Others
    - **Side-chain fluorinated polymers**
      - Fluorinated (meth)acrylate polymers
      - Fluorinated urethane polymers
      - Fluorinated oxetane polymers
    - **Perfluoropolyethers**

Environmental Issues

Environmental contamination/human exposure

- Chemical class includes thousands of different chemicals
- Highly persistent (doesn't breakdown in the environment)
- Released during production and industrial application
  - Emissions to air
  - Discharges to water
  - Widespread contamination
- Consumer product use: food packaging, stain resistant materials, non-stick cookware and firefighting foam
- Conventional drinking water (DW) treatment ineffective (Rahman et al., 2014)
- Lack validated methods for measurement of most new-generation PFAS

Human health effects for PFOA and PFOS well established based on human epidemiology and animal studies

- Low infant birth weights, effects on the immune system, liver effects, increased cholesterol levels, cancer and thyroid hormone disruption
- Largely unknown for other PFAS

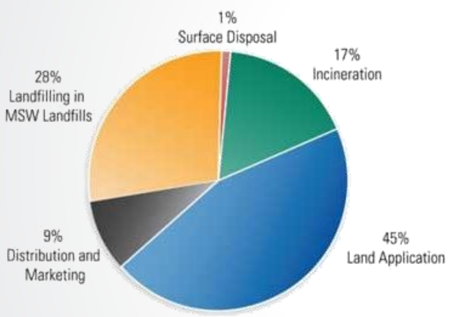
An Environmental Health Challenge

Many states are dealing with PFAS issues; some communities working to respond and asking for assistance.

Find out more: epa.gov/fedfac/technical-fact-sheet-perfluorooctane-sulfonate-pfos-and-perfluorooctanoic-acid-pfoa-0.

Overview of Management of Biosolids

U.S. Biosolids Management Practices



"Biosolids Management: Options, Opportunities & Challenges", NACWA

~55 % of residuals are land applied
~30% Landfilled
~15 % Incinerated @ low temp

Year	Dry tons generated	% Beneficial Use	Dry tons used	Acres covered
1976	3,970,000	25	992,500	330,833
1984	6,500,000	25	1,625,000	541,667
1988	5,328,429	36	1,918,234	639,411
1993	5,357,200	44	2,357,168	785,723
1998	6,900,000	60	4,140,000	1,380,000
2004	7,188,070	55	3,953,439	1,317,813
2010	7,188,070	55	3,953,439	1,317,813

- Sewage sludges applied pre-Regs (80s)
- Many fields have 20+ years of biosolids land application
- **Other wastes are also land applied – pulp/paper sludge, CAFO wastes, refinery/industrial wastes, DW residuals, etc.**

Additional Data Needs: Validating Inputs

- Influent concentrations:
  - PFASs (both removal targets and other PFASs)
  - Other competing contaminants (sulfate, nitrate)
  - Influent water characteristics (TOC)
- Study scale (RSSCT, pilot, full-scale)
- Type of GAC/resin tested
- Definition of breakthrough associated with a given bed life value. For example, does "breakthrough" mean:
  - Initial detection (and at what detection limit)
  - A specified target PFAS concentration (e.g., 70 ppt)
  - Percent breakthrough (e.g., 10% breakthrough/90% removal)
- Raw data (concentration vs time/bed volumes) are useful

Additional Data Needs: Validating Cost Outputs

- As-built costs:
  - Installed equipment cost
  - System engineering and other indirect cost
  - Annual operating cost
- The more detail, the better:
  - Detailed breakdown of cost by line item
  - Total cost with list of categories included, for example:
    - "Equipment includes vessels, piping, valves, instrumentation, concrete pad, buildings"
    - "Indirect includes engineering, permitting, pilot testing, site work, mobilization"
    - "Operating cost includes media replacement, labor, electricity"
  - Total only
- Associated flow rates, vessel sizes, materials of construction for major components (e.g., stainless steel, fiberglass)

EPA Actively Partnering with Federal, State, Tribes, and Communities

DoD

- EPA serves on their technical advisory group that oversees PFAS research.
- DoD and EPA developing analytical methods for evaluating PFAS exposure and site characterization.
- Partnering with industry to evaluate thermal treatment systems for managing contaminated soils and reactivation of GAC.
- EPA cost and performance models are being adapted with DoD for site remediation and cleanup.
- Evaluating treatment technologies for site remediation and managing emergency response waste streams .

USDA and FDA

- Initiated cross agency workgroups to focus on analytical methods, charactering exposure, and treatment/remediation.

DOE

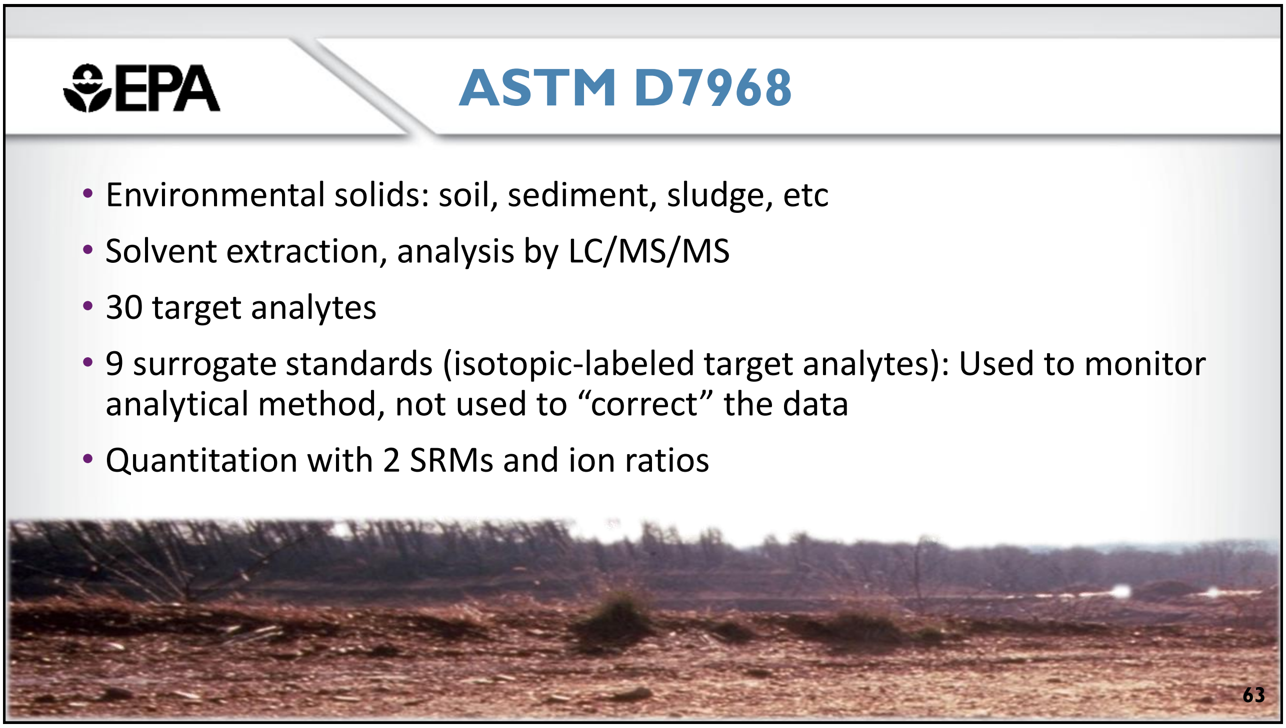
- Joint project with academia to evaluate E-beam treatment of PFAS in water.

States/Tribes/Communities

- Stack sampling of emissions from manufacturing facilities.
- State workgroups to assess drinking water and contaminated sites.

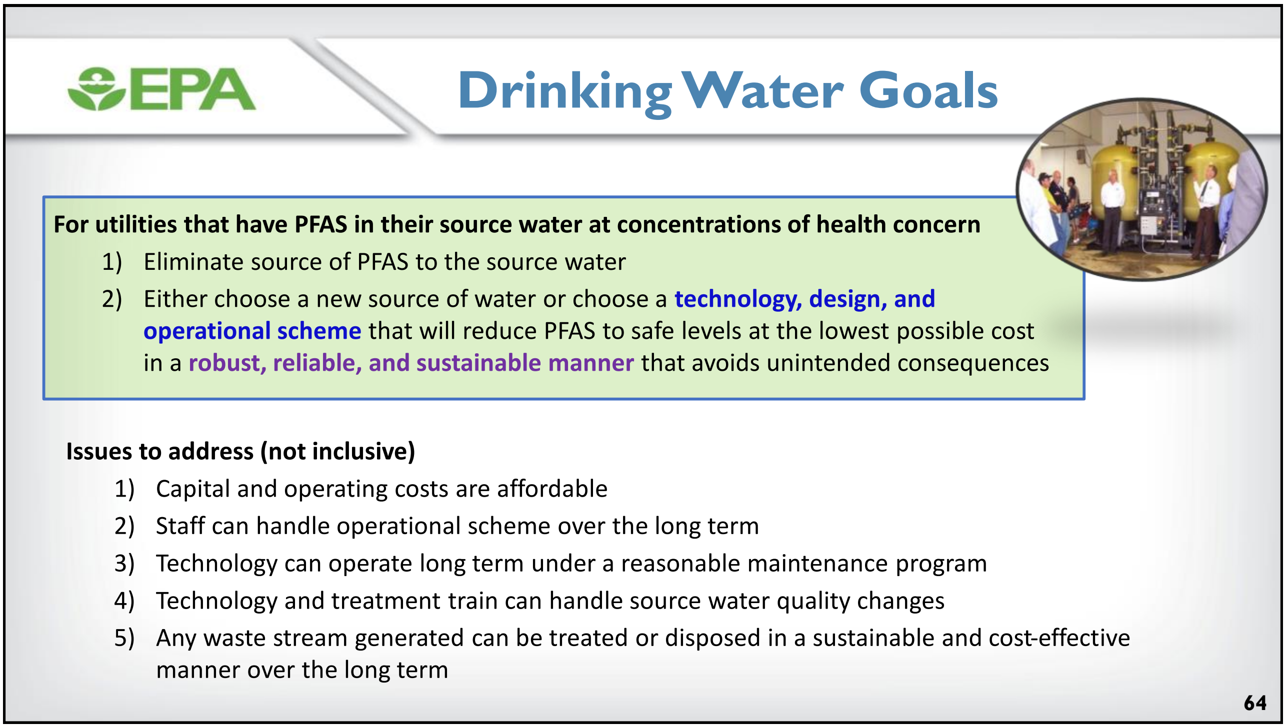
Drinking Water Method 533

Draft Method 533	Both Methods	Method 537.1
1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (8:2 FTS)	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)	N-ethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA)
1H, 1H, 2H, 2H- perfluorohexane sulfonic acid (4:2 FTS)	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS)	N-methyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA)
1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (6:2 FTS)	4,8-dioxa-3H-perfluorononanoic acid (ADONA)[3]	Perfluorotetradecanoic acid (PFTA)
Nonafluoro-3,6-dioxaheptanoic acid (NFDHA)	Hexafluoropropylene oxide dimer acid (HFPO-DA)	Perfluorotridecanoic acid (PFTrDA)
Perfluoro (2-ethoxyethane) sulfonic acid (PFEESA)	Perfluorodecanoic acid (PFDA)	
Perfluoro-3-methoxypropanoic acid (PFMPA)	Perfluorododecanoic acid (PFDoA)	
Perfluoro-4-methoxybutanoic acid (PFMBA)	Perfluorohexanoic acid (PFHxA)	
Perfluorobutanoic acid (PFBA)	Perfluoroundecanoic acid (PFUnA)	
Perfluoroheptanesulfonic acid (PFHpS)	Perfluorobutanesulfonic acid (PFBS)	
Perfluoropentanesulfonic acid (PFPeS)	Perfluoroheptanoic acid (PFHpA)	
Perfluoropentanoic acid (PFPeA)	Perfluorohexanesulfonic acid (PFHxS)	
	Perfluorononanoic acid (PFNA)	
	Perfluorooctanoic acid (PFOA)	
	Perfluorooctanesulfonic acid (PFOS)	



ASTM D7968

- Environmental solids: soil, sediment, sludge, etc
- Solvent extraction, analysis by LC/MS/MS
- 30 target analytes
- 9 surrogate standards (isotopic-labeled target analytes): Used to monitor analytical method, not used to “correct” the data
- Quantitation with 2 SRMs and ion ratios



Drinking Water Goals

For utilities that have PFAS in their source water at concentrations of health concern

1) Eliminate source of PFAS to the source water
2) Either choose a new source of water or choose a **technology, design, and operational scheme** that will reduce PFAS to safe levels at the lowest possible cost in a **robust, reliable, and sustainable manner** that avoids unintended consequences

Issues to address (not inclusive)

1) Capital and operating costs are affordable
2) Staff can handle operational scheme over the long term
3) Technology can operate long term under a reasonable maintenance program
4) Technology and treatment train can handle source water quality changes
5) Any waste stream generated can be treated or disposed in a sustainable and cost-effective manner over the long term

Avoiding Unintended Consequences

Choice of technology, design, and operations can lead to…

1) Negative impacts on the performance of the rest of the **treatment system** for other parameters (e.g., decreased control of particulates/pathogens, taste & odor compounds, other source water contaminants)
2) Negative impacts on the **distribution system** (e.g., increased lead, copper, or iron corrosion; disinfection residual maintenance difficulties)

EPA is conducting research on optimizing PFAS treatment

II.5.4 PFAS pollution, from the artic to the equator. Integrated approaches on characterisation and remediation strategies

Ian T. Cousins
Stockholm University (Sweden), Department of Environmental Science

Understanding the sources, fate and transport of per- and polyfluoroalkyl substances (PFAS) has been the subject of extensive scientific effort since the early 2000s. Among the more than 4000 PFAS on the global market, the long-chain perfluoroalkyl acids (PFAAs) have been identified as global contaminants of concern. As a result of voluntary actions by industry, and regulation, the long-chain PFAAs have been largely phased-out from use in most parts of the world (Asia being the notable exception), although legacy contamination problems in these regions associated with long-chain PFAAs will keep scientists occupied for some years to come. In addition to the long-chain PFAAs and their precursors, there has also been increasing concern regarding the thousands of other PFAS in use. This concern is driven by the lack of knowledge of chemical structures, properties, uses, and toxicological profiles of these relatively poorly studied PFAS. In this keynote presentation, I will provide an overview of the state of the science of the sources, fate and transport of PFAS, and also briefly discuss promising remediation strategies.

For perfluoroalkyl carboxylates (PFCAs), the major historical emission source was from fluoropolymer (e.g. PTFE) manufacturing. The vast majority of PFCAs that have been historically emitted reside in the global oceans, where they will be slowly vertically transported to deeper waters. Precursor degradation had a relatively lower contribution to the global presence of PFCAs, but can still make an important contribution in remote regions. For perfluoroalkane sulfonates (PFSAs), several different sources, including precursor degradation, contributed to global emissions. Similar to PFCAs, the major global reservoir and sink for PFSAs is the global oceans. A complication in understanding global fate and transport of PFAAs is the possible role of seas spray aerosols in long-range transport.

In urban regions where wastewater is often discharged into rivers, it has been shown that PFAA levels in rivers can be correlated to population density and GDP in the river catchments, which are indicators of PFAS-containing consumer product use. Remote river catchments, inland lakes/seas and inland terrestrial environments, receive inputs of PFAAs predominantly from atmospheric deposition. All PFAAs in surface waters, groundwater and soils are ultimately discharged to the oceans, but residence times of PFAAs can be highly variable depending on, for example, extent of retention in the unsaturated zone and hydrological residence times.

Contamination hot spots are, for example, known to occur where aqueous film forming foams (AFFF) have been used for fire-fighting. Key to understanding how PFAAs are transported to groundwater, which is often a drinking water resource, is understanding the transport through the unsaturated zone. PFAA sorption to soils has been shown to be affected by multiple factors and is challenging to predict. A complication for understanding the transportation of PFAAs in the unsaturated zone is the recently reported (by Brusseau and colleagues) unique retention behaviour of PFAAs due to their strong surface activity.

Many remediation techniques (activated carbon, anionic exchange resin, chemical oxidation, etc.) have been developed for removing PFAS from contaminated waters and soils. Given that there are so many PFAS with multiple uses, a proactive “upstream” strategy for remediation of PFAS would be to phase out non-essential uses of PFAS as well as to substitute PFAS uses with safer alternatives. Some essential uses of PFAS may remain and for these use cases, emissions should be minimised.

Stockholm
University

PFAS pollution, from the artic to the equator.

Integrated approaches on characterisation and remediation strategies

Ian T. Cousins

Department of Environmental Science,
Stockholm University, Sweden

Stockholm
University

Outline

- Introduction to PFAS
- Aquatic Fate and Transport
- Atmospheric Fate and Transport
- Soil/Groundwater Fate and Transport
  - AFFF contaminated sites
- Concluding remarks

What are PFAS?

- **Perfluoroalkyl and polyfluoroalkyl substances**
- **Buck et al. (2011)** – a key milestone in understanding the PFAS universe, including terminologies of several major PFAS groups
  - **PFASs** = “the **highly fluorinated aliphatic substances** that contain **1 or more C atoms** on which all the H substituents … have been replaced by F atoms, in such a manner that they contain the perfluoroalkyl moiety **C_nF_{2n+1}–” (i.e. must contain at least CF_3–)**
- **OECD (in progress)**
  - “the **highly fluorinated ~~aliphatic~~ substances** that contain **1 or more C atoms** on which all the H substituents … have been replaced by F atoms, in such a manner that they contain ~~the~~ at least one aliphatic perfluoro~~alkyl~~carbon moiety, such as: ~~C_nF_{2n+1}–~~ –C_nF_{2n}–”

OECD 2018 Report

- In 2018, OECD published an updated PFAS List
  - → Over 4,000 CAS numbers identified
  - → **Many were not mentioned in Buck et al.**

OECD
Organisation for Economic Co-operation and Development

ENV/JM/MONO(2018)7

Unclassified English - Or. English

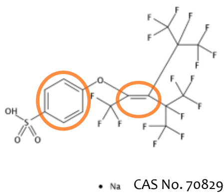
4 May 2018

ENVIRONMENT DIRECTORATE
JOINT MEETING OF THE CHEMICALS COMMITTEE AND THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY

TOWARD A NEW COMPREHENSIVE GLOBAL DATABASE OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs):

SUMMARY REPORT ON UPDATING THE OECD 2007 LIST OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs)

Series on Risk Management
No. 39



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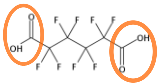

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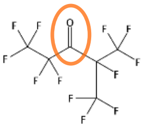

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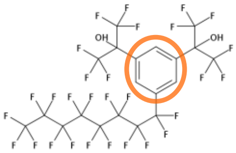

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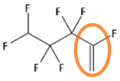

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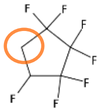
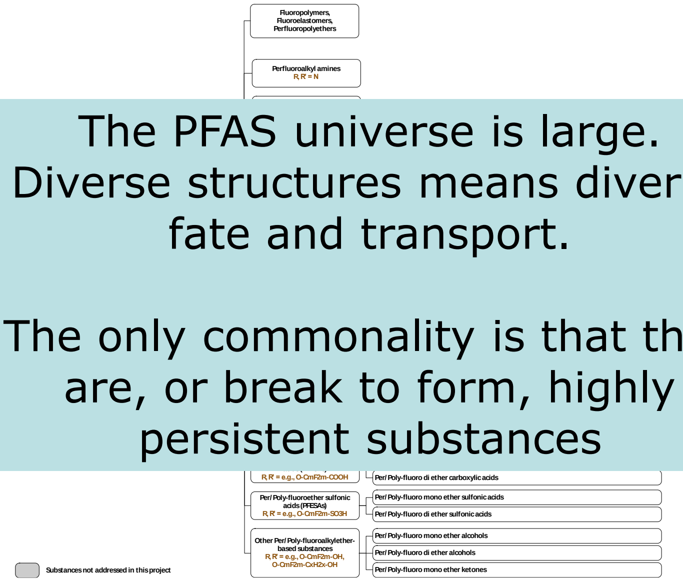


CAS No. 15290-77-4

PFAS Universe – work in progress



The PFAS universe is large. Diverse structures means diverse fate and transport.

The only commonality is that they are, or break to form, highly persistent substances

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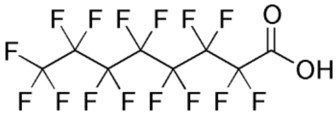
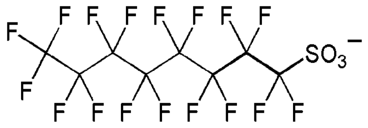
PFCAs and PFSAs – the focus of most research and this presentation



Perfluorooctanoic acid - PFOA



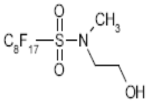
Perfluorooctane sulfonate - PFOS

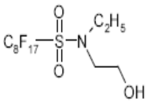
Strong surfactants with unique properties = novel environmental chemistry

They come in a range of chain lengths.

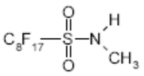
“Long-chain” PFCAs and PFSAs are persistent, bioaccumulative and toxic

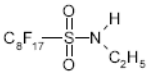
“Precursors”


Methyl FOS Alcohol

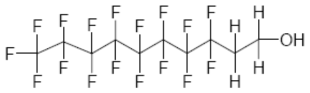

Ethyl FOS Alcohol

Perfluoroalkyl sulfonamido ethanols


Methyl FOS Amide


Ethyl FOS Amide

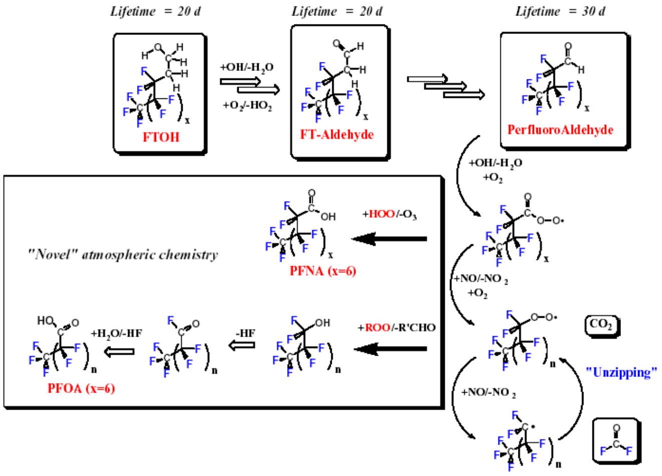
Perfluoroalkyl sulfonamides


8:2 FTOH

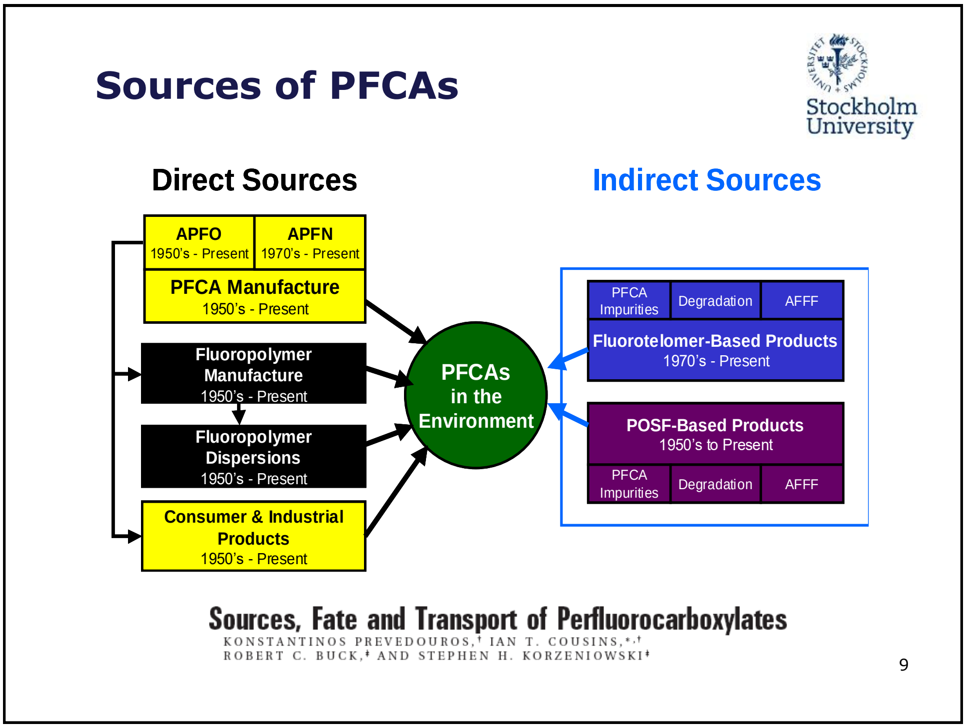
Fluorotelomer alcohols

“Precursors”

Overall Atmospheric Chemistry of FTOHs



Taken from Scott Mabury’s Fluoros presentation, Toronto, 2005



Sources of PFCAs

Direct Sources

APFO
1950's - Present

APFN
1970's - Present

PFCA Manufacture
1950's - Present

Fluoropolymer Manufacture
1950's - Present

Fluoropolymer Dispersions
1950's - Present

Consumer & Industrial Products
1950's - Present

PFCAs in the Environment

Indirect Sources

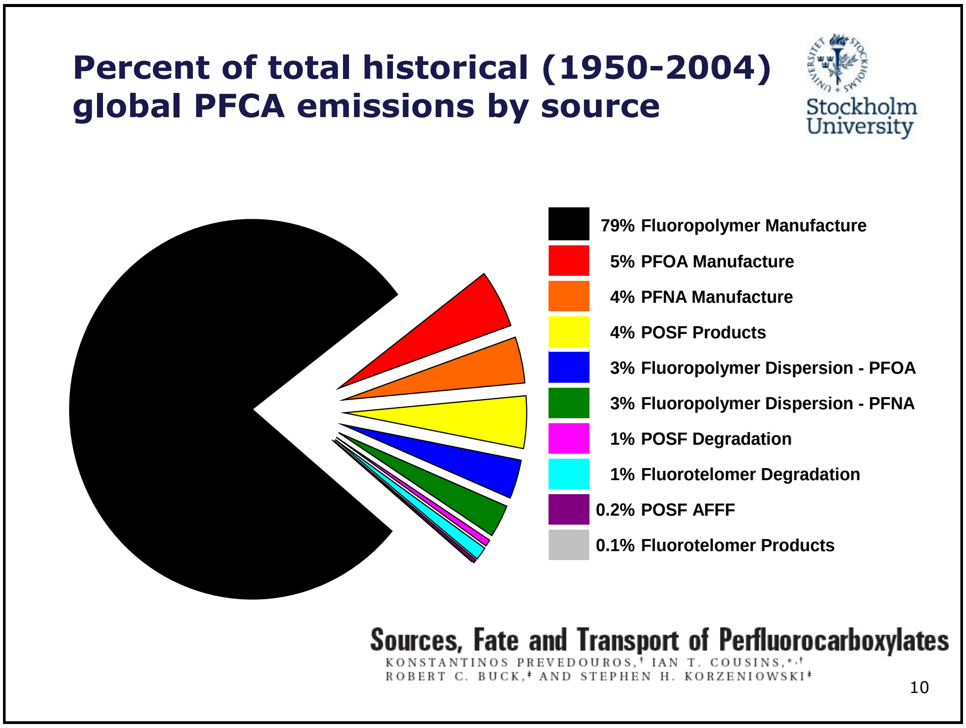
PFCA Impurities
Degradation
AFFF

Fluorotelomer-Based Products
1970's - Present

POSF-Based Products
1950's to Present

PFCA Impurities
Degradation
AFFF

Sources, Fate and Transport of Perfluorocarboxylates
KONSTANTINOS PREVEDOUROS,† IAN T. COUSINS,*,† ROBERT C. BUCK,‡ AND STEPHEN H. KORZENIOWSKI‡

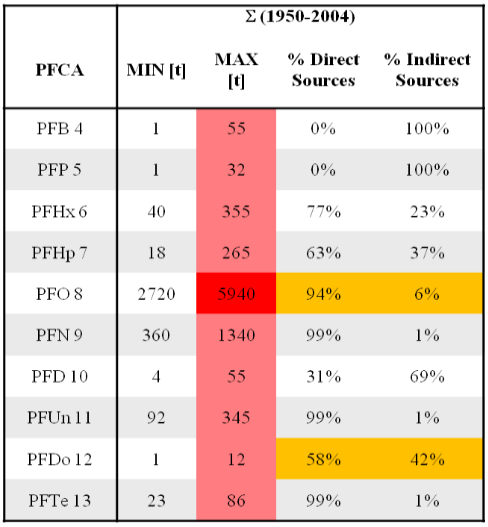


Percent of total historical (1950-2004) global PFCA emissions by source

- ■ 79% Fluoropolymer Manufacture
- ■ 5% PFOA Manufacture
- ■ 4% PFNA Manufacture
- ■ 4% POSF Products
- ■ 3% Fluoropolymer Dispersion - PFOA
- ■ 3% Fluoropolymer Dispersion - PFNA
- ■ 1% POSF Degradation
- ■ 1% Fluorotelomer Degradation
- ■ 0.2% POSF AFFF
- ■ 0.1% Fluorotelomer Products

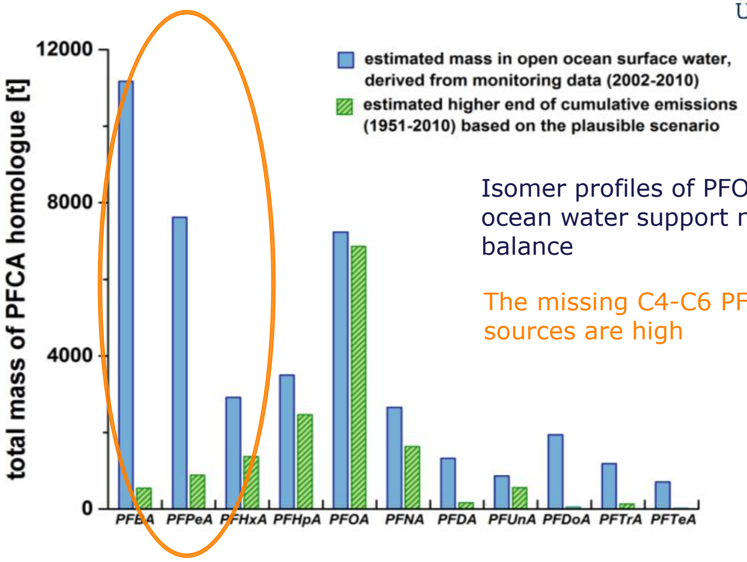
Sources, Fate and Transport of Perfluorocarboxylates
KONSTANTINOS PREVEDOUROS,† IAN T. COUSINS,*,† ROBERT C. BUCK,‡ AND STEPHEN H. KORZENIOWSKI‡

Estimated PFCA emissions by carbon chain length



PFCA	Σ (1950-2004)			
	MIN [t]	MAX [t]	% Direct Sources	% Indirect Sources
PFB 4	1	55	0%	100%
PFP 5	1	32	0%	100%
PFHx 6	40	355	77%	23%
PFHp 7	18	265	63%	37%
PFO 8	2720	5940	94%	6%
PFN 9	360	1340	99%	1%
PFD 10	4	55	31%	69%
PFUn 11	92	345	99%	1%
PFDo 12	1	12	58%	42%
PFTe 13	23	86	99%	1%

Comparison of global emissions to ocean inventory

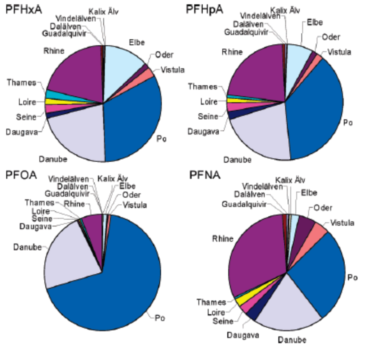


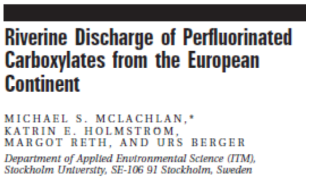
Isomer profiles of PFOA in ocean water support mass balance

The missing C4-C6 PFCAs sources are high

Wang et al. (2014)

Regional/continental scale: riverine discharge of PFCAs in Europe





Riverine Discharge of Perfluorinated Carboxylates from the European Continent

MICHAEL S. MCLACHLAN,*
KATRIN E. HOLMSTROM,
MARGOT RETH, AND URS BERGER
Department of Applied Environmental Science (ITM), Stockholm University, SE-106 91 Stockholm, Sweden

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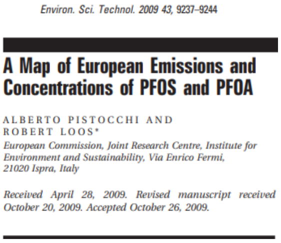
Away from manufacturing point sources, PFOS and PFOA river concentrations correlate with population density and GDP



Environ. Sci. Technol. 2009 43, 9237–9244

A Map of European Emissions and Concentrations of PFOS and PFOA

ALBERTO PISTOCCHI AND
ROBERT LOOS*
European Commission, Joint Research Centre, Institute for Environment and Sustainability, Via Enrico Fermi, 21020 Ispra, Italy

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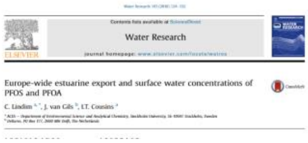

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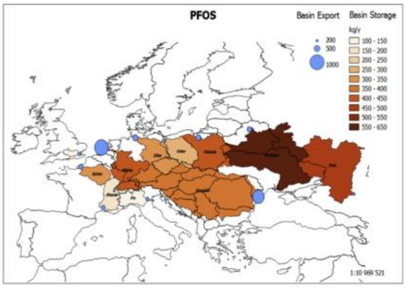
Europe-wide estuarine export and surface water concentrations of PFOS and PFOA

C. Lindim a,*, J. van Gils b, I.T. Cousins a



Regional scale: Baltic mass balance

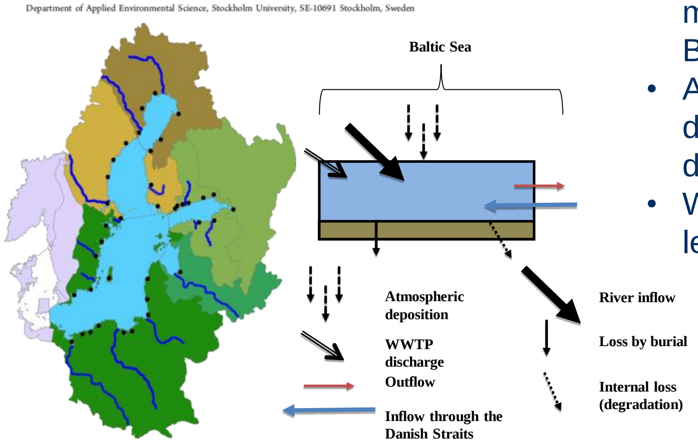
Stockholm University

Environmental Science & Technology

Mass Balance of Perfluoroalkyl Acids in the Baltic Sea

Marko Filipovic, Urs Berger, and Michael S. McLachlan*

Department of Applied Environmental Science, Stockholm University, SE-10691 Stockholm, Sweden



- No known manufacturers in Bactic region
- Atmospheric deposition dominant source
- WWTPs relatively less important

Conclusions 1: sources and fate of PFCAs and PFSAs in the aquatic environment

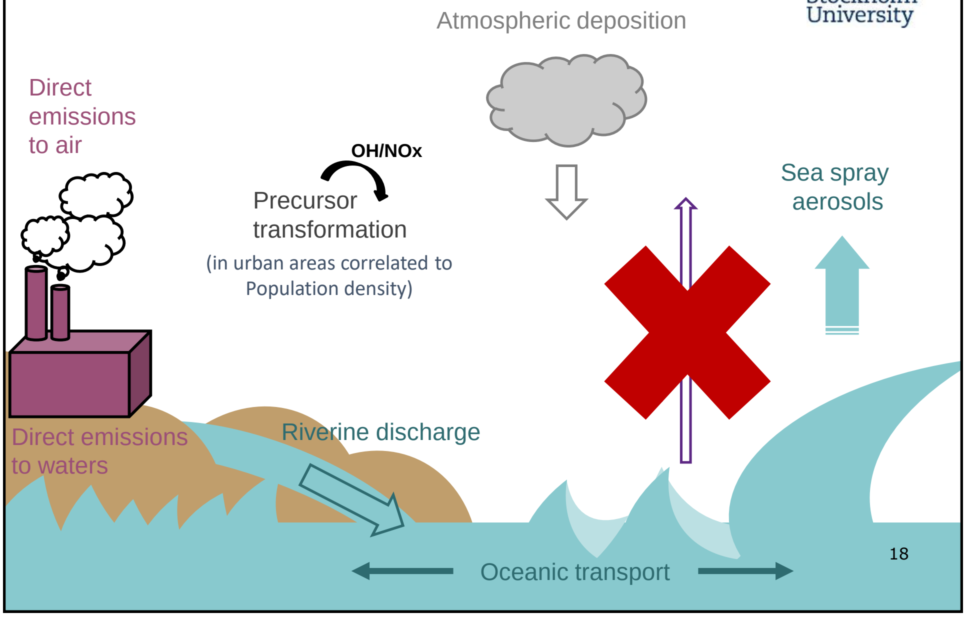
Stockholm University

- Fluoropolymer manufacturing main global historical emission source for PFCAs.
- For PFSAs, the main global historical emissions were from manufacture and use of PFSA-containing products.
- Precursors made a minor contribution
  - But can make important contributions to levels in some environments
- Global emissions of PFCAs and PFSAs substantially declined
  - But everything still in the environment. The oceans are the ultimate sink.

Conclusions 2: sources and fate of PFCAs and PFSAs in the aquatic environment

- In “urban” rivers WWTPs dominate emissions of PFCAs and PFSAs
  - Emissions can be estimated from population and GDP
- For background lakes, rivers, inland seas, atmospheric deposition dominates
  - precursors or other sources?
- Arctic, depends where you look…
  - Arctic and Arctic Ocean as whole: ocean water transport dominant (Wania et al., 2006)
  - Inland Arctic: precursor transport/degradation?

Atmospheric fate & transport processes



Atmospheric deposition

Direct emissions to air

OH/NOx

Precursor transformation

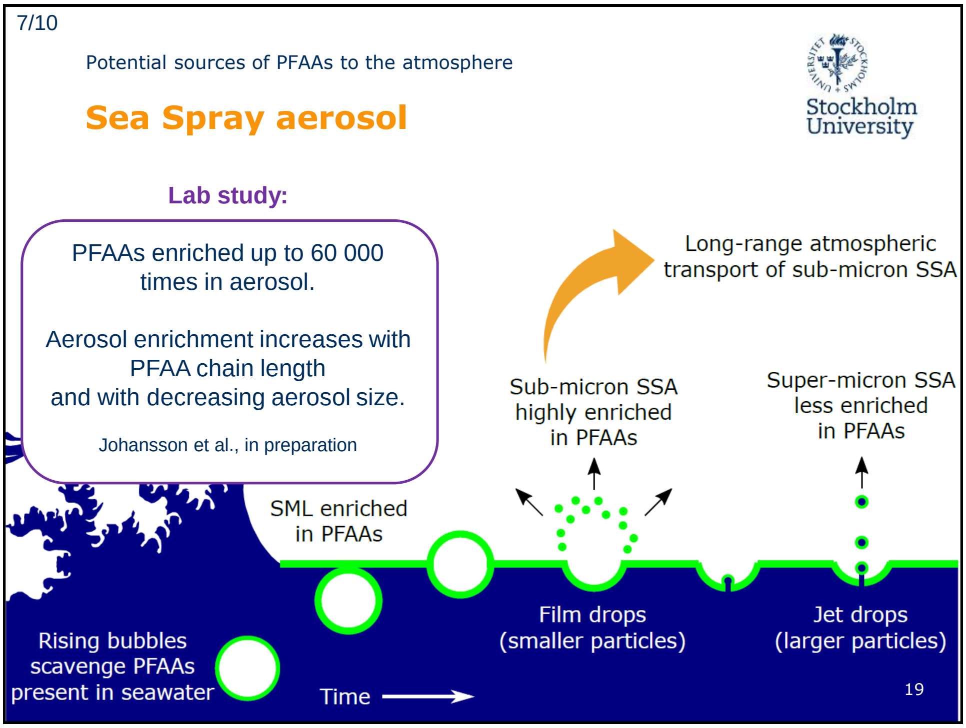
(in urban areas correlated to Population density)

Sea spray aerosols

Direct emissions to waters

Riverine discharge

Oceanic transport



Potential sources of PFAAs to the atmosphere

Sea Spray aerosol

Stockholm University

Lab study:

PFAAs enriched up to 60 000 times in aerosol.

Aerosol enrichment increases with PFAA chain length and with decreasing aerosol size.

Johansson et al., in preparation

Long-range atmospheric transport of sub-micron SSA

Sub-micron SSA highly enriched in PFAAs

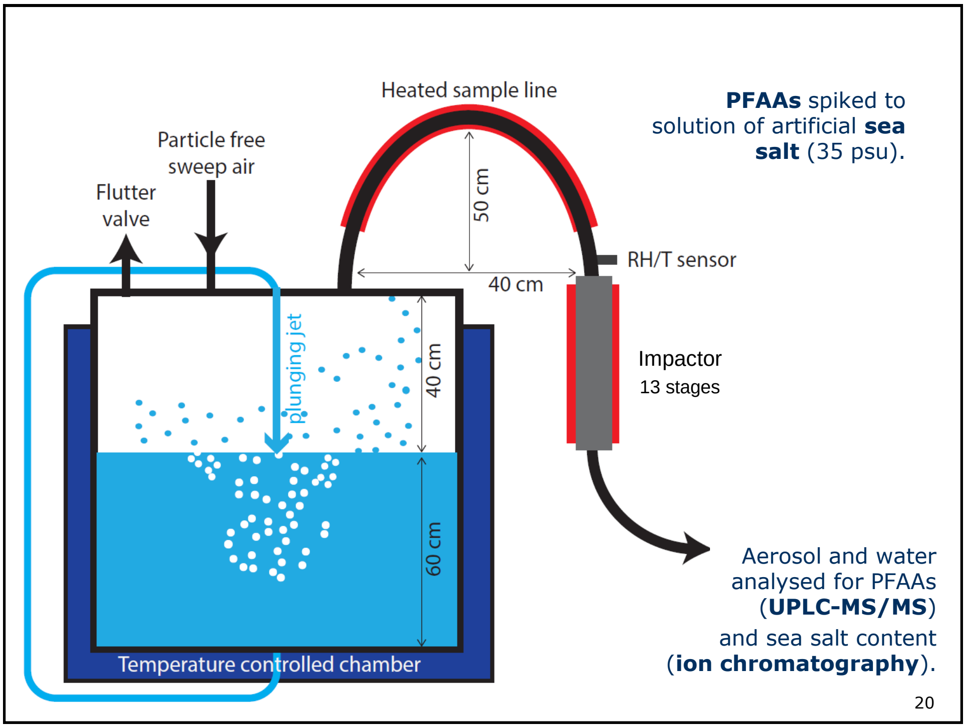
Super-micron SSA less enriched in PFAAs

SML enriched in PFAAs

Film drops (smaller particles)

Jet drops (larger particles)

Rising bubbles scavenge PFAAs present in seawater

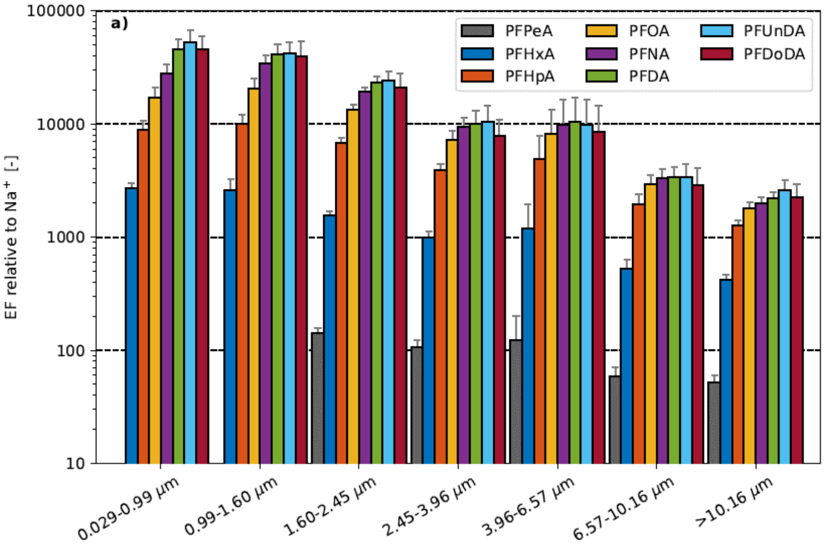


PFAAs spiked to solution of artificial **sea salt** (35 psu).

Aerosol and water analysed for PFAAs (**UPLC-MS/MS**) and sea salt content (**ion chromatography**).

Measured aerosol enrichment factors

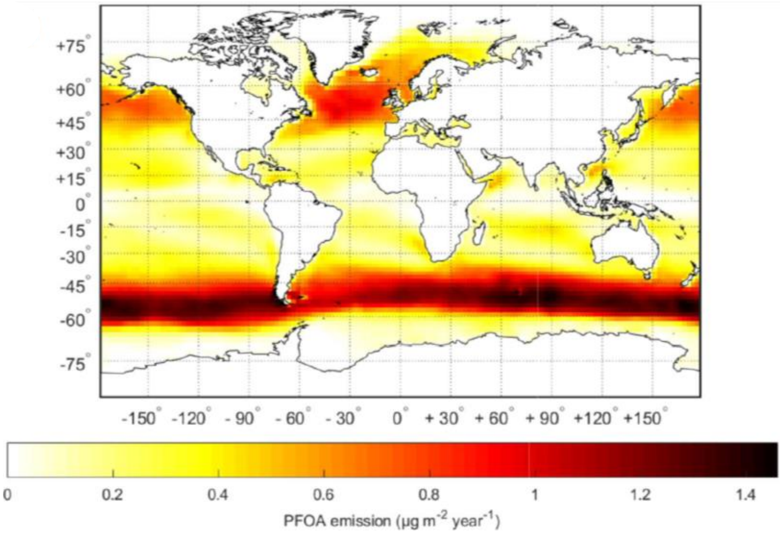
Normalised to mass of sea salt tracer Na+



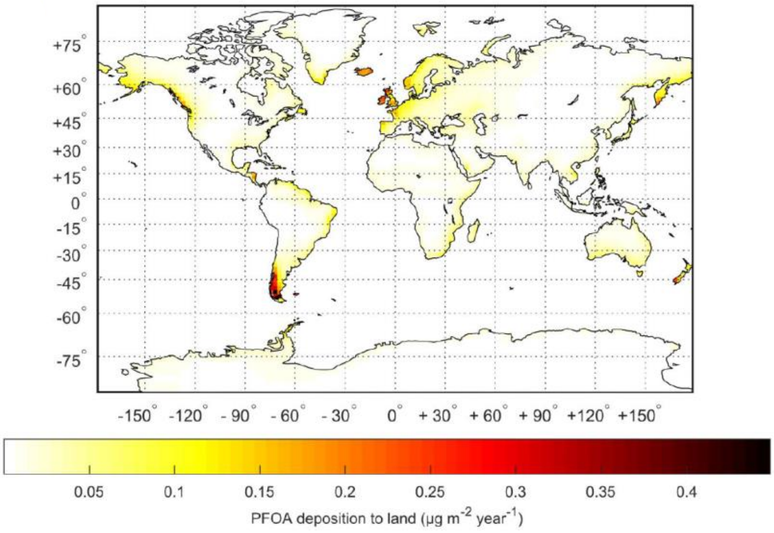
Weeks Days Hours

Atmospheric residence time

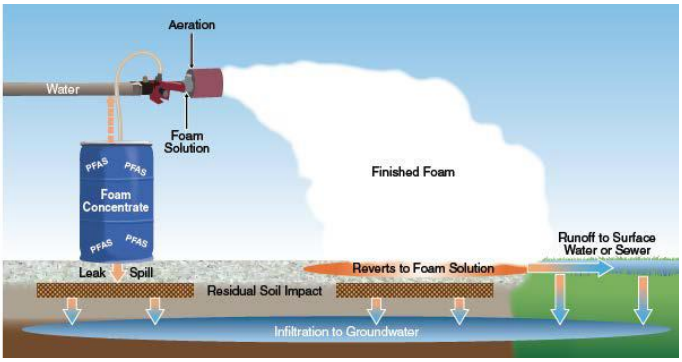
Modelled annual ocean-to-air flux



Modelled deposition to land

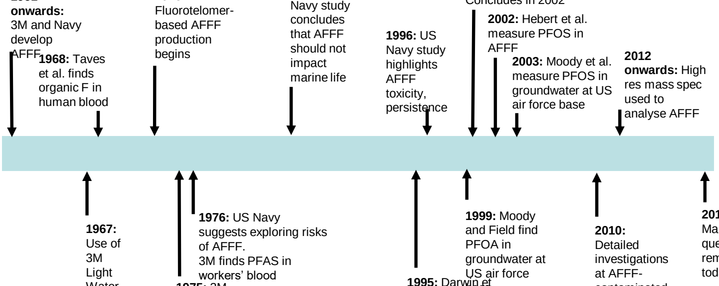


Fate & Transport of PFAS in soil & groundwater



Hunter Anderson, SETAC NA Focused Topic Meeting, Durham, NC, 2019

A short history of AFFF



1961 onwards: 3M and Navy develop AFFF

1967: Use of 3M Light Water begins

1968: Taves et al. finds organic F in human blood

1973: Fluorotelomer-based AFFF production begins

1975: 3M scientists informed of PFAS (PFOA?) in human blood. Work published soon after in Taves et al. (1976)

1976: US Navy suggests exploring risks of AFFF. 3M finds PFAS in workers' blood

1985: US Navy study concludes that AFFF should not impact marine life

1995: Darwin et al. highlight environmental concerns of AFFF

1996: US Navy study highlights AFFF toxicity, persistence

1999: Moody and Field find PFOA in groundwater at US air force base

2000: 3M phase out of C6, C8 and C10 chemistries. Concludes in 2002

2002: Hebert et al. measure PFOS in AFFF

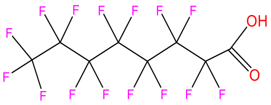
2003: Moody et al. measure PFOS in groundwater at US air force base

2010: Detailed investigations at AFFF-contaminated sites begin worldwide

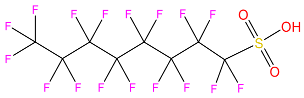
2012 onwards: High res mass spec used to analyse AFFF

2019: Many questions remain today

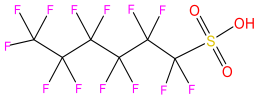
PFOS, PFHxS and PFOA – receive the most focus



Perfluorooctanoic acid - PFOA

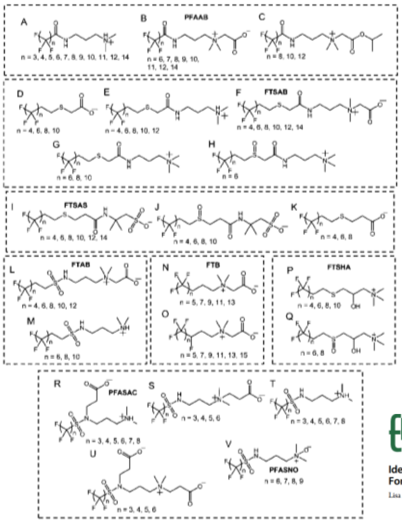


Perfluorooctane sulfonate - PFOS



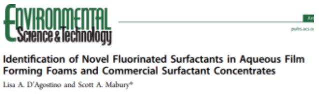
Perfluorohexane sulfonate - PFHxS

- Is this sufficient?
- What should we do instead?



PFSAs and PFCAs are not the major surfactants in AFFF

40 classes of anionic, cationic, zwitterionic PFAS ("many

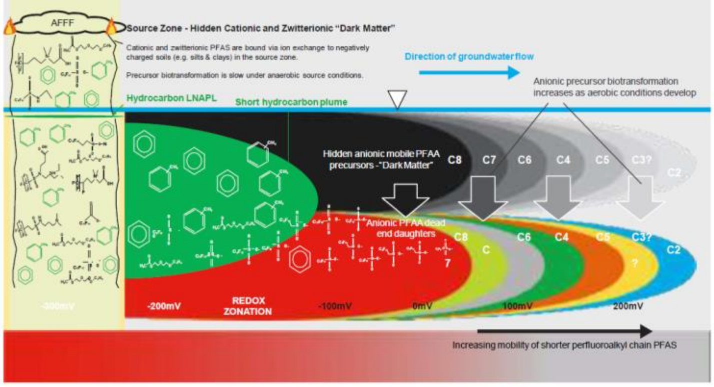


Environmental Science & Technology

Identification of Novel Fluorinated Surfactants in Aqueous Film Forming Foams and Commercial Surfactant Concentrates

Lisa A. D'Agostino and Scott A. Mabury*

Fate and transport complex!



Source Zone - Hidden Cationic and Zwitterionic "Dark Matter"

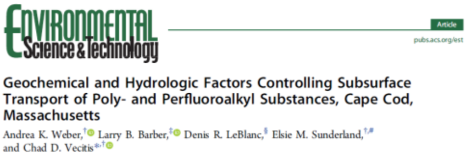
Cationic and zwitterionic PFAS are bound via ion exchange to negatively charged soils (e.g. silts & clays) in the source zone.

Precursor biotransformation is slow under anaerobic source conditions.

Anionic precursor biotransformation increases as aerobic conditions develop

Increasing mobility of shorter perfluoroalkyl chain PFAS

ARCADIS

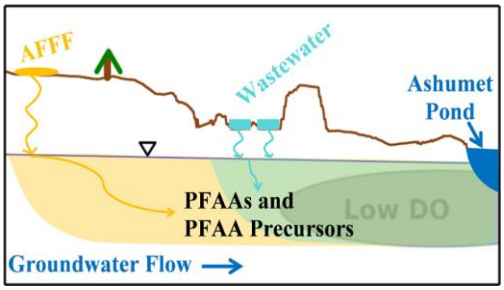


Article

pubs.acs.org/est

Geochemical and Hydrologic Factors Controlling Subsurface Transport of Poly- and Perfluoroalkyl Substances, Cape Cod, Massachusetts

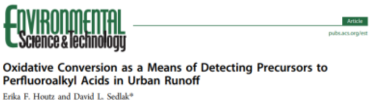
Andrea K. Weber,[†] Larry B. Barber,[‡] Denis R. LeBlanc,[§] Elsie M. Sunderland,[†,#] and Chad D. Vecitis[*,†]



- PFCAs (C_4-C_{12})
- PFBA, PFHxS, PFOS, PFDS, FOSA
- 6:2 and 8:2 FTSA

- Total Oxidizable Precursor (TOP) assay
  - converts all precursors to PFAAs

TOP Assay

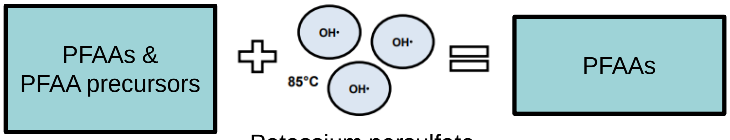


Article

pubs.acs.org/est

Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff

Erika F. Houtz and David L. Sedlak*

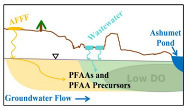


PFAAs & PFAA precursors

PFAAs

Potassium persulfate
Sodium hydroxide

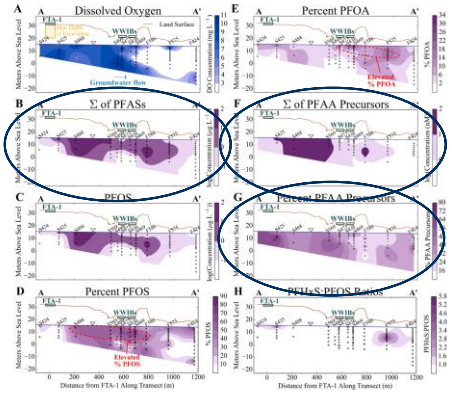
- Analyse PFAAs in sample before and after oxidation
- Difference is ΣPFAA precursors
- Developed for water but now being applied to soils



AFFF used historically

But not used for last ~ 20 years

Aren't PFAS mobile?



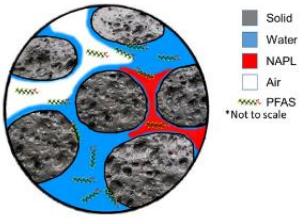
PFAS stuck in unsaturated zone

Including precursors (TOP assay)

Precursors not the major proportion of PFAS

Weber et al. (2017)

Sorption is more complicated: adsorption to air-water interfaces



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ELSEVIER

Assessing the potential contributions of additional retention processes to PFAS retardation in the subsurface

Mark L. Brusseau

- Multiple papers by Brusseau and colleagues
- Interfacial adsorption in unsaturated zone dominates over absorption to organic matter

Concluding remarks

- >4000 PFASs used in multiple applications
  - Only fate & transport of PFCAs and PFSAs understood
- Production and use of PFASs should be limited
  - Based on concerns regarding high persistence and lack of knowledge on chemical structures, properties, uses, and toxicological profiles (Madrid Statement, Blum et al. 2015).
- Although remediation techniques exist they are very energy intensive and costly
- Neither practical nor reasonable to ban all uses of PFASs in one step
  - However, if some uses of PFASs are found **not** to be **essential**, they could be eliminated without having to first find functional alternatives (Essential Use Concept: Cousins et al., 2018)

Environmental Science Processes & Impacts

CRITICAL REVIEW

View Article Online

Cite this: Environ. Sci.: Processes Impacts, 2019, 21, 1803

The concept of essential use for determining when uses of PFASs can be phased out

Ian T. Cousins, Gretta Goldenman, Dorte Herzke, Rainer Lohmann, Mark Miller, Carla A. Ng, Sharyle Patton, Martin Scheringer, Xenia Trier, Lena Vierke, Zhanyun Wang and Jamie C. DeWitt

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Thank you for your attention!

PERFORCE3

We are recruiting 15 PhD students

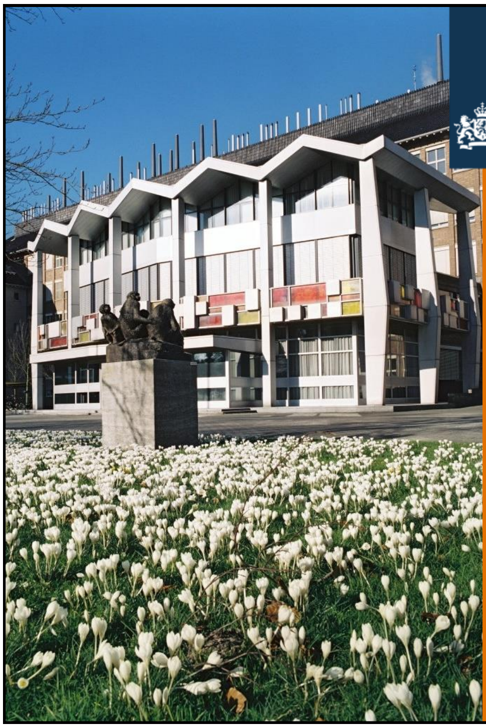
II.5.5 PFAS risk assessment what do we know and what do we want to know?

Arjen Wintersen, Frank Swartjes and Piet Otte
National Institute for Public Health and the Environment (RIVM), The Netherlands

As ever more information is becoming available on the occurrence of PFAS in our environment, regulators and environmental specialists are confronted with new questions. How do we assess the risks of these substances in different media and for the relevant applications (e.g. the re-use of soil and sediments)? What risks can we already take into account and what are we potentially still missing in our assessments? How will these substances migrate and behave in our environment over time?

Up until 2018 in The Netherlands these questions were mainly addressed by local and regional government bodies. PFAS contaminations were dealt with primarily as a problem limited to the direct surroundings of several known point sources. However, as it became ever more clear that PFAS were found quite widespread in soil, sediments, ground- and surface water and biota, the need for action by the national government became clear. In 2019 for the first time a preliminary national framework for PFAS was introduced to regulate the use of moderately contaminated soil and sediment. The PFAS framework aims to prevent health risks and to limit risks for the environment to predefined acceptable levels. At the same time the framework must ensure that existing contaminations are not spread any further through the environment.

In this presentation I will discuss the environmental and health risk limits as well as (new) background levels that were used to underpin the preliminary framework. Additionally I will discuss the research that is still ongoing in the short term to substantiate a definitive version of the framework in 2020. Finally I will go into the challenges that lie ahead in the longer term as we try to address the risks and behavior of PFAS and other substances of emerging concern. Looking forward, can we already identify the tools and methods needed to forecast and assess the risks of these substances, and what kind of data and research is still needed to fill in the blanks?



National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

PFAS risk assessment what do we know and what do we want to know?

Arjen Wintersen
Frank Swartjes
Piet Otte

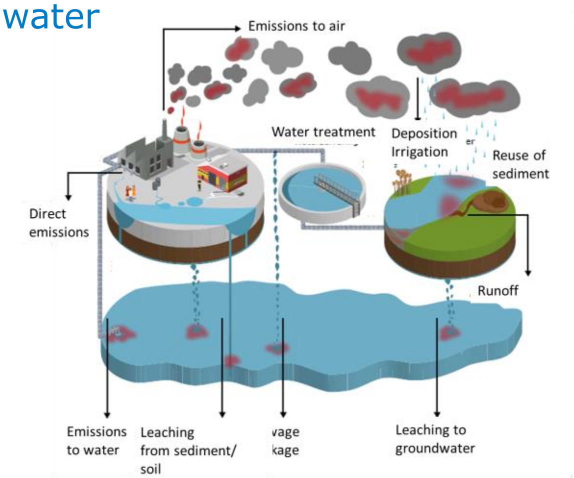
13-01-2020

Introduction – PFAS in soil and groundwater in The Netherlands

Until recently main attention focused on larger ‘point sources’

Activity	Example/type
Practicing and incidents involving AFFF	Schiphol (2008)
PFAS producing industry	Chemours Dordrecht
Landfills	PFAS in waste material
Industrial applications/processing	E.g. drying of products. metal plating
Other industrial sites	Smaller locations

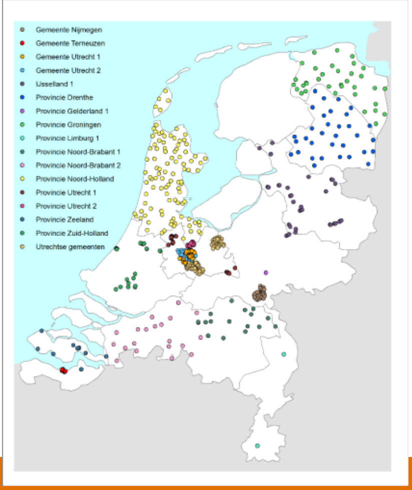
Diffuse PFAS contamination of soil, sediment and groundwater



Limit values for re-use of soils and sediments in The Netherlands

- First preliminary national framework: July 2019
- No background values available yet: LOQ serves as replacement
- Consequently large impact on market for re-usable soil and sediment

Ubiquitous concentrations of PFAS in soil: establishing preliminary background levels



- In October 2019 data was collected from available soil investigations
- November 2019: processing data:
- \- Point sources
- \- Land use
- \- Soil parameters (OC, clay)
- 1 December: preliminary values operationalized in soil policy by Ministry

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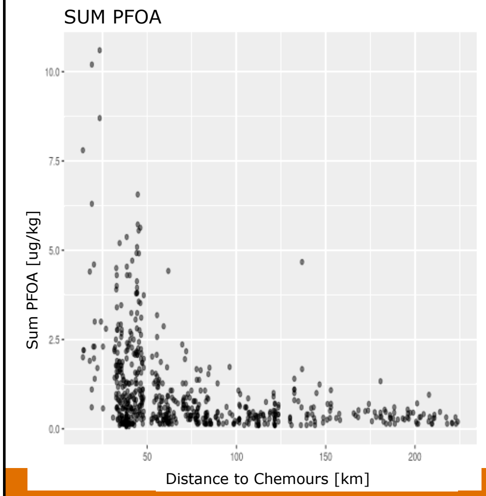
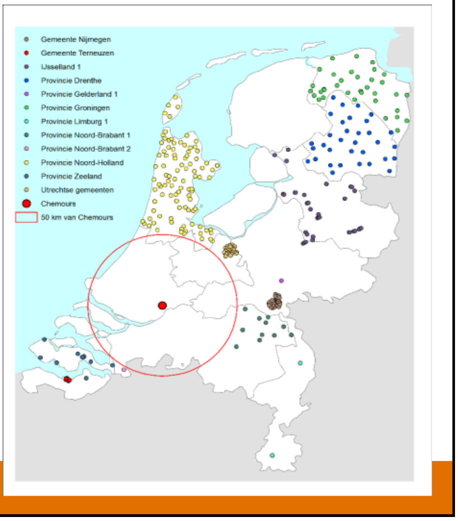
Results background values: PFOA





Results background values

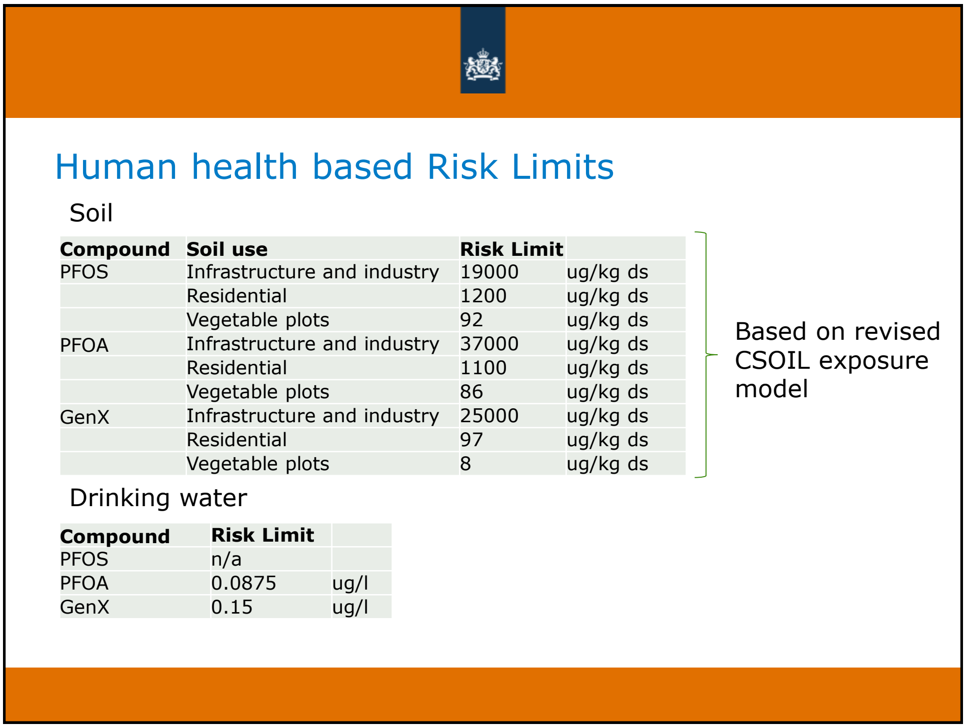
- Based on P80 of concentration distributions of PFOS and PFOA

Subst.	Prelim. bv in (µg/kg ds)	Prelim. bv (µg/kg ds) rounded to 1 decimal
PFOS	0.94	**0.9**
PFOA	0.77	**0.8**

- Definitive values will be available in july 2020
- Of ~30 PFAS only PFOS and PFOA were structurally elevated in top soil
- Stricter criteria apply for groundwater protection areas

Environmental risk limits for soil and groundwater

- Currently based on endpoints:
  - Human health
  - Direct ecotoxicity
  - Indirect ecotoxicity
- Risk limits to be (further) developed
  - Agriculture/food (in prep)
  - Leaching to groundwater and surface water (in prep)
  - Waste streams and building materials (no plans yet)



Human health based Risk Limits

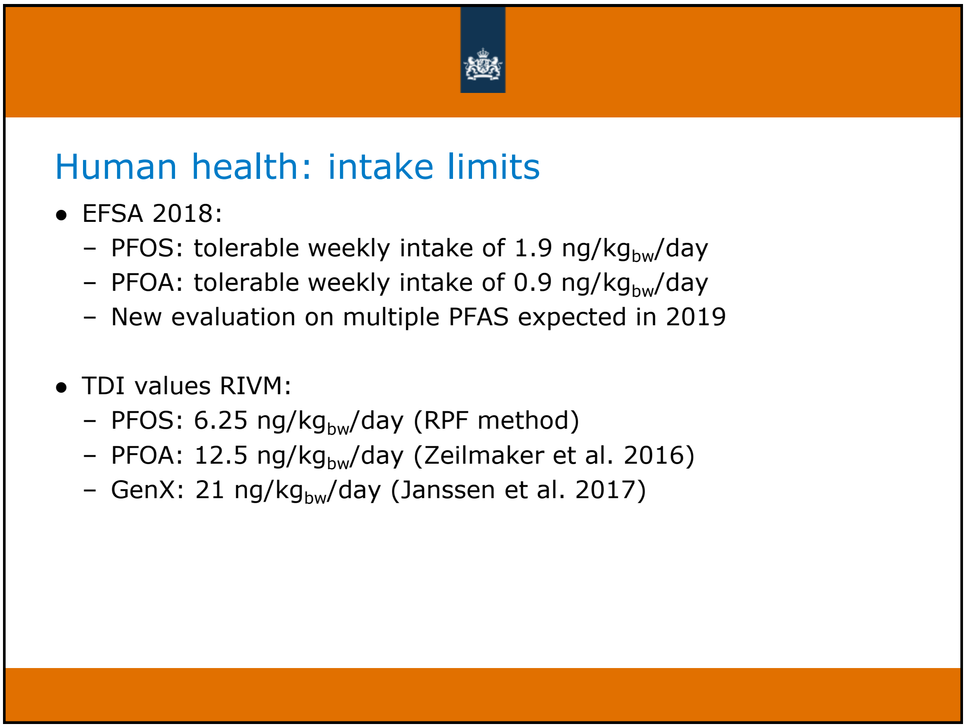
Soil

Compound	Soil use	Risk Limit	
PFOS	Infrastructure and industry	19000	ug/kg ds
	Residential	1200	ug/kg ds
	Vegetable plots	92	ug/kg ds
PFOA	Infrastructure and industry	37000	ug/kg ds
	Residential	1100	ug/kg ds
	Vegetable plots	86	ug/kg ds
GenX	Infrastructure and industry	25000	ug/kg ds
	Residential	97	ug/kg ds
	Vegetable plots	8	ug/kg ds

Based on revised CSOIL exposure model

Drinking water

Compound	Risk Limit	
PFOS	n/a	
PFOA	0.0875	ug/l
GenX	0.15	ug/l



Human health: intake limits

- EFSA 2018:
  - PFOS: tolerable weekly intake of 1.9 ng/kg$_{bw}$/day
  - PFOA: tolerable weekly intake of 0.9 ng/kg$_{bw}$/day
  - New evaluation on multiple PFAS expected in 2019

- TDI values RIVM:
  - PFOS: 6.25 ng/kg$_{bw}$/day (RPF method)
  - PFOA: 12.5 ng/kg$_{bw}$/day (Zeilmaker et al. 2016)
  - GenX: 21 ng/kg$_{bw}$/day (Janssen et al. 2017)

Ecological risk limits

Direct toxicity

Compound	Risk level	Risk Limit (ug/kg)
PFOS	HC5	16
	Intermediate/HC20	380
	HC50	9100
PFOA	HC5	500
	Intermediate/HC20	5000
	HC50	50000

Indirect toxicity

Compound	Risk level	Risk Limit (ug/kg)
PFOS	HC5	3
	Intermediate/HC20	18
	HC50	110
PFOA	HC5	7
	Intermediate/HC20	89
	HC50	1137
GenX	HC5	3
	Intermediate/HC20	54
	HC50	964

Ecological risk assessment

- PFOS:
  - Toxicity data re-evaluated in 2018/2019 (compared to earlier 2011 data)
  - New assessment method applied for indirect toxicity (Verbruggen et al. 2014)
  - High bioaccumulation
- PFOA:
  - Toxicity data evaluated in 2018 (Lijzen et al. 2018)
  - New assessment method applied for indirect toxicity (Verbruggen et al. 2014)
  - Less bioaccumulation than PFOS
- GenX:
  - Insufficient data to derive RL’s based on direct toxicity
  - RL’s based on indirect toxicity for GenX based on accumulation potential of PFOS (worst case)

Risk limits for agriculture/food production

	Risk Limit (ug/kg)	
Use	**PFOS**	**PFOA**
Arable farming	58	30
Cattle	6.8	12

- Based on transfer calculations soil/crop and crop/water/animal
- Intake derived from National Food Consumption Survey (Van Rossum et al. 2016)
- Endpoint: TDI’s
- Report: Wintersen et al. 2019

Recent and future publications

- Report Relative Potency Factors PFAS: 2018-0017
- RIVM report Risk Limits soil and groundwater GenX: 2019-0027
- RIVM report Risk Limits PFOS en PFOA in agricultural soil (2019-)
- RIVM overview report Risk Limits PFAS (2019/2020)

Rijksinstituut voor Volksgezondheid
en Milieu
Ministerie van Volksgezondheid,
Welzijn en Sport

Risicogrenzen GenX (HFPO-DA) voor grond en grondwater

RIVM Briefrapport 2019-0027
M. Rutgers et al.

National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

Mixture exposure to PFAS: A Relative Potency Factor approach

RIVM Report 2018-0070
M.J. Zeilmaker et al.

Environmental screening levels for re-use and site assessment

Re-use of soil and sediment (prelim. Framework)	PFOS	PFOA	Other PFAS (incl. GenX)
Agriculture/nature	0.9	0.8	0.8
Residential/industrial	3.0	7.0	3.0

Stof	EQC for site assessment		
	Soil (µg/kg ds)	Groundwater (µg/L)	Groundwater (µg/L)
		Including drinking water[1]	No drinking Water
PFOS	110	0.20	56
PFOA	1100	0.39	170
GenX	97	0.66	140

[1] Note that these are <u>not</u> drinking water risk limits

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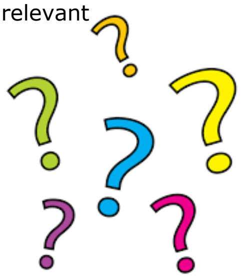
What do we still want to know?

- Analytical performance:
  - Ring test 9 laboratories (results just in)
  - Other matrices, eg waste streams: no plans but very relevant
- Sources and distribution of PFAS in the environment:
  - PFAS in products
  - PFAS in water and waste streams irt emissions
  - Definitive background values in soil (july 2020)
  - Background values in groundwater (2021)
  - PFAS in river sediments
- Environmental behavior:
  - Leaching tests from soil and sediment (2020)
  - Risk limits in soil protecting groundwater (for re-use; 2020)
- Substance risks and risk limits:
  - EFSA evaluation 2020
  - Other PFAS/combination toxicity
  - Risk limits for waste streams
- International network: align with international developments



II.5.6 The Role of Total Fluorine Measurements in Monitoring PFAS

Graham F. Peaslee
University of Notre Dame (US), Departement of Physics

Poly- and perfluoroalkyl substances (PFAS) in drinking water, soils, food and diverse consumer products are a major concern globally. Although PFAS are a large chemical class of more than 4,700 compounds, most measurements have focused on less than 30 PFAS using targeted LC-MS/MS methods. These targeted PFAS often account for <10% of the total organofluorine burden in environmental samples and <1% in consumer products. Several research groups are using non-targeted high-resolution mass spectrometry to identify unknown chemical structures that are not typically quantified using targeted methods. However, without standards these techniques are only semi-quantitative and have not been considered suitable for regulatory decisions. To fill this gap, methods for quantifying the total fluorine and total organofluorine burden in different matrices are being developed. Many of these methods show promise. For example, total fluorine measurements have the unique ability to allow development of mass balance assessments of the total environmental reservoirs of PFAS, or to rapidly screen samples for the presence of any PFAS, or to monitor levels of all PFAS. However, these methods have not yet been standardized in publicly available protocols (e.g. EPA methods) that include rigorous quality assurance/control and interlaboratory comparison. Systematic evaluations of which method(s) are most suitable for different applications and different media are also needed. A brief review of one promising new technology - Particle Induced Gamma-ray Emission (PIGE) spectroscopy will be presented with examples of where this (and other total fluorine techniques) can complement traditional LC-MS/MS techniques and provide the most utility for consumers, regulators and research scientists.

The Role of Total Fluorine Measurements in Monitoring PFAS

Graham F. Peaslee – University of Notre Dame

January 13, 2020

Outline

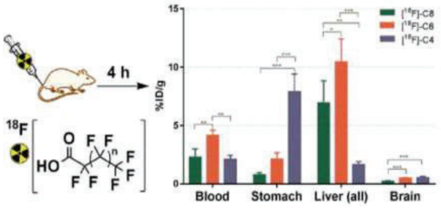
- Motivation Why is a "Total Fluorine" method needed?
- Some common total fluorine methods
- Some potential applications
- Conclusions
- Questions

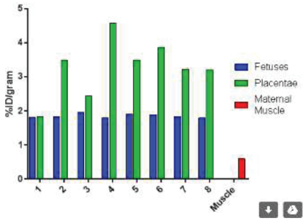
Why is a “Total Fluorine” method needed?

- There are 4700+ known PFAS…less than 1% are currently targeted
- All are **persistent** (C-F bond)…
- Most are **bioaccumulative** as far as we can tell…
- Most are **toxic** as far as we can tell...
  - *e.g. Immunotoxicity (Grandjean et al.)*
  - *C8 → C6 “regrettable substitution”*

more soluble, more used, goes to every organ…

(Burkemper et al.)

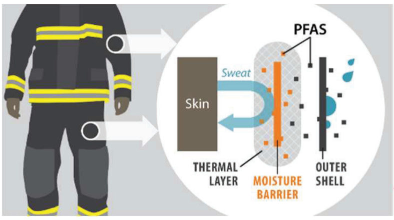




Why is a “Total Fluorine” method needed?

- Non-targeted analytes can be precursors to regulated PFAS
  - Example of textile side-chain fluoropolymers

n-Et-FOSE → n-Et-FOSAA → PFOA



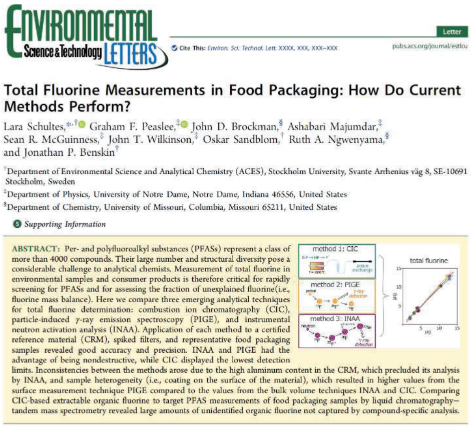
- Potential for **screening**: Complement to LC-MS/MS analysis € € € !
- Potential for **monitoring**: Remediation and treatment
- Potential for **regulating:** Drinking water safety…

Several methods have been developed…

- Total Oxidizable Precursor Assay (TOPA)
  - Add oxidant and heat sample – convert “all” PFAS to known PFAS
  - Very sensitive – uses LC-MS/MS
- Combustion Ion Chromatography (CIC)
  - Combust sample – convert “all” fluorine to flouride
  - Quicker – uses IC, less expensive
- Particle Induced Gamma-ray Emission (PIGE) Spectroscopy
  - Spectroscopic measurement of ^{19}F
  - Rapid, measures solid targets in air

Several methods have been developed…

- Comparisons are published… all will be commercially available…



Environmental Science & Technology LETTERS

Letter

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Total Fluorine Measurements in Food Packaging: How Do Current Methods Perform?

Lara Schultes,[*,†] Graham F. Peaslee,[‡] John D. Brockman,[§] Ashabari Majumdar,[‡] Sean R. McGuinness,[‡] John T. Wilkinson,[‡] Oskar Sandblom,[†] Ruth A. Ngwenyama,[§] and Jonathan P. Benskin[†]

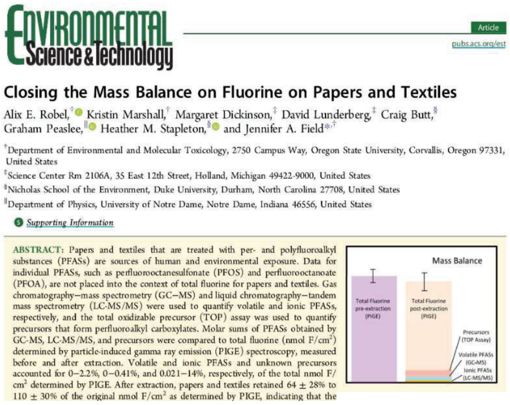
[†] Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, Svante Arrhenius väg 8, SE-10691 Stockholm, Sweden

[‡] Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, United States

[§] Department of Chemistry, University of Missouri, Columbia, Missouri 65211, United States

Supporting Information

ABSTRACT: Per- and polyfluoroalkyl substances (PFASs) represent a class of more than 4000 compounds. Their large number and structural diversity pose a considerable challenge to analytical chemists. Measurement of total fluorine in environmental samples and consumer products is therefore critical for rapidly screening for PFASs and for assessing the fraction of unexplained fluorine(i.e., fluorine mass balance). Here we compare three emerging analytical techniques for total fluorine determination: combustion ion chromatography (CIC), particle-induced γ-ray emission spectroscopy (PIGE), and instrumental neutron activation analysis (INAA). Application of each method to a certified reference material (CRM), spiked filters, and representative food packaging samples revealed good accuracy and precision. INAA and PIGE had the advantage of being nondestructive, while CIC displayed the lowest detection limits. Inconsistencies between the methods arose due to the high aluminum content in the CRM, which precluded its analysis by INAA, and sample heterogeneity (i.e., coating on the surface of the material), which resulted in higher values from the surface measurement technique PIGE compared to the values from the bulk volume techniques INAA and CIC. Comparing CIC-based extractable organic fluorine to target PFAS measurements of food packaging samples by liquid chromatography–tandem mass spectrometry revealed large amounts of unidentified organic fluorine not captured by compound-specific analysis.



Environmental Science & Technology

Article

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Closing the Mass Balance on Fluorine on Papers and Textiles

Alix E. Robel,[†] Kristin Marshall,[†] Margaret Dickinson,[‡] David Lunderberg,[‡] Craig Butt,[§] Graham Peaslee,[‖] Heather M. Stapleton,[§] and Jennifer A. Field[*,†]

[†] Department of Environmental and Molecular Toxicology, 2750 Campus Way, Oregon State University, Corvallis, Oregon 97331, United States

[‡] Science Center Rm 2106A, 35 East 12th Street, Holland, Michigan 49422-9000, United States

[§] Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States

[‖] Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, United States

Supporting Information

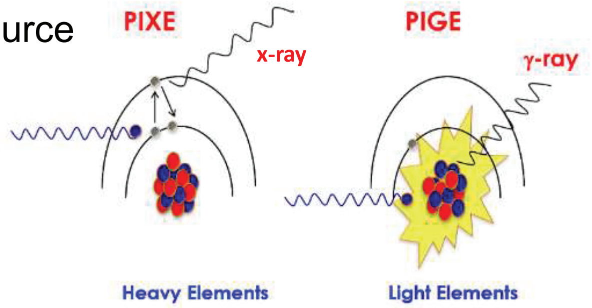
ABSTRACT: Papers and textiles that are treated with per- and polyfluoroalkyl substances (PFASs) are sources of human and environmental exposure. Data for individual PFASs, such as perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA), are not placed into the context of total fluorine for papers and textiles. Gas chromatography–mass spectrometry (GC–MS) and liquid chromatography–tandem mass spectrometry (LC-MS/MS) were used to quantify volatile and ionic PFASs, respectively, and the total oxidizable precursor (TOP) assay was used to quantify precursors that form perfluoroalkyl carboxylates. Molar sums of PFASs obtained by GC-MS, LC-MS/MS, and precursors were compared to total fluorine (nmol F/cm^2) determined by particle-induced gamma ray emission (PIGE) spectroscopy, measured before and after extraction. Volatile and ionic PFASs and unknown precursors accounted for 0–2.2%, 0–0.41%, and 0.021–14%, respectively, of the total nmol F/cm^2 determined by PIGE. After extraction, papers and textiles retained 64 ± 28% to 110 ± 30% of the original nmol F/cm^2 as determined by PIGE, indicating that the

Several methods have been developed…

- All methods are fairly recent…
- There is a need for total F standards, interlaboratory comparisons, typical quality assurance/quality control protocols, etc.
  - ➔ EPA, NIST, DoD workshop on Total F Methods (March 2020).

Specific Example: What is PIGE?

- **Particle Induced Gamma-ray Emission (PIGE) Spectroscopy**
- Accelerated Protons as excitation source
- Nuclear de-excitation of ^{19}F
- Identification of characteristic γ-rays



Sensitive, specific, rapid, non-destructive

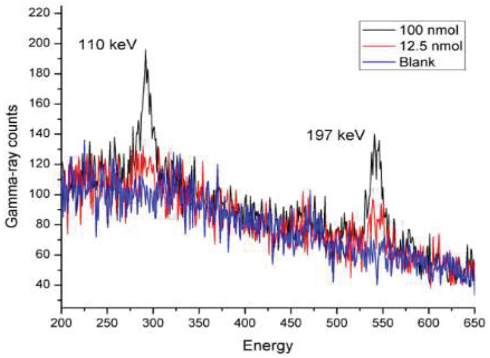
What is PIGE?

- Particle Induced Gamma-ray Emission (PIGE) Spectroscopy @ ND

What is PIGE?

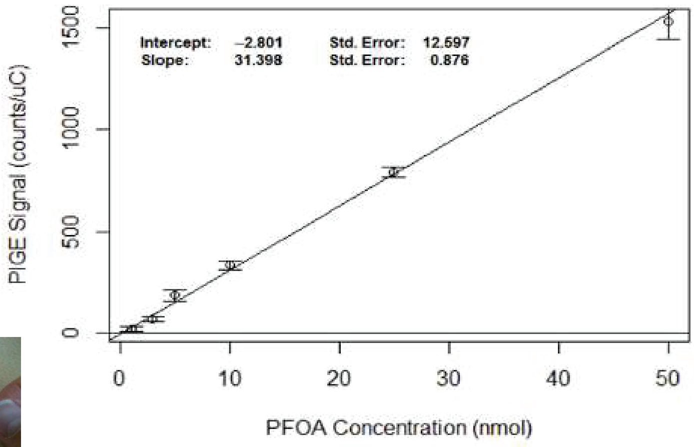
- **Specificity**
- 50 mL aliquot
- Concentrated by SPE
- Analyzed for 3 min
- No interferents
- No matrix effects
- Identifies all PFAS on SPE
- Inorganic F removed by wash

Figure 3: PIGE spectra of PFOA extracted onto the surface of WAX cartridges. The two gamma rays detected at 110 keV and 197 keV arise from excitations of ^{19}F nuclei.



What is PIGE?

- **Sensitivity**
- 50 mL aliquot
- Concentrated by SPE
- Analyzed for 3 min
- MDL = 5 ppb F



Advantages/Disadvantages

- PIGE is spectroscopic: **Rapid** > 500 samples per day possible
- PIGE is non-destructive: Same sample can be extracted for LC-MS/MS
- PIGE is inclusive: All PFAS (known and unknown) simultaneously
- PIGE MDL depends on volume sampled…70 ppt any PFAS = 3 L

- PIGE is largely academic tool to date – limited commercialization
- PIGE is laboratory-based to date – large & specialized equipment

Recent Development Advances

- **Determine MDL for PIGE as a Function of Sample Volume**

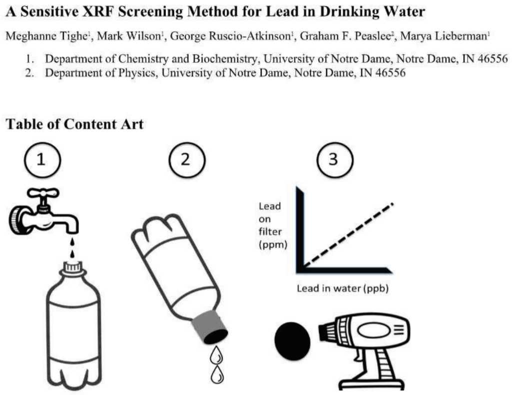
- We have identified faster and more complete preconcentration method:

= Commercially available GAC felt

Cost < 10 cents / sample

Can gravity filter 5 L in less than 3 min

PFAS stick to felt very well….



A Sensitive XRF Screening Method for Lead in Drinking Water

Meghanne Tighe[1], Mark Wilson[1], George Ruscio-Atkinson[1], Graham F. Peaslee[2], Marya Lieberman[1]

1. Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556
2. Department of Physics, University of Notre Dame, Notre Dame, IN 46556

Table of Content Art

Commercialization of Process

- Significant progress in demonstrating PIGE as a viable total F method
- Partner with medical cyclotron manufacturer:
- Use GENTrace cyclotron (100,000 samples/yr)

Run 3 L of water through GAC felt filter (minutes in field)

Dry filters (hours)

Send filters for PIGE analysis (1-2 minutes per sample)

Identify all sum of all PFAS present > 50 ng/L

(If targeted analytes needed, can elute PFAS for LC-MS/MS)

GE Healthcare

Conclusions

- Total fluorine measurements are a powerful screening tool for drinking water

If there is no fluorine, there are no PFAS…

- Save LC-MS/MS analysis only for those samples with elevated total F levels…
- Complements targeted LC-MS/MS analysis, doesn't replace it…
- Techniques must be robust, sensitive and widely available…
- If we develop standards and QA/QC protocols – this could be in place within a year
- Nothing like this was feasible even a year ago…

Questions?

gpeaslee@nd.edu

II.5.7 Characterization of PFAS in groundwater, surface water and drinking water, including approaches for total assessment of organofluorines

Anna Kärrman
Örebro University (Sweden), Man-Technology-Environment Research Centre

Per- and polyfluorinated alkyl substances (PFAS) are used in a variety of applications as new unique properties are obtained when fluorine atoms are introduced into a molecule, such as increased electronegativity, stability, and bioavailability (Kissa 2001). As a result there is a widespread contamination of PFAS in the environment with potential risks associated with persistence, bioaccumulation and toxicity. The sampling techniques and standardized analysis methods currently in place for determination of selected target PFAS in water will be discussed including representative sampling, how to maintain sample integrity, partitioning between dissolved and particulate phase, and extraction efficiency impacted by co-contaminants.

The OECD has recently updated the list of PFAS to apply to 4730 CAS numbers (OECD 2018). As many as 3000 structures could be relevant from a human- and environmental exposure point of view. Due to the large number of PFAS in production, several studies have used methods to estimate the total amount of fluorine instead of individual PFAS substances.

Total fluorine (TF) has been analysed in food packaging by non-specific methods that measures the total amount of fluoride (Schultes et al. 2019). For most other sample types, such as water, one needs to isolate and concentrate the PFAS substances (organofluorine) and there are in general two methods that are currently discussed: extractable organic fluorine (EOF) and total oxidizable precursor assay (TOPA). In EOF the organofluorine is extracted and inorganic fluorine is excluded, after which the fluorine is measured by combustion ion chromatography (CIC). In TOPA the sample is oxidized with the intention that all PFASs form perfluorinated carboxylic- and sulfonic acid which can then be quantified using standard analysis methods.

CIC measures fluoride that is formed after combustion of the sample in 1100 degrees Celsius and it is therefore assumed that all PFASs extracted from the sample will be measured. The TOPA method includes a chemical reaction that presumably will transform (oxidize) all PFASs to perfluorinated acids. TOPA is often performed in parallel with standard analysis to be able to evaluate known PFAS (standard assay) and unknown precursors (difference between standard assay and TOP assay).

In a study of the Nordic environment using standardized sampling and extraction protocols, it was shown that 73 known PFAS substances could explain 68% of EOF in marine bird eggs (Kärrman et al. 2019). The corresponding explanation percentage was 42% for marine mammals, 28% for fish and 18% for terrestrial mammals. In outgoing wastewater and sludge, only 11% and 9% could be explained by known PFAS, and in surface water, known PFAS accounted for only 5% of the extracted organic fluorine. There is therefore a need to include the total amount of PFAS in risk assessments and to identify the fraction of unknown organofluorine in water and other environmental compartments.

References

Kissa E. (2001) Fluorinated Surfactants and Repellents. 2nd ed. New York:Marcel Dekker Inc.

Kärrman et al. (2019) Screening of poly- and perfluoroalkyl substances (PFASs) and extractable organic fluorine (EOF) in the Nordic environment. Nordic Council of Ministers 2019.

OECD (2018) Toward a new comprehensive global database of per-and ployfluoroalkyl substances (PFAS): Summary report on updating the OECD 2007 list of per-and ployfluoroalkyl substances (PFAS), in Series on Risk Management.

Schultes L, Peaslee GF, Brockman JD, Majmudar A, McGuinness SR, Wilkinson JT, Sandblom O, Ngwenyama RA, Benskin JP. (2019) Total fluorine measurements in food packaging: How do current methods perform? Environmental Science Technology Letters, 6, 2, 73-78.

Characterization of PFAS in surface water, groundwater, and drinking water

Anna Kärrman
MTM Research Centre, Örebro University, Sweden

Workshop on PFAS Monitoring in water and other media 2020-01-14

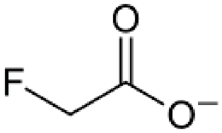
Characterization of PFAS in waters

1. Sampling, storage, and pre-treatment
    - representative sampling, how to maintain sample integrity, partitioning between dissolved and particulate phase, and extraction efficiency impacted by co-contaminants
2. Extraction, analysis, and quality control
    - solid-phase extraction protocols, target analysis, total PFAS analysis (EOF, TOPA), quality control

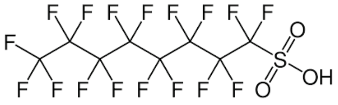
Introduction PFAS

F^-

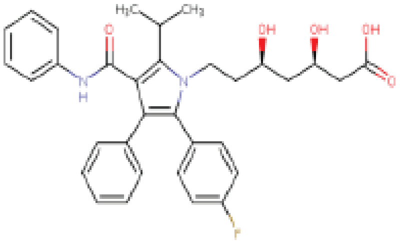
most common form
found in nature

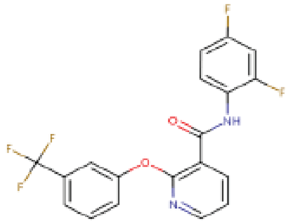


Example of natural
occuring organofluorine



Antropogenic organofluorine





Organofluorine is present in:

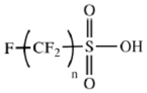
~20% pharmaceuticals

30-40% agrochemicals

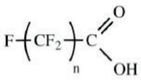
PFAS

Perfluoroalkyl acids

Examples:

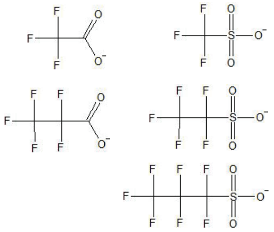


PFSAs



PFCAs

Ultra-short-chain acids ≤3 carbons

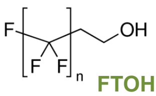


Precursors

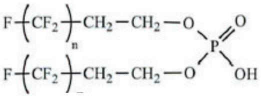
Examples of precursors to PFSAs:

Et-FOSA

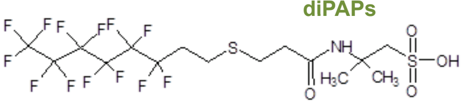
Example of precursors to PFCAs:



FTOHs



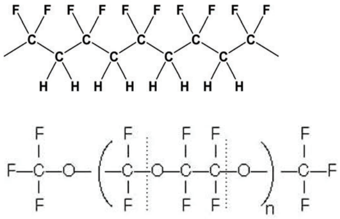
diPAPs



6:2 FTSAS

Others

Polymers:



Sampling

Contamination prevention and control

- sample equipment
- field blank

Temporal and spatial variation

- influence of point-source or hot spot
- concentration profiles and distribution in aquifier

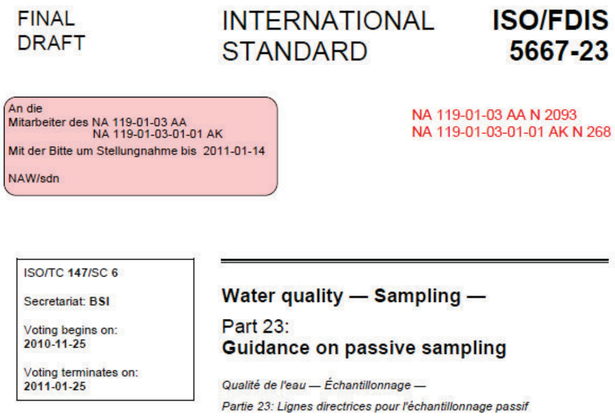
How to compensate for variations

- increase number of samples, pool composite samples
- passive samplers – e.g. polar organic chemical integrative samples (POCIS)

Passive sampling

Reflects concentration over time as well as availability and affinity

Equilibrium or kinetic modes



FINAL
DRAFT

INTERNATIONAL
STANDARD

ISO/FDIS
5667-23

An die
Mitarbeiter des NA 119-01-03 AA
NA 119-01-03-01-01 AK
Mit der Bitte um Stellungnahme bis 2011-01-14

NAW/sdn

NA 119-01-03 AA N 2093
NA 119-01-03-01-01 AK N 268

ISO/TC **147/SC 6**

Secretariat: **BSI**

Voting begins on:
2010-11-25

Voting terminates on:
2011-01-25

Water quality — Sampling —

Part 23:
Guidance on passive sampling

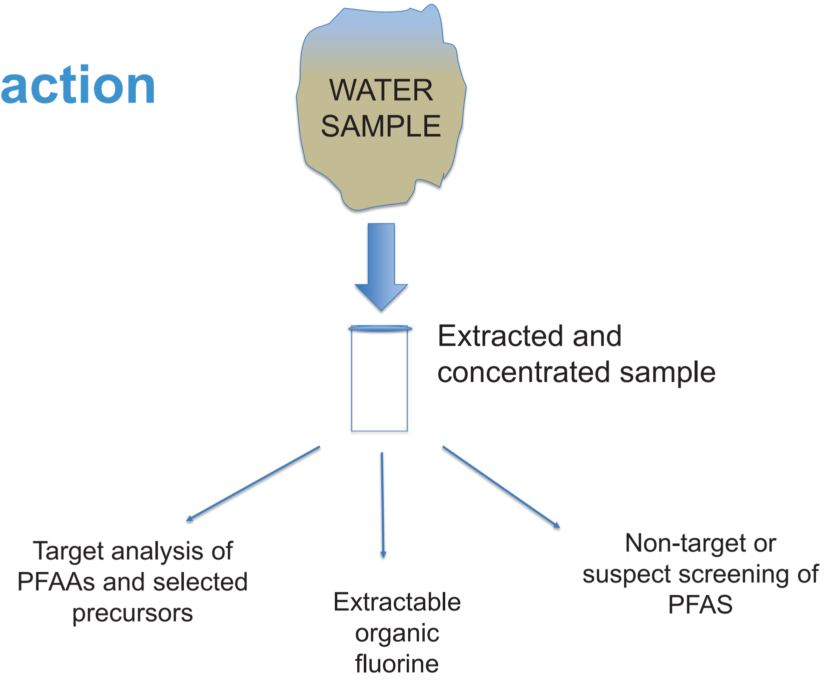
Qualité de l'eau — Échantillonnage —

Partie 23: Lignes directrices pour l'échantillonnage passif

Storage and pre-treatment

- Sorption to the sample container, and consequences of sub-sampling
- Transformation of precursors to PFAAs during storage
- Filtration of the sample – separation of dissolved and particulate phase
- pH
- Removal of competitive ions

Extraction



WATER SAMPLE

Extracted and concentrated sample

Target analysis of PFAAs and selected precursors

Extractable organic fluorine

Non-target or suspect screening of PFAS

Performance of extraction method

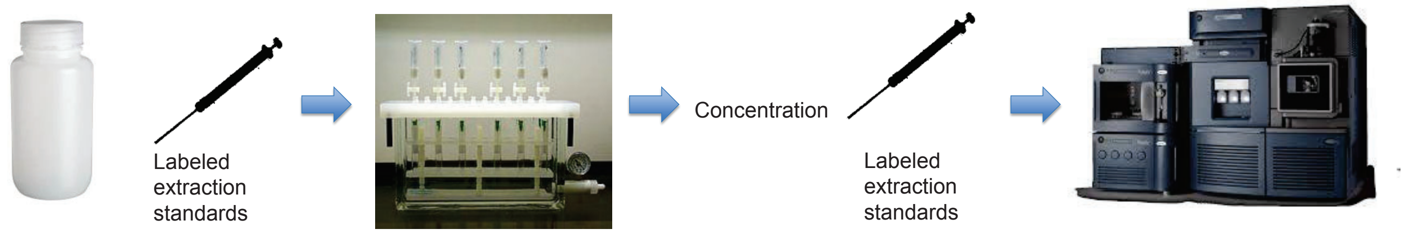
Spike recovery tests:
- recovery of target PFAS
- removal of inorganic PFAS

Recovery of total PFAS
- compare with direct injection

Solid-phase extraction

ISO 25101 – PFOS and PFOA in unfiltered water

ISO 21675 – PFAS in unfiltered water, incl. isomer (PFOA, PFOS) quantification and normative method if suspended material > 2 g/L



Labeled extraction standards

Concentration

Labeled extraction standards

SPE using mixed weak-anion exhange and hydrophobic interaction

- Good performance for many target PFAAs and precursors
- Possibility to wash out inorganic fluoride
- A more extensive extraction method needed for some PFASs
- Include suspended materials for full characterization of PFAS contamination in water
  - Sorption to organic carbon, charged mineral surfaces depends on size and functional group
  - Non-polar extraction solvents needed to extract strongly bound PFAS

PFAS analysis using LC-MS/MS

Perfluoroalkylsulfonic acids (PFSAs) (*n*=8)

PFBS (C4), PFPeS (C5), PFHxS (C6), PFHpS (C7), PFOS (C8), PFNS (C9), PFDS (C10), PFDoDS (C12)

Precursors of PFSAs (*n*=5)

FOSA, FOSAA, MeFOSAA, EtFOSAA, diSAmPAP

Perfluorinated phosphonic acids (PFPAs) (*n*=3)

PFHxPA (C6), PFOPA (C8), PFDPA (C10)

Perfluorinated phosphinic acids (PFPiAs) (*n*=3)

6:6, 6:8, 8:8 PFPiA

Perfluoroalkyl carboxylates (PFCAs) (*n*=13)

PFBA (C4), PFPeA (C5), PFHxA (C6), PFHpA (C7), PFOA (C8), PFNA (C9), PFDA (C10), PFUnDA (C11), PFDoDA (C12), PFTrDA (C13), PFTDA(C14), PFHxDA (C16), PFOcDA (C18)

Precursors of PFCAs (*n*=32)

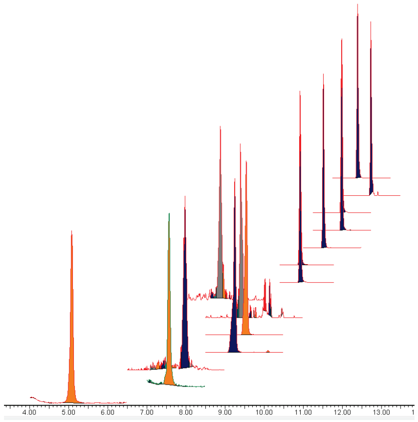
FTSAs (*n*=3), FTCAs (*n*=2), FTUCAs (*n*=3), PAPs (*n*=24)

Novel PFASs (*n*=6)

ADONA, HFPO-DA, HFPO-TA, F-53B, PFECHS

Scotchguard side-chain co-polymers

PFAS analysis using LC-MS/MS



Precursors of PFCAs (*n*=32)

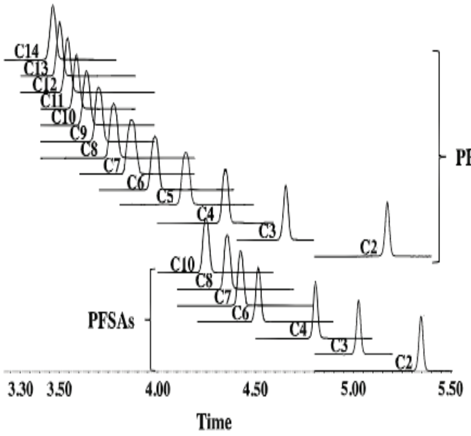
PAPs (*n*=24)

Precursors of PFSAs (*n*=5)

FOSA, FOSAA, MeFOSAA, EtFOSAA, diSAmPAP

Ionisation in ESI improved by increased proportion of organic solvent in the extract

Supercritical fluid chromatography for ultra-short-chain PFASs



Yeung et al. 2017

UPC²-MS/MS

Perfluoroalkylsulfonic acids (PFSAs)

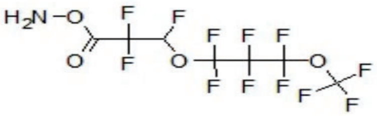
PFMeS (C1), PFEtS (C2), PFPrS (C3)

Perfluoroalkyl carboxylates (PFCAs)

TFA (C2), PFPrA (C3)

Analysis of novel PFASs

HFPO-DA and ADONA can be analyzed together with PFOS, but are sensitive to in-source fragmentation resulting in high LOD



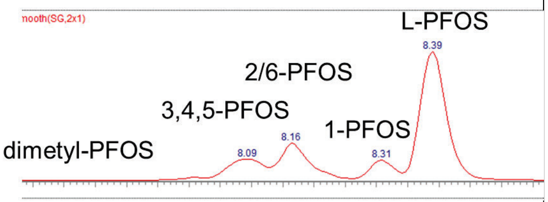
Target analysis

LC-MS/MS

- sensitive and specific, but one method can not cover all PFAS
- in-source fragmentation

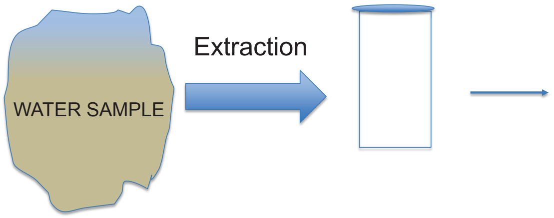
Quantification

- isotope dilution – labeled standards
- matrix ionisation effects
- branched isomers important for water samples
  - PFOS, PFHxS, PFOA, other PFCAs after TOP Assay

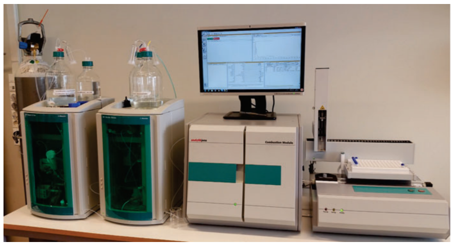


L-PFOS 9.5 ng/L
totPFOS 19.9 ng/L

Extractable Organic Fluorine – Combustion Ion Chromatography (EOF-CIC)



Measure fluoride after pyrolysis 1000-1100° C



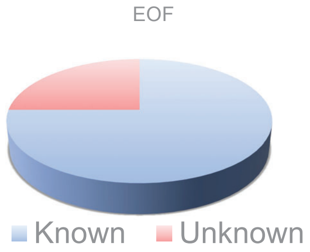
Ion chromatograph

Autoinjector

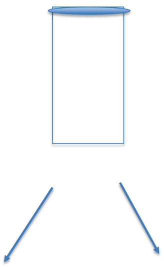
Furnace
Pyrolysis 1000-1100° C
Thermal oxidation

- No discrimination between F from PFAS, labelled PFAS, or inorganic fluoride.
- Careful control of background F
- Determination of F using IC less sensitive compared to PFAS determination with LC-MS/MS

Concept of mass balance



Mass balance = C_F target / C_F EOF



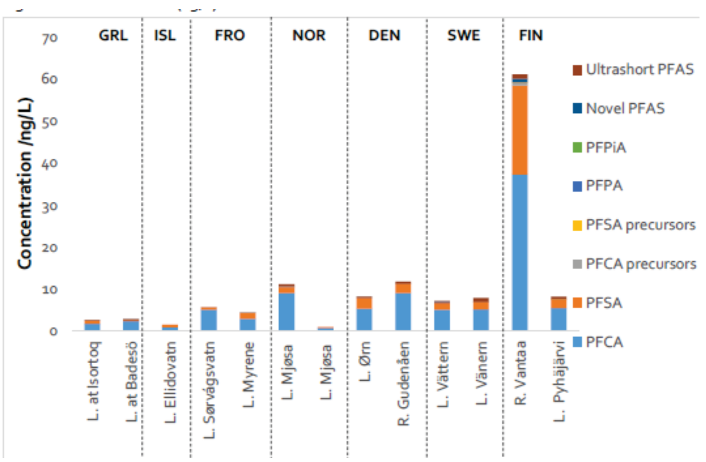
Fluoride measured after combustion 1100° C

Target PFAS by LC-MS/MS converted to fluoride

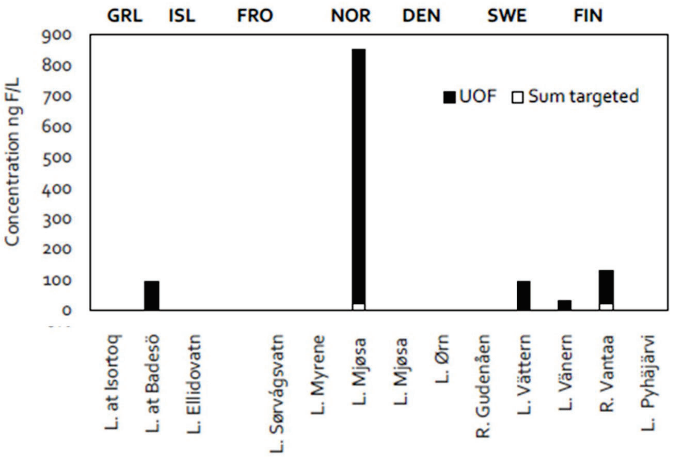
Not recovery corrected

Example, surface water

Target PFAS



EOF-CIC



LOD 41 ng F / l

Kärrman et al. 2019. Screening of Poly- and Perfluoroalkyl Substances (PFASs) and Extractable Organic Fluorine (EOF) in the Nordic Environment. TemaNord, ISSN 0908-6692 ; 2019:515

EOF-CIC observations for water samples

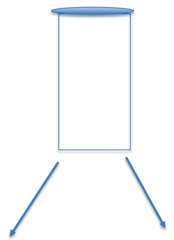
Target $\sum_{73}$PFAS explained on average 8% of EOF in a screening of surface water [1]

Correlation between low levels of target PFAS and EOF observed for some samples, surface water around 10 ng/L are under detection limit for EOF.

For some samples a relatively high EOF are observed, regardless of low target PFAS concentration

Kärrman et al. 2019. Screening of Poly- and Perfluoroalkyl Substances (PFASs) and Extractable Organic Fluorine (EOF) in the Nordic Environment. TemaNord, ISSN 0908-6692 ; 2019:515

Total oxidizable precursor (TOP) assay



Target analysis using LC-MS/MS

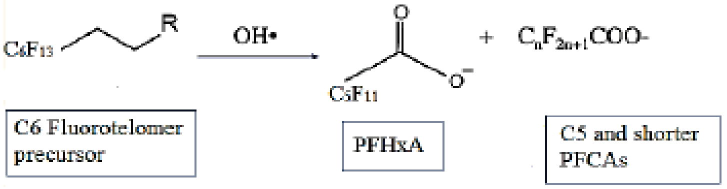
Oxidation reaction with hydroxyl radicals followed by target analysis using LC-MS/MS

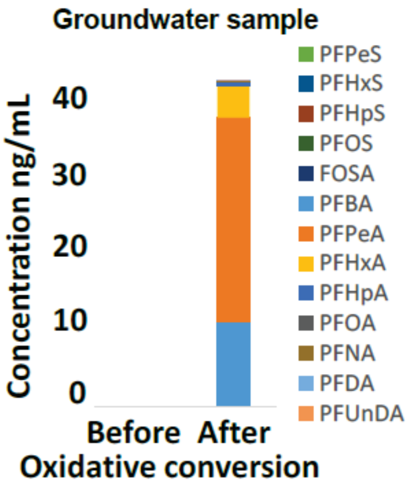
$$S_2O_8^{2-} + heat \rightarrow 2SO_4^{-\cdot}$$

$$SO_4^{-\cdot} + OH^{-} \rightarrow SO4^{2-} + {}^{\cdot}OH$$

- Chemical oxidation by hydroxyl radicals of precursors to PFCA
- 85° C at high pH (12)
- Sulfonamides form PFCA (incl branched)
- Telomers form a series of PFCAs
- Reaction performance depends on structure of precursors and matrix

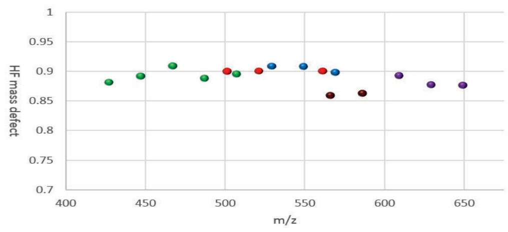
Example, contaminated ground water

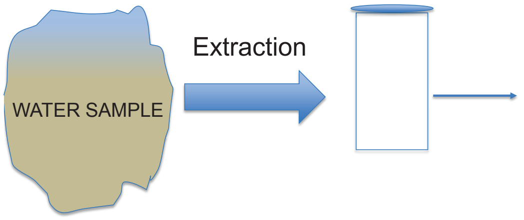




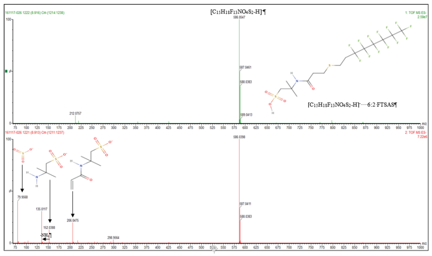
- Highest conc. for C(n-1)
    - (eg 6:2 FTSA to PFPeA)

Suspect and non-target screening





High resolution accurate mass analysis



Data mining and reduction through:

- mass defects
- fragmentation flagging
- suspect lists
    - *Norman lists*

Summary Analysis

	Target analysis of PFAAs and selected precursors	Total oxidizable precursor assay	Extractable organic fluorine	Non-target or suspect screening of PFAS
Qualitative	High	Indicates precursor origins	No	Confidence level varies
Quantitative	High	PFCA oxidation products by LC-MS	Fluoride Lower sensitivity than LC-MS	No, or semi-quantitative
Quality control	Interlab studies, CRM´s	Positive control(s) of precursor compounds pH monitoring	Removal of inorganic F Background control Positive control	Sensitivity Multiple ionisation modes

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Email: anna.karrman@oru.se

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II.5.8 Characterisation of PFAS in food, crops, feed (including packing material)

Dorte Herzke
Norwegian Institute for Air Research (NILU), Department of Environmental Chemistry

It is increasingly apparent that to effectively protect the public from the wide range of possible PFAS-related health effects, dietary items including packing materials require a close inspection. Since our understanding of the extend of the PFAS universe and their toxic effects is under constant improvement, methods, guidelines and thresholds need to be adapted continuously. No status quo has been reached and we expect the scientific expertise on PFAS to grow even more in the near future. The technological improvements in analytical instrumentation and data processing also allow big leaps in understanding of how PFAS exposure effects humans.

As for many pollutants, PFAS characterisation in food and feed is governed by the question you want to answer:

1. Does the food/ feed contain any PFAS?
2. Which PFAS can be found in food and feed?
3. Are there any unknown PFAS in food and feed?
4. Is the food safe to be consumed?

All four questions ask for strategies to group PFAS to either deliver a sum parameter for all PFAS (1), a suspect screening approach (2), non-target screening for so far unknown PFASs (3) or for regulation purposes a targeted measurement of the regulated compounds (4).

Following techniques resulting in increasing resolution of information on PFAS composition and concentration will be discussed during the presentation:

1. *Total organic fluorine and extractable organic fluorine approaches*
   Total fluorine (TF) comprises the sum of all inorganic and organic fluorinated substances in a sample (McDonough et al., 2018). Today, TF is used by the Danish Ministry of the Environment and Food with an indicator value of 0.1 µg/cm^2 for food packaging (Fluorinated substances in paper and cardboard food contact materials (FCM). (www.fvst.dk). This indicator can screen if PFAS levels are increasing or at levels that justify further analyses needed for risk assessment. Depending on the sample type, a certain fraction of the TF can be extracted using organic solvents (extractable organic fluorine, EOF) or by using a sorbent, which is then analysed for TF (adsorbable organic fluorine, AOF).
2. *Total Oxidizable Precursor Assay*
   The total oxidizable precursor (TOP) assay was developed to quantify PFAS precursors that oxidize to PFAAs in water samples and has further been applied to a wider range of sample types as for example soil (Janda, J. et al., 2019). Samples are quantified for PFAAs using targeted analysis before and after application of the TOP-assay. The difference between the levels of PFAAs before and after treatment is considered to be the total concentration of the oxidizable PFAA-precursors.
3. *Non-target screening (NTS) of PFASs*
   Non-target approaches aim to identify the unknown PFASs present in a given sample based on high resolution mass spectrometry coupled to either LC (for ionic) or GC (neutral PFASs). NTS is based on applying HRMS database searches, recursive molecular feature extraction

(MFE)) and suspect screening applying mass defect, MS/MS fragmentation patterns or homologue search methodologies to identify some of these unknown structures (McCord & Strynar, 2019).

4. *Suspect screening and targeted analysis of known PFAS*

   Ultra-trace concentrations of PFAS can be measured today in every food-, feed- and food packing item on the marked, enabling a thorough monitoring of known PFAS. Modern analytical instrumentation and automated sample handling allow for fast and (relatively) cheap analysis of many samples. However, the lack of international methods is hampering the comparability of reported data.

The aims of this presentation are to discuss 1) grouping approaches for PFAS measurements and 2) outline the way forward and remaining challenges in measuring PFAS in food, feed and food packaging.

References

McDonough, C. A.; Guelfo, J. L.; Higgins, C. P. (2018) Measuring Total PFASs in Water: The Tradeoff between Selectivity and Inclusivity. Current Opinion in Environmental Science & Health

Janda, J. et al. (2019) Closing the gap – inclusion of ultrashort-chain perfluoroalkyl carboxylic acids in the total oxidizable precursor (TOP) assay protocol Environmental Science: Processes & Impacts, 21, 1926-1935

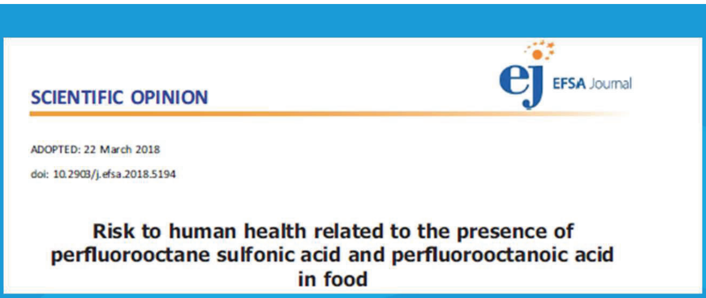
McCord, J.. Strynar, M. (2019) Identification of Per- and Polyfluoroalkyl Substances in the Cape Fear River by High Resolution Mass Spectrometry and Nontargeted Screening James, Environmental Science & Technology 53 (9), 4717-4727

Characterisation of PFAS in food, crops, feed (including packing material)

Dorte Herzke
dhe@nilu.no

NILU
Norsk institutt for luftforskning
Norwegian Institute for Air Research

PFAS Global Science Panel



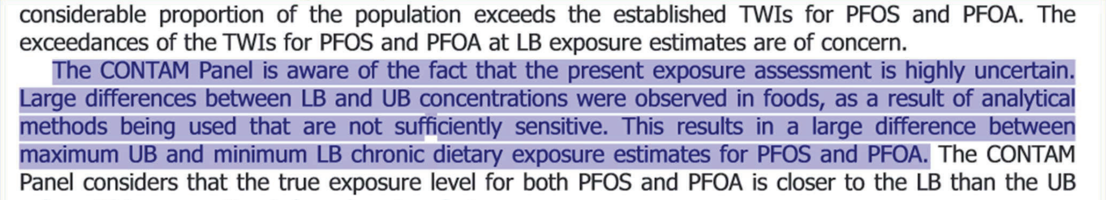
SCIENTIFIC OPINION

EFSA Journal

ADOPTED: 22 March 2018

doi: 10.2903/j.efsa.2018.5194

Risk to human health related to the presence of perfluorooctane sulfonic acid and perfluorooctanoic acid in food



considerable proportion of the population exceeds the established TWIs for PFOS and PFOA. The exceedances of the TWIs for PFOS and PFOA at LB exposure estimates are of concern.

The CONTAM Panel is aware of the fact that the present exposure assessment is highly uncertain. Large differences between LB and UB concentrations were observed in foods, as a result of analytical methods being used that are not sufficiently sensitive. This results in a large difference between maximum UB and minimum LB chronic dietary exposure estimates for PFOS and PFOA. The CONTAM Panel considers that the true exposure level for both PFOS and PFOA is closer to the LB than the UB

TWI; tolerable weekly intake:

PFOS 13 ng/kg bw per week

PFOA 6 ng/kg bw per week

NILU

https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2018.5194

Sources to PFAS in food

- By bioaccumulation in aquatic and terrestrial food chain
- By degradation of precursors
- By contamination from food packaging
- During processing
- Others?

→ Result is a different PFAS composition

Content

1) Sampling techniques and protocols
2) Analytical methods and target parameters (PFAS total, PFAS sum, individual components)
3) Reference samples
4) New insights into BCF & MRL

Short history of conventional PFAS analysis until early 2010s

1950s Total organic F analyzed by combustion

1968 Taves postulates two forms of fluoride in human serum (Nature *217* (1968) 1050-1051)

1976 Taves *et al.* suggest that organic fluorine in human serum is PFOA

1990s Moody *et al.* use GC/MS after derivatization and later ^{19}F-NMR and LC/MS/MS for analysis of PFAAs in water

2001 Hansen *et al.* publish the first trace analytical method for PFASs based on HPLC/MS/MS (ES&T *35* (2001) 766-770)

2003 First international meeting of scientists in Hamburg, Germany, discussing analytical challenges in the determination of PFOA (and other PFASs)

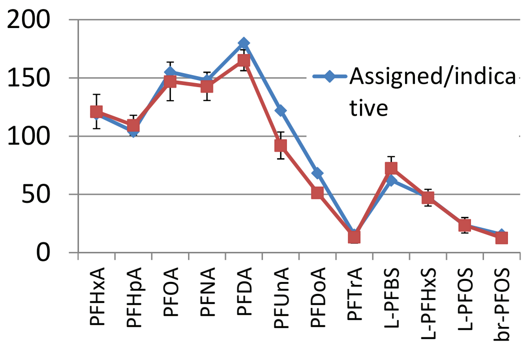
2004 Detection limits of ppq (pg/L/kg) achieved after elemination of instrumental blanks etc by Yamashita *et al.*, (ES&T *38* (2004) 5522-5528)

Ever since: exponential increase in number of papers per year including/reflecting continuous improvements of detection limits and measured nr. of PFAS in multianalyses runs and advanced HRMS techniques

→ Everything is under controll

Improved QA/QC and sensitivities

PERFOOD Interlab study, vegetables (ng/kg):



Z-scores between 0.06 and 1.4

LOQs (ng/kg)	
PFHxA	6.5
PFHpA	1.4
PFOA	0.1
PFNA	0.4
PFDcA	2.4
PFUnA	1.1
PFDoA	1.9
PFTrA	7.4
PFTeA	1.4
PFOSA	0.2
PFBS	0.4
PFHxS	0.5
PFOSlin	1.4
PFDcS	3.0

→ Everything is under controll

Growing PFAS universe…

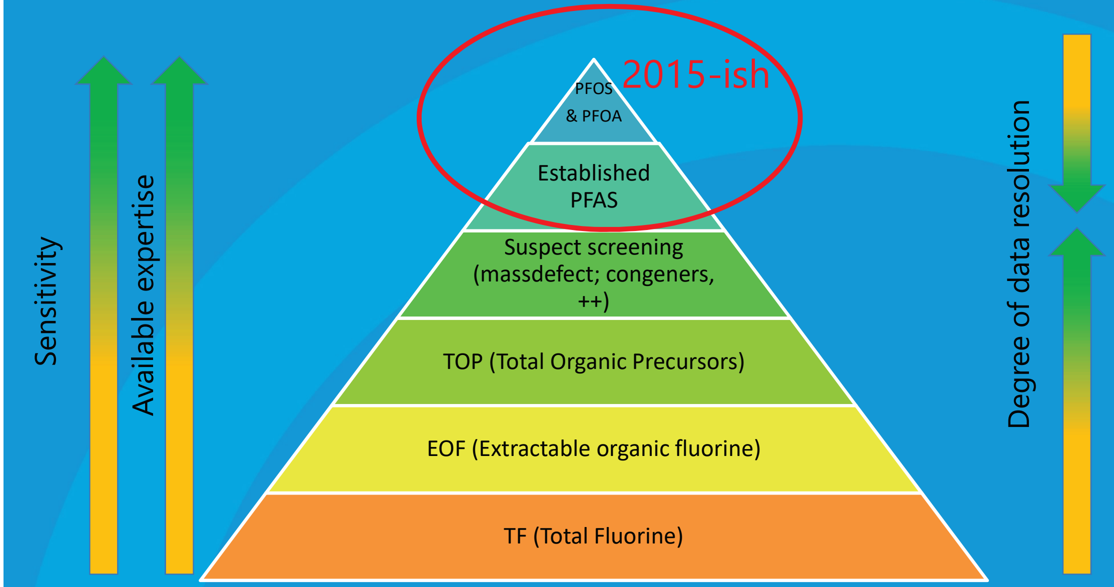
Will they all be in food too?

4730 PFAS related CAS nrs

Ranging from volatiles to very water soluble to polymers

…growing analytical challenge

New tools needed…



Sensitivity

Available expertise

2015-ish

PFOS & PFOA

Established PFAS

Suspect screening (massdefect; congeners, ++)

TOP (Total Organic Precursors)

EOF (Extractable organic fluorine)

TF (Total Fluorine)

Degree of data resolution

What is the question?

I. Does the food/ feed/ packaging contain any PFAS?
II. Which PFAS can be found in food and feed?
III. Are there any unknown PFAS in food and feed?
IV. Is the food safe to be consumed ?
V. Which dietary items are most relevant (regulation, dietary advice)?

Choice of Project Design

I. Sampling design
   (agegroup, raw/ cooked, period, monitoring, research, random/ selective)
II. Sample clean up method
   (extraction, matrix removal, concentration steps)
III. Required MDLs
   (As good as possible vs. good enough)
IV. Required resolution of data
   (sumPFAS, single known, unknowns)

I. Selection of Sampling design

- Uniform sampling and sample treatment:
  - COMMISSION RECOMMENDATION 2010/161/EU of 17 March 2010
  - Annex I to Commission Regulation (EC) No 1883/2006 of 19 December 2006
  - Grouping of food items according to EFSA → guarantee later use of results
  - Documentation at each step of sample treatment assured

INSTITUTE OF CHEMICAL TECHNOLOGY PRAGUE

Sampling meat - the PERFOOD project.

Prepared by:
Vladimir Kocourek (vladimir.kocourek@vscht.cz) and Jana Hajslova (jana.hajslova@vscht.cz)

based on Teleconference (22nd April 2010, 11.00 UTC)

A. PORK MEAT

1. Part to be taken from each animal: about 250 - 300 g (boneless, unpacked).
2. In 2 – 3 supermarkets, buy fresh pork loin (centre part) from 4 – 5 animals.

Loin cutlet

3. Put all samples individually in polyethylene (microtene) bags and transport them to the laboratory the same day. Temperature during transportation shall be kept at 2-4 °C but not exceeding 7 °C for more than 60 min.
4. Fill in Sampling records with information on individual samples.
5. Remove the rest of bones (if any) and weight the meat. At least 250 g is necessary from each (individual) animal.
6. Cut-off all fatty (lard) parts. Weight muscle tissue fraction and calculate the ratio of "pure" (lean as much as possible) meat.

1

Sampling Protocol for food items for the PERFOOD project.

1. **General**

In this manual a detailed sampling protocol is presented for the sampling of food items in Europe for measurement of perfluor compounds, in order to generate data that allow to make a risk evaluation of PFCs present in food for human consumption.

Although the European Comisson has published a recommendation on the monitoring of perfluoralkynated substances in food (COMMISSION RECOMMENDATION 2010/161/EU of 17 March 2010) this is not fully applicable for the present study.
The recommendation refers to the sampling procedure as laid down in Annex I to Commission Regulation (EC) No 1883/2006 of 19 December 2006 laying down methods of sampling and analysis for the official control of levels of dioxins and dioxin-like PCBs in certain foodstuffs (2) in order to ensure that the samples are representative for the sampled lot. That procedure however, is developed for another purpose, i.e. to analyse pollutants in certain lots of food. Since the PERFOOD aims to get a preliminary global idea of the risks posed by consumption of food with respect of the PFC content., we prefer to follow a food basket study. However, some general sampling principles used in that document are withdrawn for our sampling strategy.

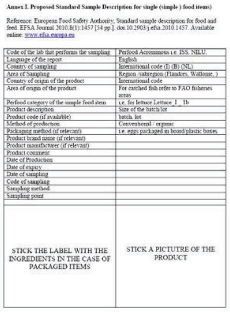
- Four countries, each representing a European region, are selected (N, Cz, B, I) where food items will be sampled.
- The two most important food distribution companies in a country have to be selected e.g.: for Belgium this are Colruyt; Delhaize or Carrefour
  Food items are divided in 14 categories and sampling strategy and sample treatment will depend on the category

During the first sampling period only raw samples and no composite samples neither couldrons are collected.
For all categories a sub-sample of each homogenized item (of a certain lot, which can be a single brassica or 100g homogenized peas) is preserved for later individual analysis if needed. Only edible parts of the food items will be selected for homogenization and analyses.

Food packaging consisting of cardboard or other paper-like material has to be stored for later analyses (10 x 10cm^2) of each article. Storage: cool and dry.

In the selected supermarkets randomly 3-10 items are sampled, depending on the number of lots or marks present in both supermarkets together (see table 1).
In the list of items the category will be specified
All samples (pools) are extracted in duplicate.

The food samples will be analyzed by three different labs. Each lab will analyze certain matrices. In the sample list is indicated which lab is measuring what type of matrices.

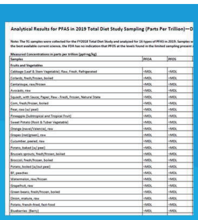


Annex I. Proposed Standard Sample Description for single (simple) food items)

Reference: European Food Safety Authority; Standard sample description for food and feed. EFSA Journal 2010;8(1):1457 [54 pp.]. doi:10.2903/j.efsa.2010.1457. Available online: www.efsa.europa.eu

Code of the lab that performs the sampling	Perfood Acronimous i.e. ISS, NILU,
Language of the report	English
Country of sampling	International code (I) (B) (NL)
Area of Sampling	Region /subregion (Flandres, Wallone,)
Country of origin of the product	International code
Area of origin of the product	For catched fish refer to FAO fisheries areas
Perfood category of the simple food item	i.e. for lettuce Lettuce_I_1b
Product description	Size of the batch/lot
Product code (if available)	batch, lot
Method of production	Conventional / organic
Packaging method (if relevant)	i.e. eggs packaged in board/plastic boxes
Product brand name (if relevant)	
Product manufacturer (if relevant)	
Product comment	
Date of Production	
Date of expiry	
Date of sampling	
Code of sampling	
Sampling method	
Sampling point	
STICK THE LABEL WITH THE INGREDIENTS IN THE CASE OF PACKAGED ITEMS	STICK A PICTUTRE OF THE PRODUCT

I. Sampling campaign:



Analytical Results for PFAS in 2019 Total Diet Study Sampling (Parts Per Trillion)—D

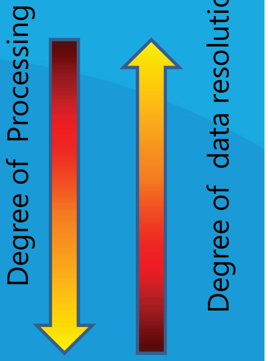
Note: The 91 samples were collected for the FY2018 Total Diet Study and analyzed for 16 types of PFAS in 2019. Samples w
the best available current science, the FDA has no indication that PFOS at the levels found in the limited sampling present

Measured Concentrations in parts per trillion (ppt=ng/kg)

Samples	PFOA	PFOS
Fruits and Vegetables		
Cabbage (Leaf & Stem Vegetable); Raw, Fresh, Refrigerated	<MDL	<MDL
Collards, fresh/frozen, boiled	<MDL	<MDL
Cantaloupe, raw/frozen	<MDL	<MDL
Avocado, raw	<MDL	<MDL
Squash, with Sauce; Paper; Raw - Fresh, Frozen, Natural State	<MDL	<MDL
Corn, fresh/frozen, boiled	<MDL	<MDL
Pear, raw (w/ peel)	<MDL	<MDL
Pineapple (Subtropical and Tropical Fruit)	<MDL	<MDL
Sweet Potato (Root & Tuber Vegetable)	<MDL	<MDL
Orange (navel/Valencia), raw	<MDL	<MDL
Grapes (red/green), raw	<MDL	<MDL
Cucumber, peeled, raw	<MDL	<MDL
Potato, baked (w/ peel)	<MDL	<MDL
Brussels sprouts, fresh/frozen, boiled	<MDL	<MDL
Broccoli, fresh/frozen, boiled	<MDL	<MDL
Potato, boiled (w/out peel)	<MDL	<MDL
BF, peaches	<MDL	<MDL
Watermelon, raw/frozen	<MDL	<MDL
Grapefruit, raw	<MDL	<MDL
Green beans, fresh/frozen, boiled	<MDL	<MDL
Onion, mature, raw	<MDL	<MDL
Potato, french-fried, fast-food	<MDL	<MDL
Blueberries (Berry)	<MDL	<MDL

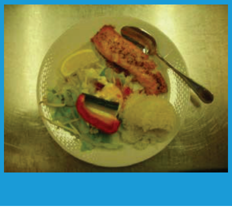
- Raw items randomly selected in supermarkeds (Total Diet Study)
- Hot spot samples (worst case scenario)
- Composite food (Ready to eat/cook food items):
- Cauldrons (whole meals, parallel sampling)
- Food packaging

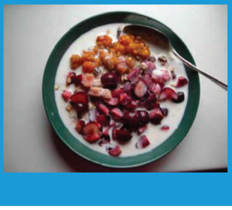
→ once, 24 hours, a week



Degree of Processing

Degree of data resolution





II. Examples for Sample clean up methods for ionic PFAS (C4 – C16)

U.S. FOOD & DRUG ADMINISTRATION

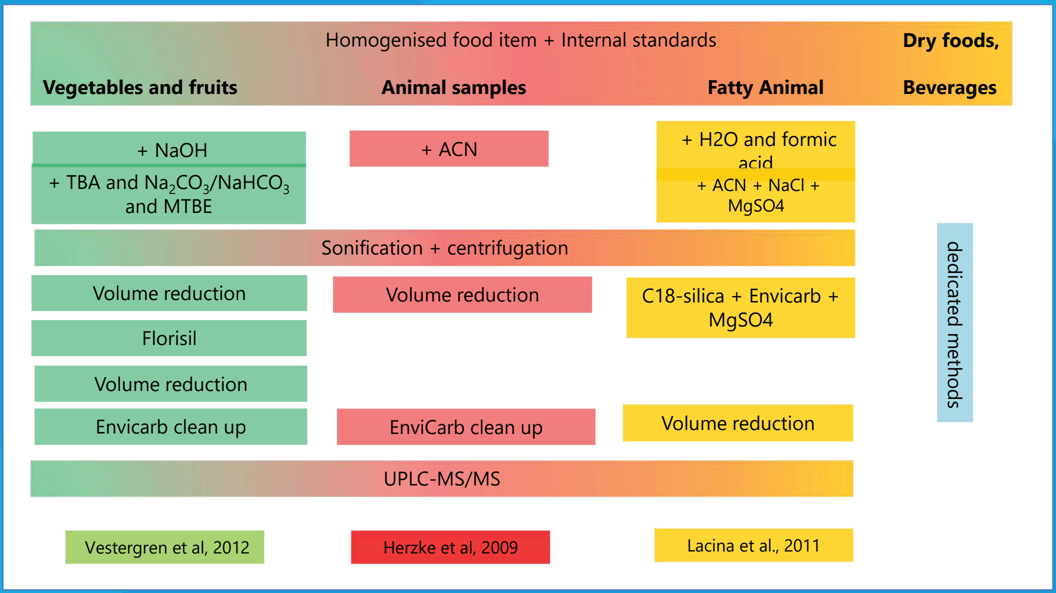
FDA Foods Program Compendium of Analytical Laboratory Methods: Chemical Analytical Manual (CAM)

ETHOD NUMBER:

OSTING DATE:

OSTING EXPIRATION DATE:

OGRAM AREA: Chemical Contaminants



Homogenised food item + Internal standards

Vegetables and fruits | **Animal samples** | **Fatty Animal** | **Dry foods, Beverages**

Vegetables and fruits:
+ NaOH
+ TBA and $Na_2CO_3/NaHCO_3$ and MTBE

Animal samples:
+ ACN

Fatty Animal:
+ H2O and formic acid
+ ACN + NaCl + MgSO4

Dry foods, Beverages: dedicated methods

Sonification + centrifugation

Vegetables and fruits:
Volume reduction
Florisil
Volume reduction
Envicarb clean up

Animal samples:
Volume reduction
EnviCarb clean up

Fatty Animal:
C18-silica + Envicarb + MgSO4
Volume reduction

UPLC-MS/MS

Vestergren et al, 2012 | Herzke et al, 2009 | Lacina et al., 2011

… other methods for neutral, very volatile, ultra short/ long chained, polymers ++

NILU

What is the question?

I. Does the food/ feed contain any PFAS?
II. Which PFAS can be found in food and feed?
III. Are their any unknown PFAS in food and feed?
IV. Is the food safe to be consumed ?
V. Which dietary items are most relevant?

Many techniques available →
choose appropriately for the question

NILU

Project design

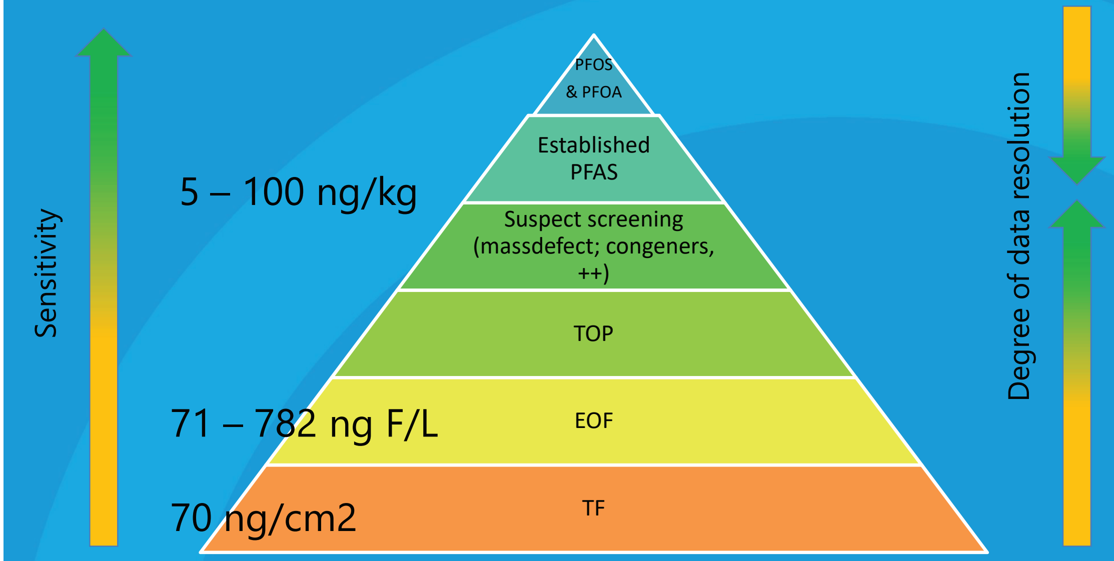
I. Sampling design
(agegroup, raw/ cooked, period, monitoring, research)

II. Sample clean up method
(extraction, matrix removal, concentration steps)

III. Required MDLs
(as low as possible → ≈LB)

IV. Required resolution of data
(sumPFAS, single known, unknowns, total organic F)

III. Required MDLs



Sensitivity

PFOS & PFOA

Established PFAS

Suspect screening (massdefect; congeners, ++)

TOP

EOF

TF

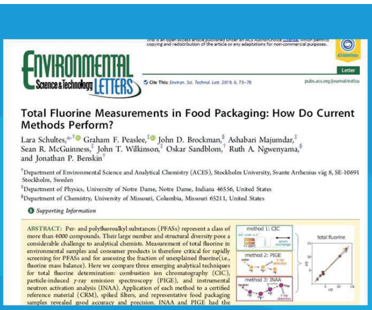
5 – 100 ng/kg

71 – 782 ng F/L

70 ng/cm2

Degree of data resolution

Total Fluorine (TF)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Environmental Science & Technology Letters

Letter

Cite This: Environ. Sci. Technol. Lett. 2019, 6, 73−78

pubs.acs.org/journal/estlcu

Total Fluorine Measurements in Food Packaging: How Do Current Methods Perform?

Lara Schultes,*[†] Graham F. Peaslee,[‡] John D. Brockman,[§] Ashabari Majumdar,[‡] Sean R. McGuinness,[‡] John T. Wilkinson,[‡] Oskar Sandblom,[†] Ruth A. Ngwenyama,[§] and Jonathan P. Benskin[†]

[†] Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, Svante Arrhenius väg 8, SE-10691 Stockholm, Sweden

[‡] Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, United States

[§] Department of Chemistry, University of Missouri, Columbia, Missouri 65211, United States

Supporting Information

ABSTRACT: Per- and polyfluoroalkyl substances (PFASs) represent a class of more than 4000 compounds. Their large number and structural diversity pose a considerable challenge to analytical chemists. Measurement of total fluorine in environmental samples and consumer products is therefore critical for rapidly screening for PFASs and for assessing the fraction of unexplained fluorine (i.e., fluorine mass balance). Here we compare three emerging analytical techniques for total fluorine determination: combustion ion chromatography (CIC), particle-induced γ-ray emission spectroscopy (PIGE), and instrumental neutron activation analysis (INAA). Application of each method to a certified reference material (CRM), spiked filters, and representative food packaging samples revealed good accuracy and precision. INAA and PIGE had the

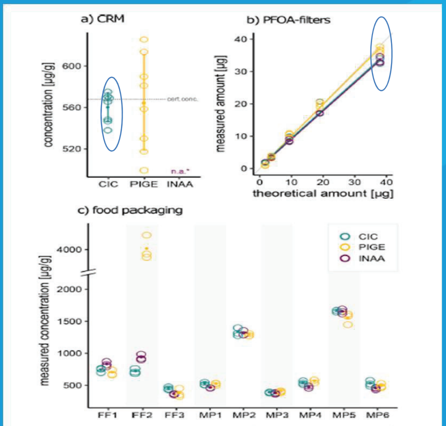


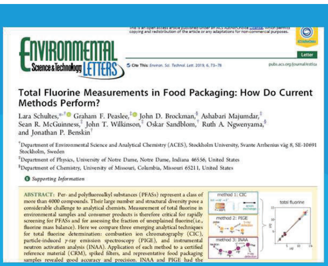
Figure 1. Comparison of TF methods (CIC, PIGE, and INAA) by means of (a) certified reference material (CRM) measurements (n = 8; circles) and means (dots) (the error bar represents the standard deviation, and the gray line indicates the certified concentration), (b) PFOA-spiked filter measurements vs theoretical concentrations (the gray line indicates slope = 1 and intercept = 0), and (c) food packaging samples (circles, data points; dots, means). Note the discrepancy in FF2 by PIGE due to the thickness and heterogeneity of this paperboard sample. *n.a., not analyzed due to interference.

1. Combustion ion chromatography (CIC)
2. Particle-induced γ-ray emission (PIGE) spectroscopy
3. Instrumental neutron activation analysis (INAA)

CIC is more precise but destructive,
INAA is sensitive to disturbances caused by Aluminium,
PIGE measures only F on surface (overestimate sample with surface coating)

NILU

TF example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Environmental Science & Technology Letters

Letter

Cite This: Environ. Sci. Technol. Lett. 2019, 6, 73−78

pubs.acs.org/journal/estlcu

Total Fluorine Measurements in Food Packaging: How Do Current Methods Perform?

Lara Schultes,*[†] Graham F. Peaslee,[‡] John D. Brockman,[§] Ashabari Majumdar,[‡] Sean R. McGuinness,[‡] John T. Wilkinson,[‡] Oskar Sandblom,[†] Ruth A. Ngwenyama,[§] and Jonathan P. Benskin[†]

[†] Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, Svante Arrhenius väg 8, SE-10691 Stockholm, Sweden

[‡] Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, United States

[§] Department of Chemistry, University of Missouri, Columbia, Missouri 65211, United States

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Environmental Science & Technology Letters

Letter

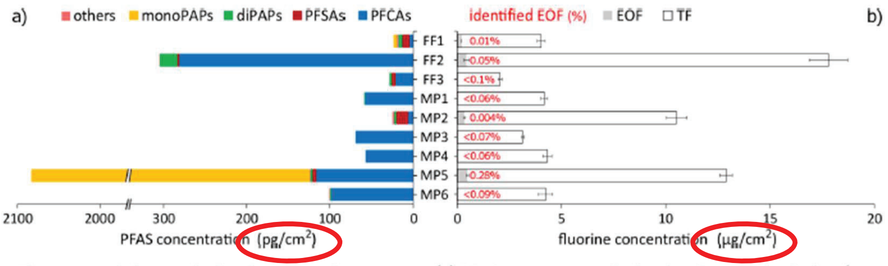
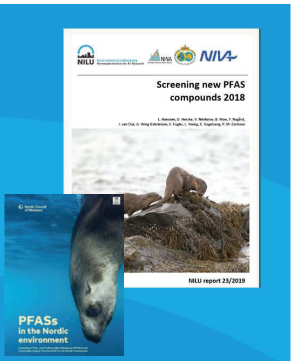


Figure 2. Fluorine mass balance in food packaging samples comprising (a) PFAS concentrations displayed as the sum of each class (in picograms per square centimeter) as measured by UHPLC−MS/MS and (b) total fluorine and extractable organic fluorine contents (error bars represent the standard deviation of triplicate measurements) in micrograms per square centimeter as measured by CIC. The percentage of EOF identified by the sum of target PFAS (ΣC_{F_PFAS}) is indicated in red.

Used by the Danish Ministry of the Environment and Food;
total fluorine indicator value of 0.1 µg/cm^2 in food packaging
No information on source of Fluorine.
Additional instrumentation is needed

NILU

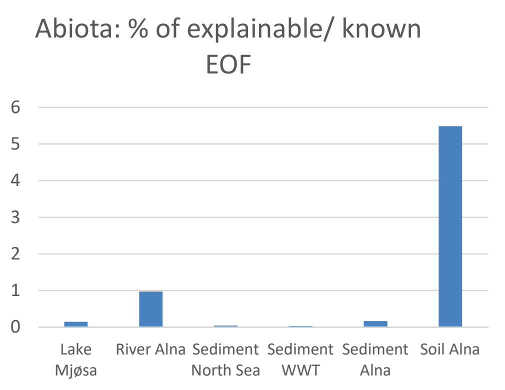
Extractable Organic Fluorine (EOF)→ TF of a PFAS extract

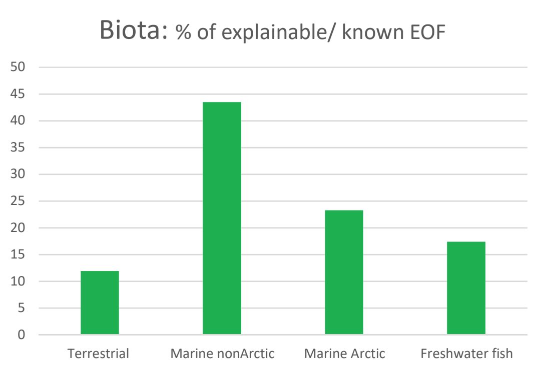

Screening new PFAS compounds 2018

L. Hanssen, D. Herzke, V. Nikiforov, B. Moe, T. Nygård, J. van Dijk, G. Wing Gabrielsen, E. Fuglei, L. Yeung, C. Vogelsang, P. M. Carlsson

NILU report 23/2019

PFASs in the Nordic environment

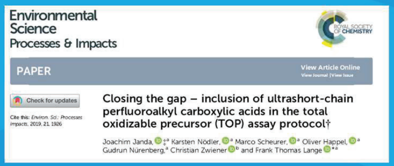




Can be used for food extracts,
2 extracts needed using the same clean up procedure
Information on PFAS ID is lost
Need additional instrumentation

NILU

Total oxidisable precursor assay (TOP)


Environmental Science Processes & Impacts

PAPER

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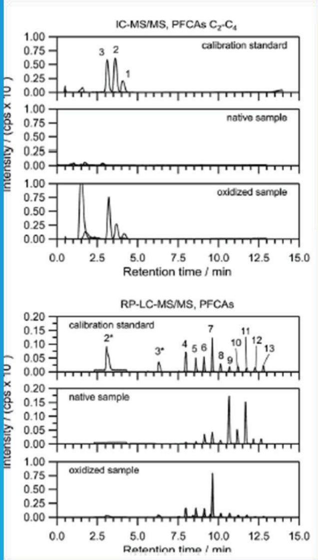
Cite this: *Environ. Sci.: Processes Impacts*, 2019, 21, 1926

Closing the gap – inclusion of ultrashort-chain perfluoroalkyl carboxylic acids in the total oxidizable precursor (TOP) assay protocol†

Joachim Janda,‡[a] Karsten Nödler,[a] Marco Scheurer,[a] Oliver Happel,[a] Gudrun Nürenberg,[a] Christian Zwiener[b] and Frank Thomas Lange*[a]



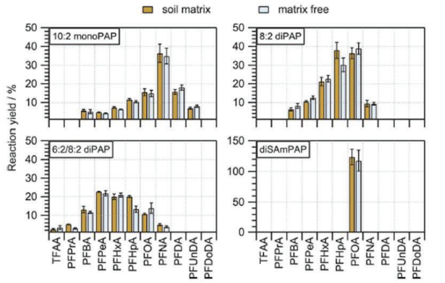


Fig. 3 Molar reaction yields for PFCAs formed from oxidation of PAPs and diSAmPAP by the top assay in presence and absence (matrix free) of a soil matrix. The recoveries are based on the maximum achievable concentrations from the applied PAPs and diSAmPAP; error bars: 1σ, $n = 3$.

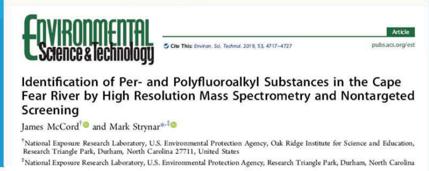
- Matrix does not infer (soil)
- A broad range of PFCA chainlengths are formed
- Not well tested for a broad variety of dietary items
- Information of precursor ID is lost

NILU

Suspect- and Non target screening using HRMS

Facilitation of specific similarities of per- and polyfluorinated organic molecules:

Massdefect
Isomeric structures
Specific molecular sites
Data mining



Environmental Science & Technology

Article

Cite This: Environ. Sci. Technol. 2019, 53, 4717−4727

pubs.acs.org/est

Identification of Per- and Polyfluoroalkyl Substances in the Cape Fear River by High Resolution Mass Spectrometry and Nontargeted Screening

James McCord[†] and Mark Strynar[*,‡]

[†] National Exposure Research Laboratory, U.S. Environmental Protection Agency, Oak Ridge Institute for Science and Education, Research Triangle Park, Durham, North Carolina 27711, United States

[‡] National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, Durham, North Carolina

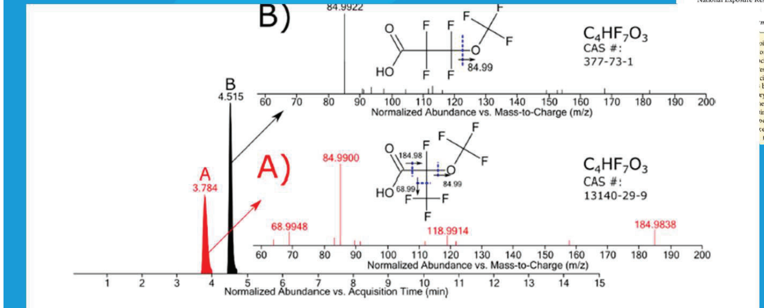


Figure 1. Determination of isomeric branching of perfluorinated ether compounds based on MS/MS fragmentation patterns. Compound 2A elutes at 3.8 min and has multiple major mass fragments. Compound 2B elutes later at 4.5 min and fragments only at the terminal ether linkage.

Requires special training, advanced instrumentation and computational capacities → research state → PFAS ID is available

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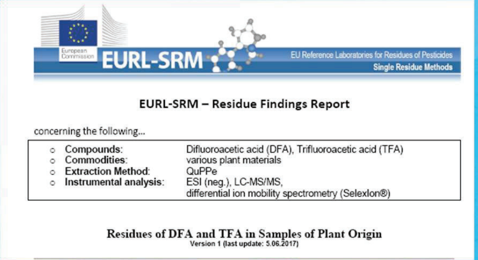
And some other examples



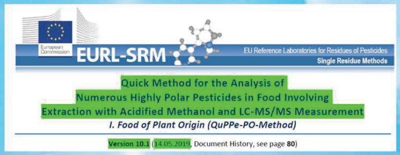
European Commission EURL-SRM EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

EURL-SRM – Residue Findings Report

concerning the following...

○ **Compounds:**	Difluoroacetic acid (DFA), Trifluoroacetic acid (TFA)
○ **Commodities:**	various plant materials
○ **Extraction Method:**	QuPPe
○ **Instrumental analysis:**	ESI (neg.), LC-MS/MS, differential ion mobility spectrometry (Selexlon®)

Residues of DFA and TFA in Samples of Plant Origin
Version 1 (last update: 5.06.2017)



European Commission EURL-SRM EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

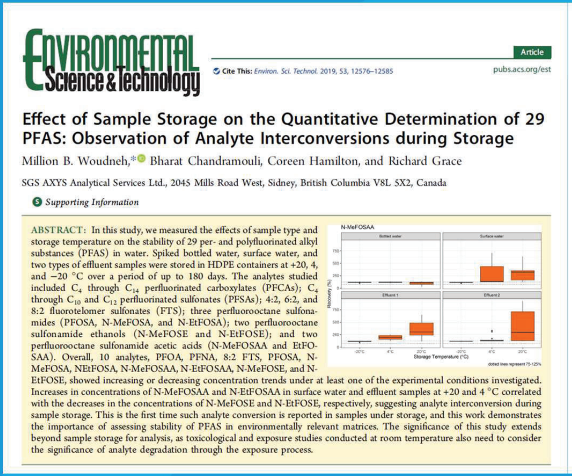
Quick Method for the Analysis of
Numerous Highly Polar Pesticides in Food Involving
Extraction with Acidified Methanol and LC-MS/MS Measurement
I. Food of Plant Origin (QuPPe-PO-Method)

Version 10.1 (14.05.2019, Document History, see page **80**)

… TFA and DFA as breakdown products from pesticides and HCFCs, fluoropolymers and others (> 140 compounds identified by EFSA)

- Reporting limit for TFA in fruit and vegetables : 40 µg/kg (40 ng/g) found in 50% of all samples (n > 1000)
- The samples were extracted via the QuPPe method (Quick Polar Pesticides Method) and measured by LC-MS/MS

Recent findings on storage and analysis conditions



Environmental Science & Technology

Article

Cite This: Environ. Sci. Technol. 2019, 53, 12576−12585

pubs.acs.org/est

Effect of Sample Storage on the Quantitative Determination of 29 PFAS: Observation of Analyte Interconversions during Storage

Million B. Woudneh,* Bharat Chandramouli, Coreen Hamilton, and Richard Grace

SGS AXYS Analytical Services Ltd., 2045 Mills Road West, Sidney, British Columbia V8L 5X2, Canada

Supporting Information

ABSTRACT: In this study, we measured the effects of sample type and storage temperature on the stability of 29 per- and polyfluorinated alkyl substances (PFAS) in water. Spiked bottled water, surface water, and two types of effluent samples were stored in HDPE containers at +20, 4, and −20 °C over a period of up to 180 days. The analytes studied included C_4 through C_{14} perfluorinated carboxylates (PFCAs); C_4 through C_{10} and C_{12} perfluorinated sulfonates (PFSAs); 4:2, 6:2, and 8:2 fluorotelomer sulfonates (FTS); three perfluorooctane sulfonamides (PFOSA, N-MeFOSA, and N-EtFOSA); two perfluorooctane sulfonamide ethanols (N-MeFOSE and N-EtFOSE); and two perfluorooctane sulfonamide acetic acids (N-MeFOSAA and EtFOSAA). Overall, 10 analytes, PFOA, PFNA, 8:2 FTS, PFOSA, N-MeFOSA, NEtFOSA, N-MeFOSAA, N-EtFOSAA, N-MeFOSE, and N-EtFOSE, showed increasing or decreasing concentration trends under at least one of the experimental conditions investigated. Increases in concentrations of N-MeFOSAA and N-EtFOSAA in surface water and effluent samples at +20 and 4 °C correlated with the decreases in the concentrations of N-MeFOSE and N-EtFOSE, respectively, suggesting analyte interconversion during sample storage. This is the first time such analyte conversion is reported in samples under storage, and this work demonstrates the importance of assessing stability of PFAS in environmentally relevant matrices. The significance of this study extends beyond sample storage for analysis, as toxicological and exposure studies conducted at room temperature also need to consider the significance of analyte degradation through the exposure process.

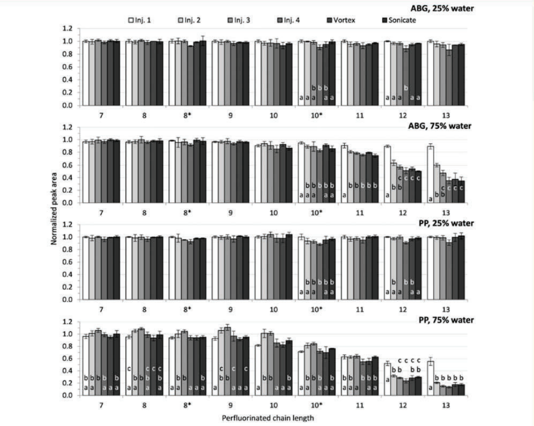


Fig. 2 Mean (*n* = 3) normalized peak areas *vs.* PFAA perfluorinated chain length for each vial material and solvent composition tested. For each material type, plotted values for each compound are normalized to the mean peak area for that compound in the first injections from the solutions containing 25% water. Bars represent sequential injections from day one (Inj. 1–3), day two (Inj. 4), day 2 after vortexing for 2 min (vortex), and day 2 after sonicating for 2 min (Sonicate). Embedded letters signify groups likely to be different based on multiple comparison testing (Tukey,

… storage temperature and - vessel and water content matter

Environmental Science
Water Research & Technology

PAPER

View Article Online

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Towards the development of a standardized method for extraction and analysis of PFAS in biological tissues†

Adam D. Point, Thomas M. Holsen, Sujan Fernando, Philip K. Hopke and Bernard S. Crimmins

---

Content

1) Sampling techniques and protocols

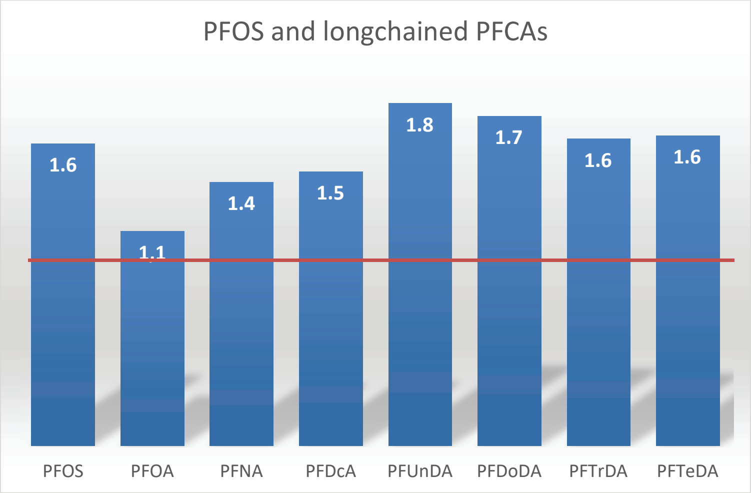
2) Analytical methods and target parameters (PFAS total, PFAS sum, individual components)

3) Reference samples → fish (NIST; IRMM) only few PFAS

4) New insights into BCF & MRL

BCF: Short chained PFAS→ vegetables (<C8)
Long chained PFAS → foodchain (>C9)

TMFs in a terrestrial foodchain (worm, small bird, bird of prey)

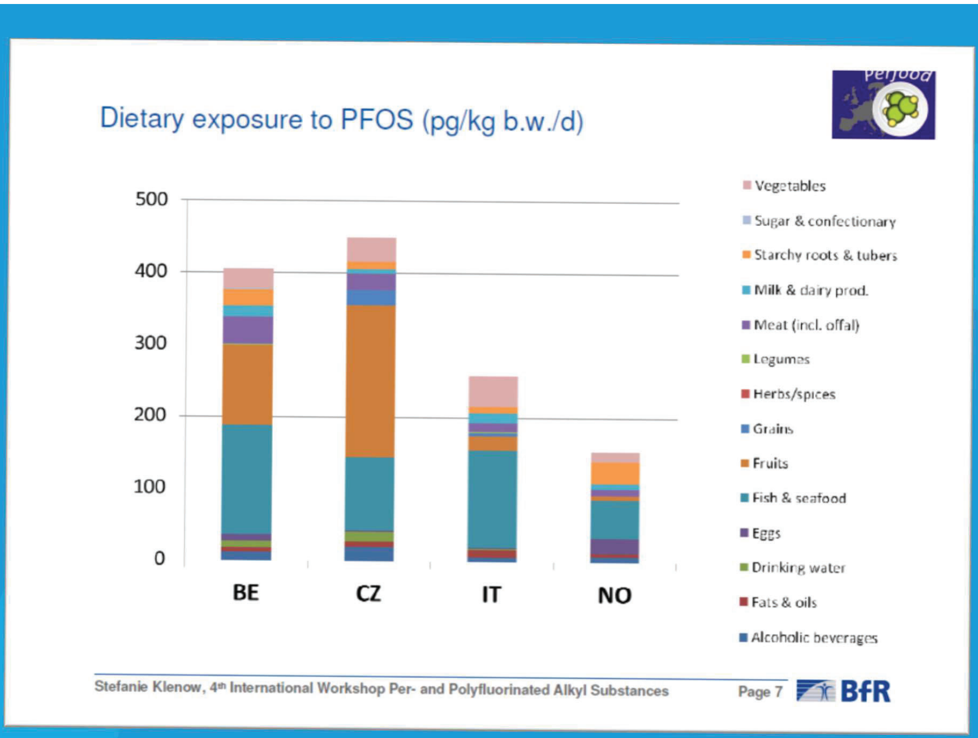



Environmental pollutants in the terrestrial and urban environment 2018

Content

1) Sampling techniques and protocols
2) Analytical methods and target parameters (PFAS total, PFAS sum, individual components)
3) Reference samples → fish (NIST) only few PFAS
4) New insights into BCF & MRL

Maximum Residue Levels is the highest level of a pesticide residue that is legally tolerated in or on food or feed when pesticides are applied correctly (Good Agricultural Practice). → TWI → need good dietary consumption data/ input data in the EFSA database / add countries who are not reporting to identify important contributors to the local dietary exposure scenario → PERFOOD data

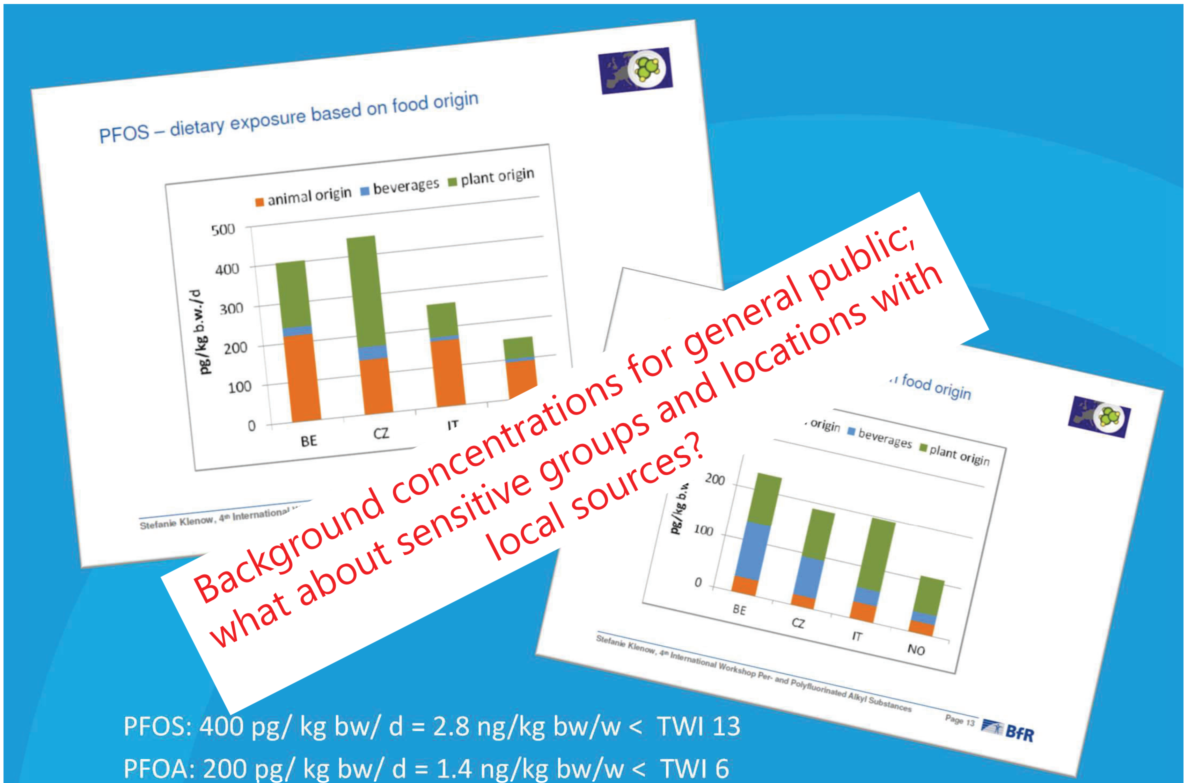


Dietary exposure to PFOS (pg/kg b.w./d)

Stefanie Klenow, 4th International Workshop Per- and Polyfluorinated Alkyl Substances

Page 7 BfR

400 pg/ kg bw/ d = 2.8 ng/kg bw/w < TWI 13



PFOS – dietary exposure based on food origin

Stefanie Klenow, 4th International

… food origin

Stefanie Klenow, 4th International Workshop Per- and Polyfluorinated Alkyl Substances

Page 13 BfR

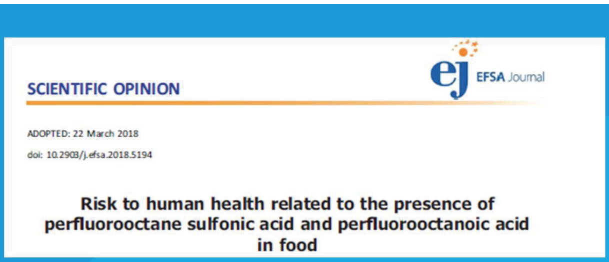
Background concentrations for general public;
what about sensitive groups and locations with
local sources?

PFOS: 400 pg/ kg bw/ d = 2.8 ng/kg bw/w < TWI 13

PFOA: 200 pg/ kg bw/ d = 1.4 ng/kg bw/w < TWI 6

Main contributing food categories differ with respect to regions and compounds

→ Good and comparable consumption data are not easily available throughout Europe

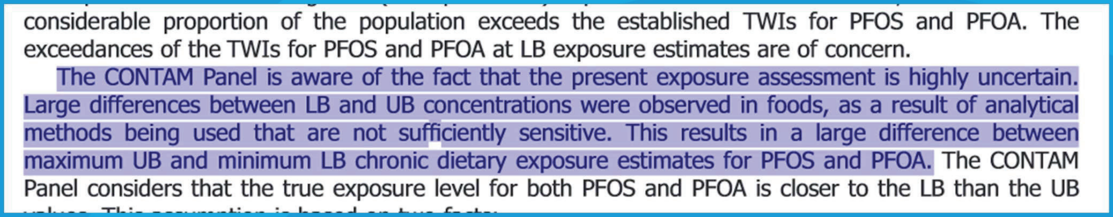

SCIENTIFIC OPINION

EFSA Journal

ADOPTED: 22 March 2018

doi: 10.2903/j.efsa.2018.5194

Risk to human health related to the presence of perfluorooctane sulfonic acid and perfluorooctanoic acid in food


considerable proportion of the population exceeds the established TWIs for PFOS and PFOA. The exceedances of the TWIs for PFOS and PFOA at LB exposure estimates are of concern.

The CONTAM Panel is aware of the fact that the present exposure assessment is highly uncertain. Large differences between LB and UB concentrations were observed in foods, as a result of analytical methods being used that are not sufficiently sensitive. This results in a large difference between maximum UB and minimum LB chronic dietary exposure estimates for PFOS and PFOA. The CONTAM Panel considers that the true exposure level for both PFOS and PFOA is closer to the LB than the UB

LB ≠ UB is caused by:

1. **High rate of non detects → unsuitable instrumentation, methodology used**
2. **Elevated LOQ due to contamination and high variability of contamination (high STDEV)**

- **→ Methods and instrumentation are good enough today to avoid this for most PFAAs and PFSAs, not for others**
  - **→ Quality of data?**

https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2018.5194

… And other PFAS– challenges

- Isotopically mass-labeled and quantification standards not available for a number of new PFAS
- Pure standards not available for branched isomers

- Matrix effects in ionization problematic
- Sorption effects due to low solubility for PFDS and PFCAs > C12 problematic, varies for glass and PP
- Water content in final extract can cause issues
- Quantification of a mixture of isomers problematic
- No qualifier transition available for < C6 PFAS
- Very volatile PFAS … Are very volatile …

«Elements for an EU-strategy for PFASs December 2019

Member states are encouraged to share their monitoring data, via e.g. IPCheM35.

A standardised method should be developed for monitoring total PFASs concentration **with a low detection limit** in various matrices **including food**, products and human blood. Standardised analytical methods by CEN for PFASs need to be developed for enforcement to assure compliance with legislation. «

https://www.eea.europa.eu/themes/human/chemicals/emerging-chemical-risks-in-europe

Water and marine environment

Emerging chemical risks in Europe — 'PFAS'

It is currently not possible to perform in-depth environmental and health risk assessments of all chemical substances in use in Europe because of the great variety of chemicals and their diverse uses. New and legacy chemicals continue to be released into Europe's environment, adding to the total chemical burden on Europe's citizens and ecosystems. Early identification of emerging risks is one of the activities of the European Environment Agency (EEA). This briefing summarises the known and potential risks to human health and the environment in Europe posed by a group of very persistent chemicals, the per- and polyfluorinated alkyl substances (PFAS).

Briefing — Published 12 Dec 2019 — Last modified 12 Dec 2019 — 20 min read

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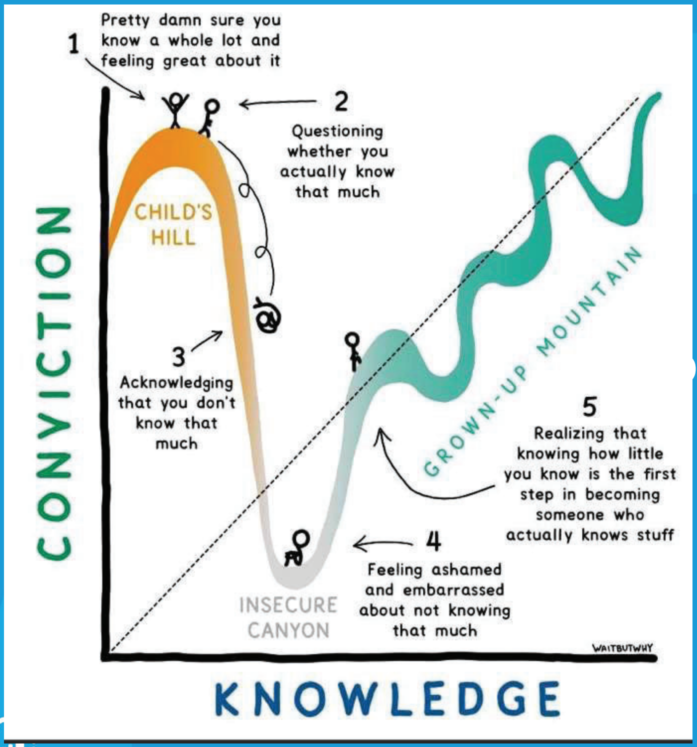
Take home messages

1) We deal with a potentially huge number of chemicals → not all of them are stable in biological samples
2) Study objective governs choice of protocols and techniques
3) PFAS in food and packaging is very simple and very complex at the same time
4) A broad variety of sampling designs and analytical protocols are available
5) Still challenges for an adequate QA/QC (lack of suitable SRMs, ISTD, methods available for all kinds of PFAS; LB = UB)
6) Robust and harmonised input data for European countries are the basis for PFAS intake estimates and also need to fullfill quality requirements (identify key fooditems)



Thank you for your attention

Dorte Herzke
dhe@nilu.no

By Maxolin97

II.5.9 Characterisation of PFAS in other matrices / media - alternatives substitutes for PFAS

Thomas P. Knepper, Tobias Frömel, Isabelle J. Neuwald, Raphael Janousek, Daniel Zahn
Hochschule Fresenius (Germany)

Per- and polyfluoroalkyl substances (PFASs) are applied in a large variety of industries since 1950 and gained worldwide attention due to their unique properties, such as persistency, hydrophobicity and concomitant lipophobicity. As an inevitable consequence, PFASs are released into the environment from various places, often through unconscious or inadvertent release. Due to the toxic and bioaccumulative properties of some longer chain PFASs ($>C_8$), a voluntary phase-out started that led to an increased usage of shorter chain homologs ($<C_8$) and other replacement chemicals. Quite often replacement chemicals are more mobile than their longer chain representatives and thus more likely to enter the water cycle. Additionally, analytical information and knowledge about environmental occurrence of these alternatives to legacy PFASs is still scarce. Thus, various high-resolution non-target and suspect-screening approaches for PFASs are deployed and successfully applied to various non-environmental and environmental samples to screen for C1-C17 PFASs.

This work presents a high-resolution screening approach combined with fragmentation flagging to identify PFASs and other fluorinated substances in a large variety of environmental samples, such as soil, manure, sludge and aerosols.

Further monitoring of non-environmental media included paints, sealants, awnings, public transport seat covers, foils, coatings, durable water repellent textiles, fire-fighting foams. If available, reference materials were used to confirm the structure of novel PFASs and other fluorinated substances and facilitate their quantification. For example, nine liquid building materials, 16 fabrics and foils, and 21 SW's (some sampled repeatedly) were used for the experiments in this work. Sample selection was performed based on the results of finalized and ongoing PFAS monitoring campaigns. Data of their release into the aquatic environment has been determined too.

Additionally, data on fluorinated ionic liquids (ILs), which are a so far only scarcely studied group of fluorinated chemicals, is presented.. Commonly, ILs are used in electrochemistry, for example in batteries or supercapacitors, as a 'green' lubricant replacement for petroleum-based lubricants or as extraction agent for industrial wastes.

Finally, various polyfluorinated substances are shown and discussed in relation to their potential as replacement chemicals for PFOA and PFOS. Also possible transformation pathways are discussed with respect to identify any resulting dead-end products. Also non-fluorinated chemicals as potential replacements will be introduced and critically evaluated.

The authors thank the Federal Ministry of Education and Research (BMBF) for funding the PROTECT project (FKZ: 02WRS1495B) and acknowledge the funding provided by the German Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety (FKZ: 3716644300). Furthermore we thank Merck, Darmstadt, for the supply of solvents and the Hessian Agency for Nature Conservation, Environment and Geology (HLNUG) for the provision of water samples.

HOCHSCHULE FRESENIUS
UNIVERSITY OF APPLIED SCIENCES

4.9 CHARACTERISATION OF PFAS IN OTHER MATRICES / MEDIA - ALTERNATIVES SUBSTITUTES FOR PFAS

WORKSHOP ON PFAS MONITORING IN WATER AND OTHER MEDIA
EC, BRUSSELS
13-14.01.2020

THOMAS P. KNEPPER,
TOBIAS FRÖMEL, RAPHAEL JANOUSEK, ISABELLE J. NEUWALD, DANIEL ZAHN

HOCHSCHULE FRESENIUS, IDSTEIN, GERMANY

HOCHSCHULE FRESENIUS
UNIVERSITY OF APPLIED SCIENCES

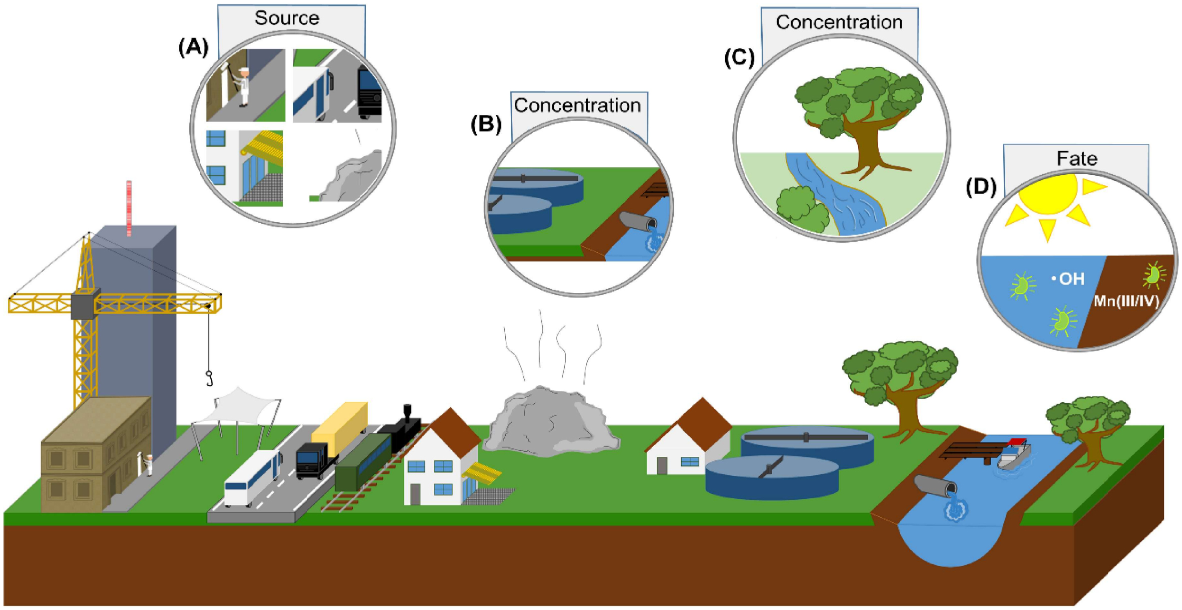
AGENDA

4.9.1. PFAS in non-environmental media (*20 min , break*)

4.9.2. PFAS in other environmental matrices (e.g. soil, manure) (*15 min, break*)

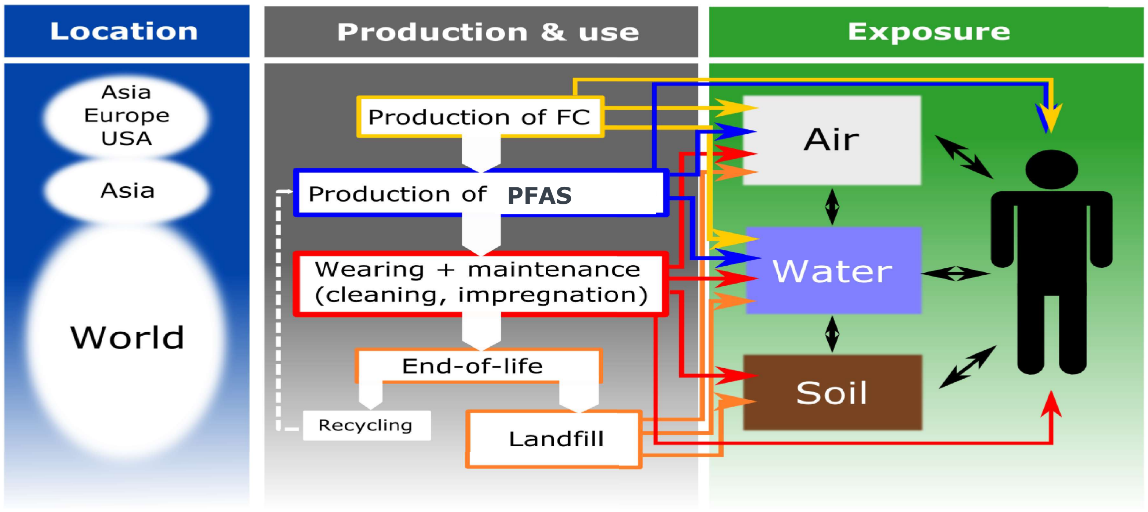
4.9.3. Alternative solutions (e.g. PFAS free products, substitution) (*10 min, break*)

4.9 CHARACTERISATION OF PFAS IN OTHER MATRICES / MEDIA - ALTERNATIVES SUBSTITUTES FOR PFAS



4.9.1. PFAS IN NON-ENVIRONMENTAL MEDIA

OUTDOOR JACKETS AS A SOURCE OF PFAS IN THE ENVIRONMENT



Location

Asia
Europe
USA

Asia

World

Production & use

Production of FC

Production of PFAS

Wearing + maintenance
(cleaning, impregnation)

End-of-life

Recycling

Landfill

Exposure

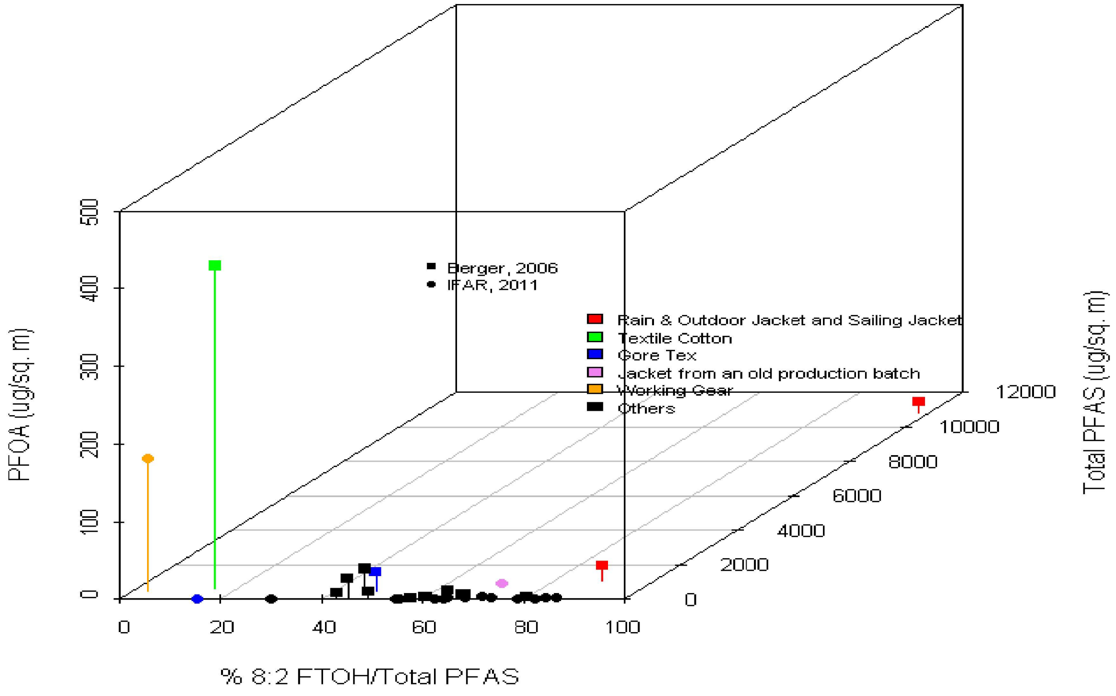
Air

Water

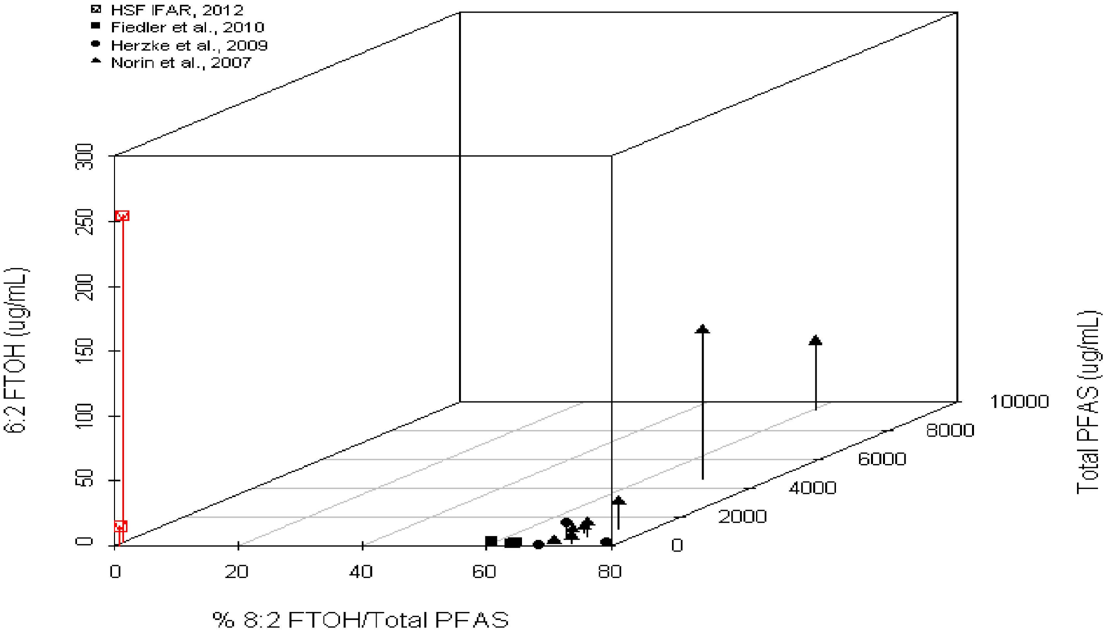
Soil

Erfassung der Expositionspfade von per- und polyfluorierten Chemikalien (PFC) durch den Gebrauch PFC-haltiger Produkte – Abschätzung des Risikos für Mensch und Umwelt (FKZ: 3711 63 418)

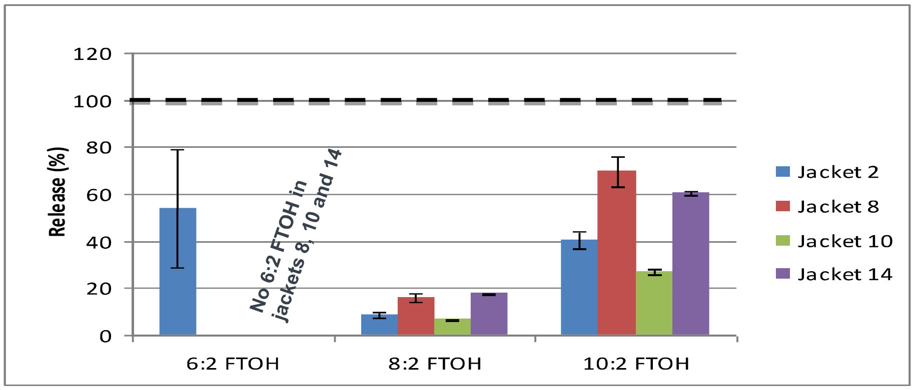
DWR TEXTILES (JACKETS)



IMPREGNATING SPRAYS



RESULTS
AIR EMISSIONS



RESULTS
WASHING WATER

APPROX. 100% RELEASE OF PFAAS

	6:2 FTOH	8:2 FTOH	10:2 FTOH
Jacket 2	0.71	3.46	5.69
Jacket 8	<LOQ	5.83	7.95
Jacket 10	n.d.	4.26	2.74
Jacket 14	n.d.	**90.6**	**110**

Concentrations in μg/m²

CONCLUSION DWR TEXTILE STUDY

SHIFT C-8 TO C-6 CHEMISTRY MEASURABLE

NO ORIGINAL PFAS VALUE DETECTABLE SINCE LOSSES DURING TRANSPORT AND STORAGE

POTENTIAL SVHC IN THE ENVIRONMENT AND PRODUCTS: ANALYSIS AND OCCURRENCE

HOCHSCHULE FRESENIUS
UNIVERSITY OF APPLIED SCIENCES

PFASs:
-23 building material samples (**BM**)
-28 industrial textile samples (**IT**)

Source?

Umwelt Bundesamt

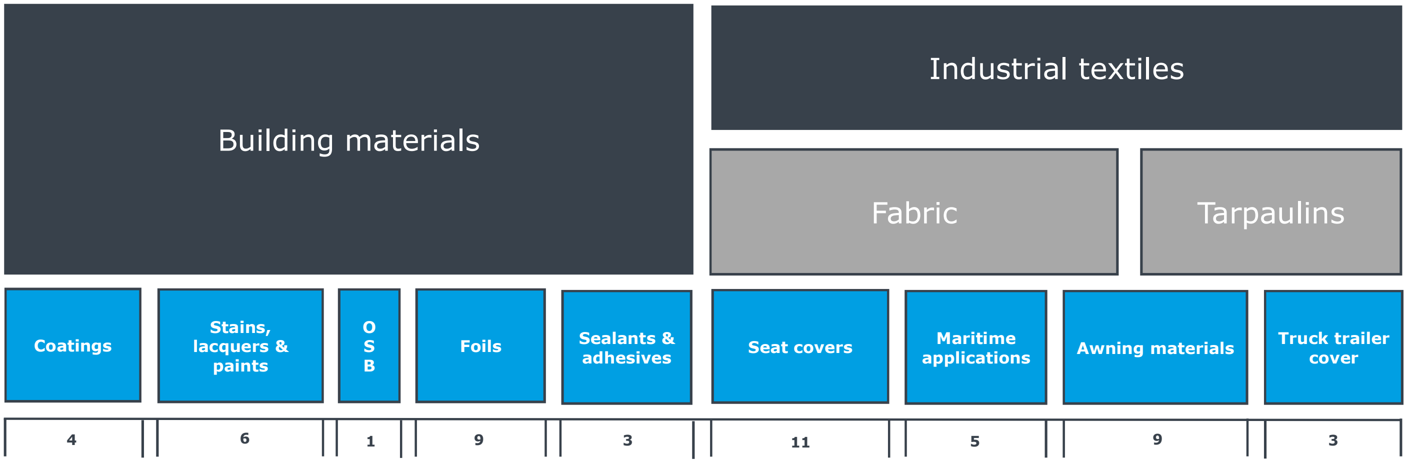
FKZ: 3716644300

Sample Preparation

Extraction prior to analysis of perfluoroalkyl acids (PFAAs) with **$MeOH + H_2O$**

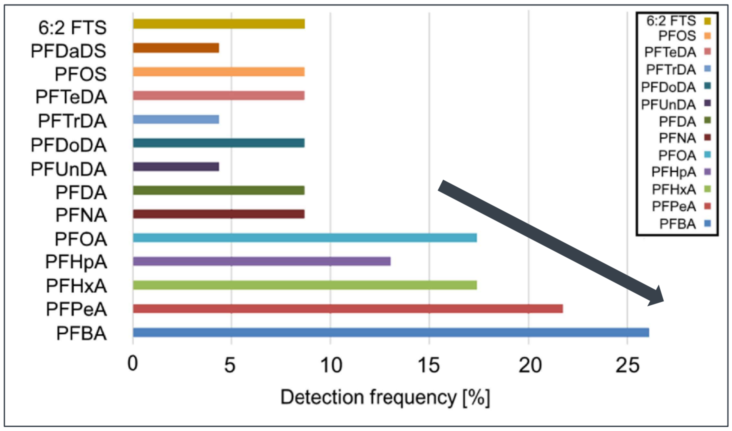
HOCHSCHULE FRESENIUS
UNIVERSITY OF APPLIED SCIENCES

OVERVIEW SAMPLES FOR THE ANALYSIS OF PFAS IN BUILDING MATERIALS AND INDUSTRIAL TEXTILES

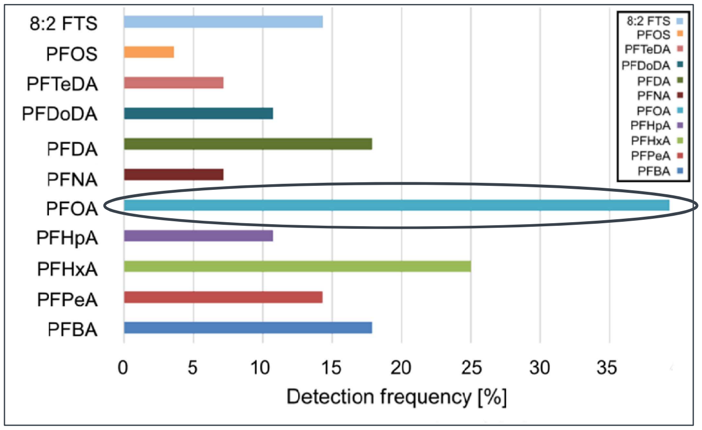


Coatings	Stains, lacquers & paints	OSB	Foils	Sealants & adhesives	Seat covers	Maritime applications	Awning materials	Truck trailer cover
4	6	1	9	3	11	5	9	3

DETECTED PFAAs IN BUILDING MATERIAL AND INDUSTRIAL TEXTILE SAMPLES
(I/IV)



Detection frequency of individual PFAAs detected in **building material** samples; Sorted by PFASs class and chain length



Detection frequency of individual PFAAs detected in **industrial textile** samples; Sorted by PFASs class and chain length

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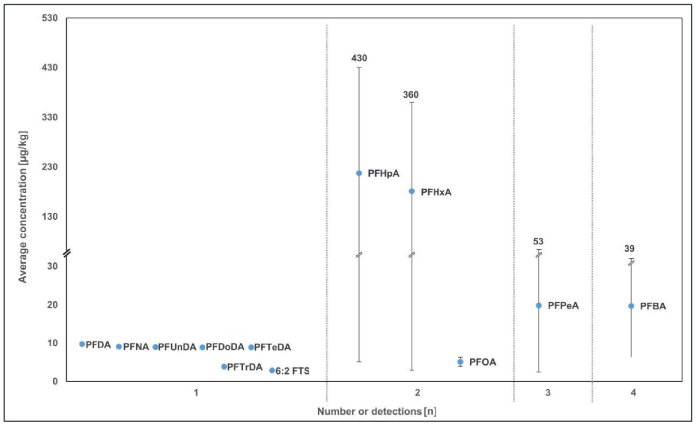
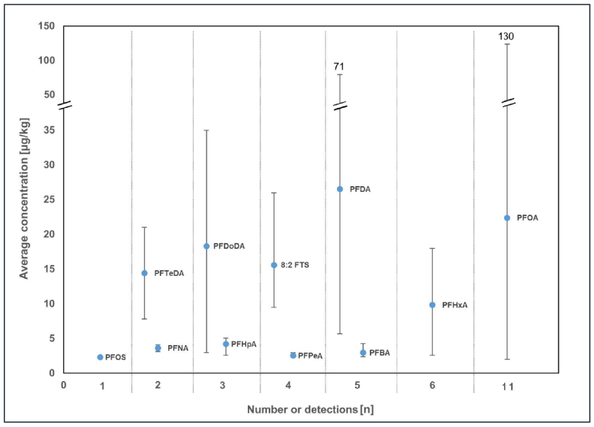
DETECTED PFAAs IN BUILDING MATERIAL AND INDUSTRIAL TEXTILE SAMPLES
(II/IV)



Average concentration and number of detection for all PFAAs in **building material samples** that were detected ≥LOQ in methanol extracts; bars indicate highest and lowest concentration, which was detected



Average concentration and number of detection for all PFAAs in **industrial textile samples** that were detected ≥LOQ in methanol extracts; bars indicate highest and lowest concentration, which was detected

DETECTED PFAAs IN BUILDING MATERIAL AND INDUSTRIAL TEXTILE SAMPLES (III/IV)

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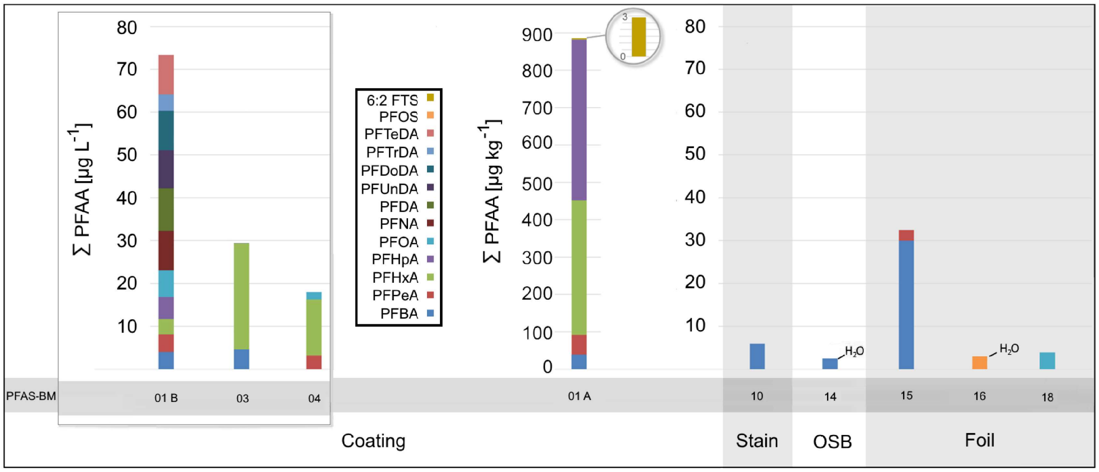
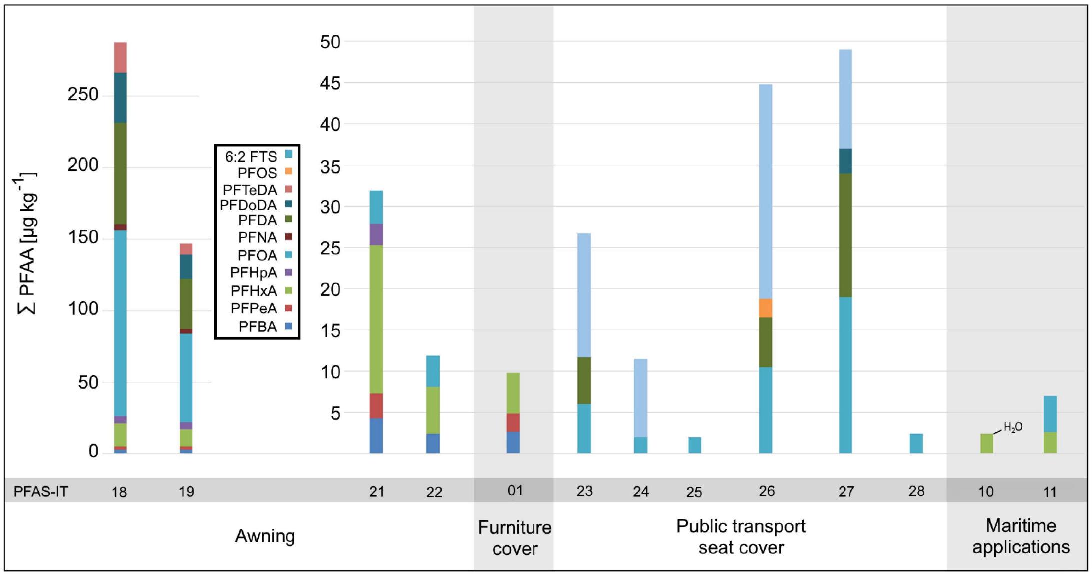


Sum of PFAAs for **building material** samples with positive findings; concentration shown in µg/kg or µg/L

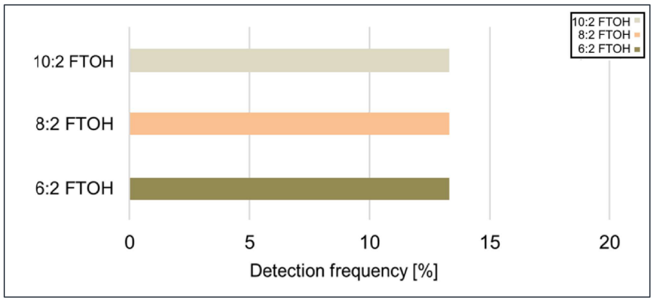
DETECTED PFAAs IN BUILDING MATERIAL AND INDUSTRIAL TEXTILE SAMPLES (IV/IV)

HOCHSCHULE FRESENIUS
UNIVERSITY OF APPLIED SCIENCES

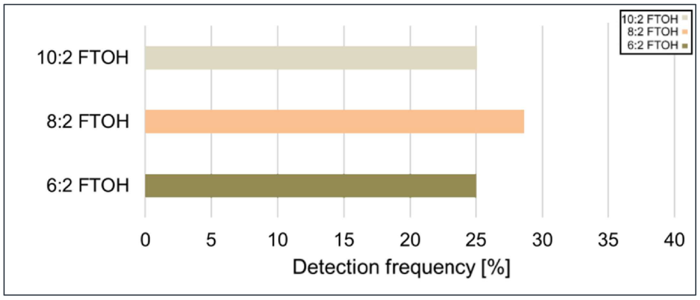


Sum of PFAAs for **industrial textile** samples with positive findings; concentration shown in µg/kg

DETECTED FTOHs IN BUILDING MATERIAL AND INDUSTRIAL TEXTILE SAMPLES (I/II)



Detection frequency of individual FTOHs detected in **building material** samples; Sorted by PFASs class and chain length



Detection frequency of individual FTOHs detected in **industrial textile** samples; Sorted by PFASs class and chain length

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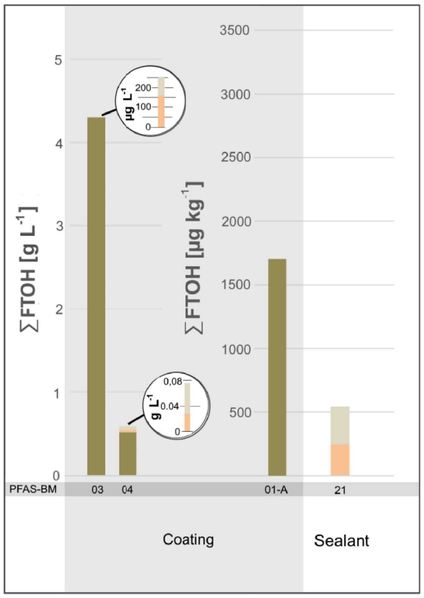
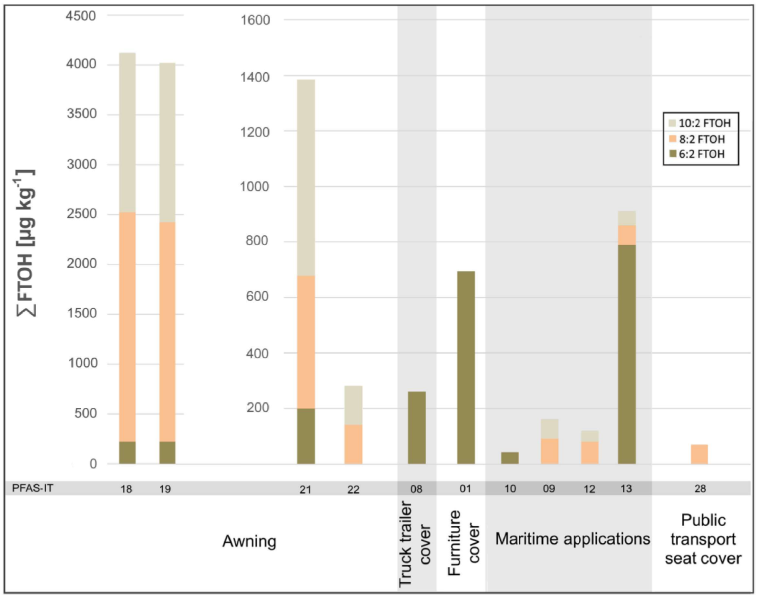
DETECTED FTOHs IN BUILDING MATERIAL AND INDUSTRIAL TEXTILE SAMPLES (II/II)

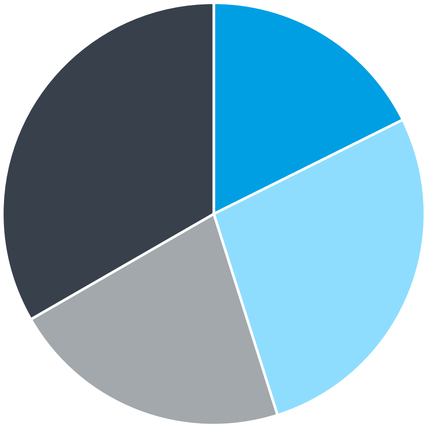


Sum of FTOHs for **building material** samples with positive findings; concentration shown in µg/kg or g/L



Sum of FTOHs for **industrial textile** samples with positive findings; concentration shown in µg/kg

SUMMARY RESULTS BM AND IT



Share of samples

Positive findings

🟦 Building materials
⬛ Industrial textiles

No PFASs detected

🟦 Building materials
◼ Industrial textiles

DF: 51%

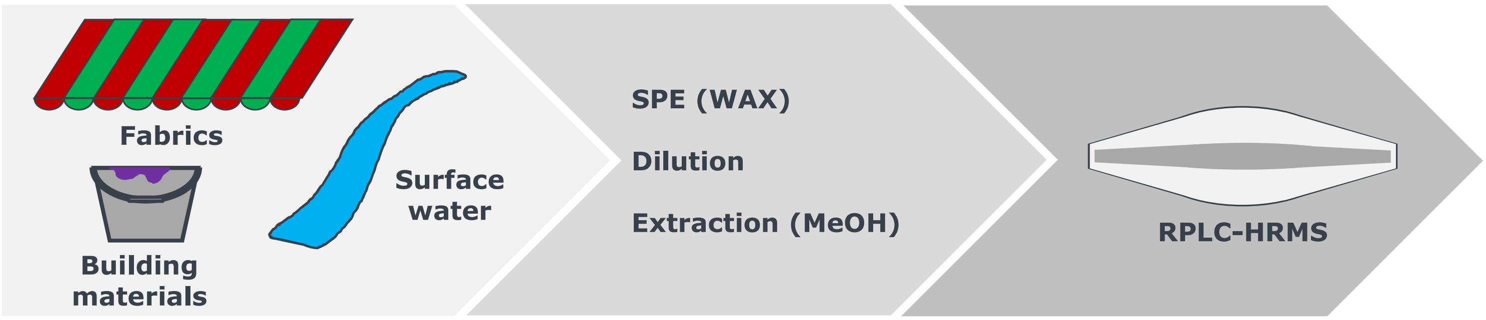
C_4-C_{14} in both BM and IT samples

C_8 chemistry with highest DF

Predominantly short-chain PFASs in BMs

High load of PFASs in awning and coating samples

SHIFTING FROM TARGET TO NON-TARGET ANALYSIS



Fabrics

Building materials

Surface water

SPE (WAX)

Dilution

Extraction (MeOH)

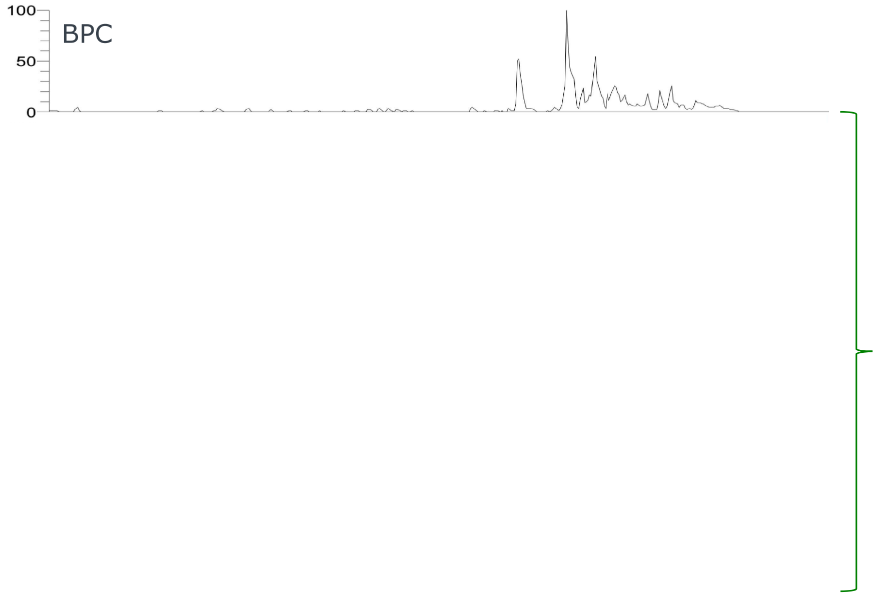
RPLC-HRMS

Sample selection

Sample preparation

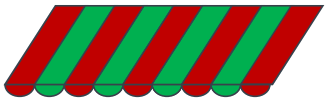
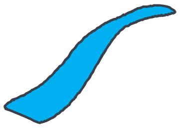
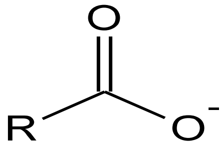
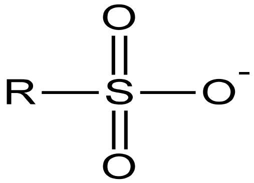
Detection & Identification

INDICATIVE PFAS FRAGMENTS - FRAGMENTATION FLAGGING



Indicative PFASs fragments

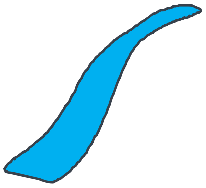
WELL-KNOWN PFAS CLASSES

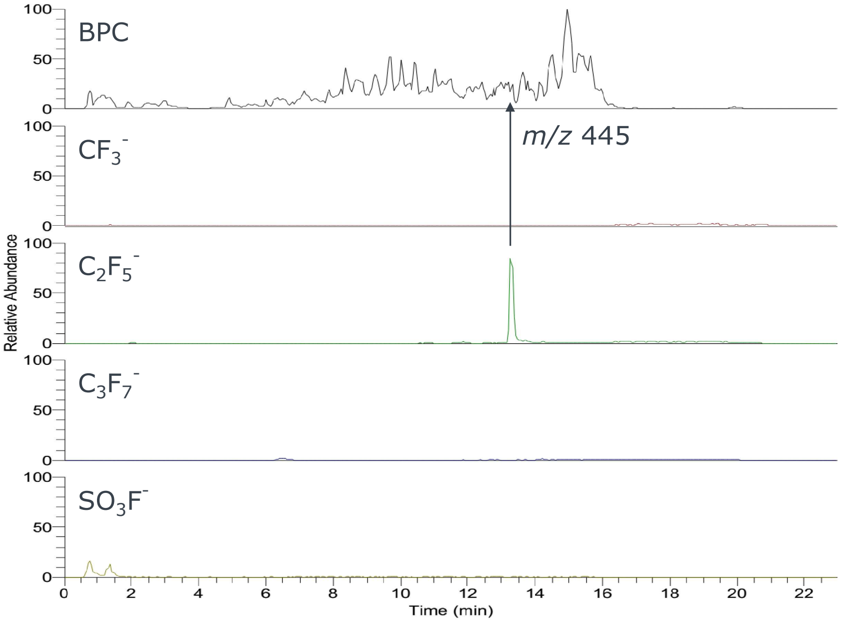
			
	C_3, C_4, C_8	$C_3 - C_{16}$	$C_4 - C_8$
	**C_1**, C_4	-	**C_1**, C_4, C_6, C_8

Most detected PFASs are well known

$R = C_nF_{2n+1}$

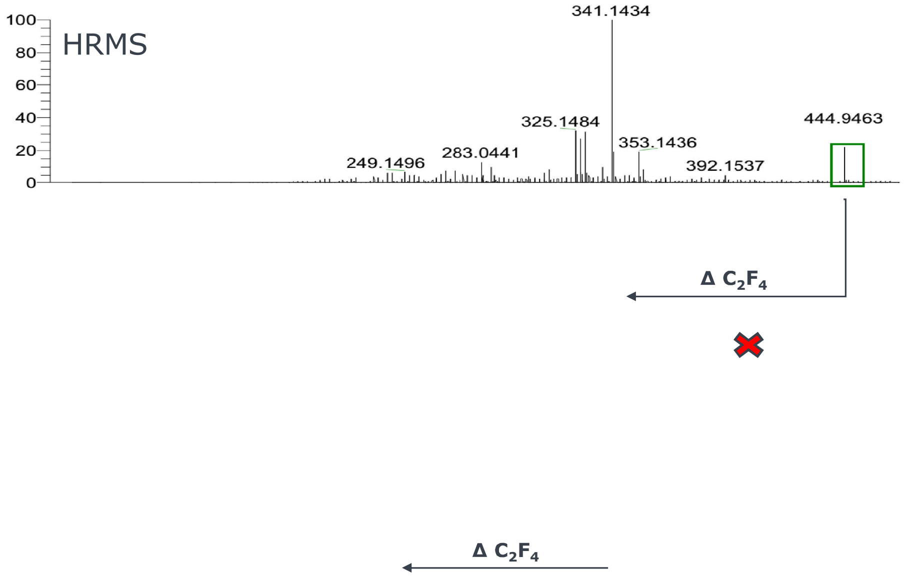
DETECTION OF "NOVEL" PFAS

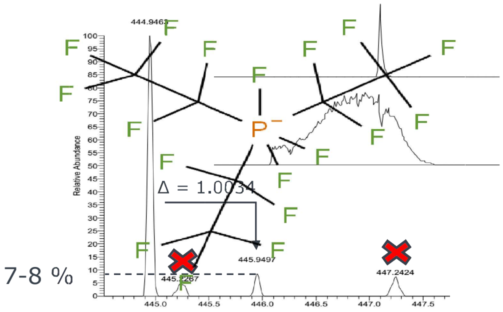




X45 does not match the mass of any typical PFASs class

STRUCTURAL ELUCIDATION OF *M/Z* 445

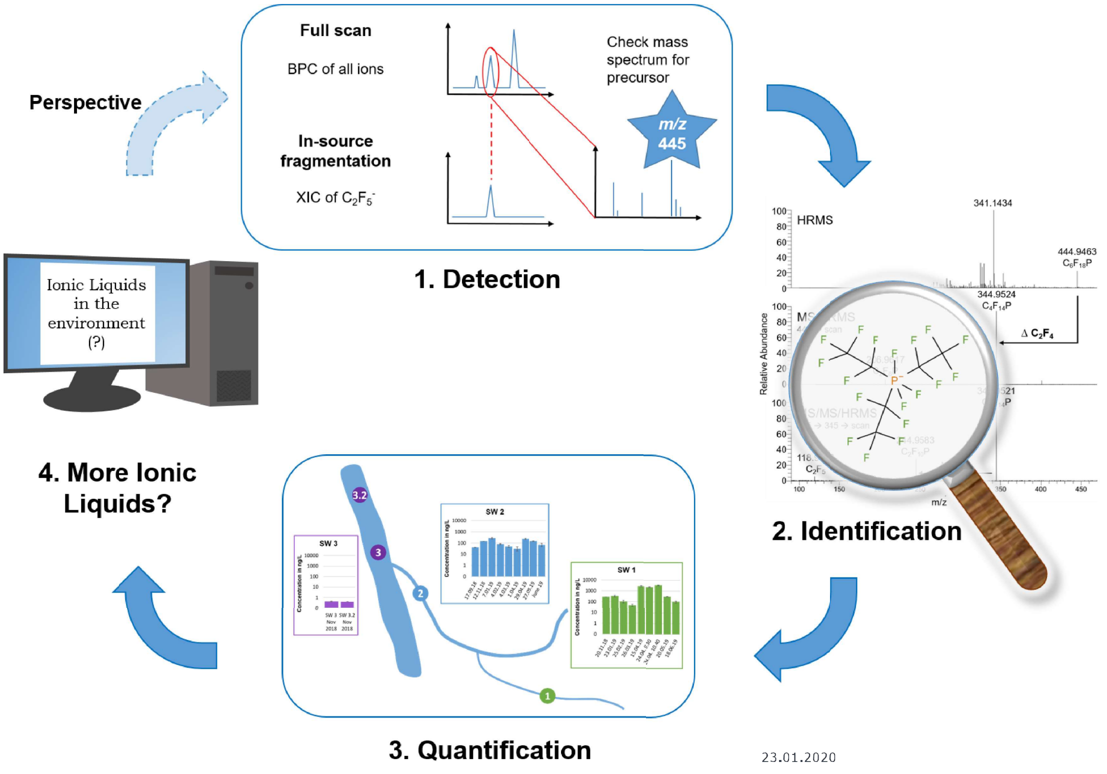




What do we know:

ca. 6-7 C atoms
Only monoisotopic elements
Cleavage of C_2F_4
$C_6PF_{18}^-$

TRIS(PERFLUOROALKYL)TRIFLUOROPHOSPHATE



Perspective

1. Detection

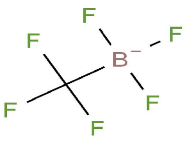
2. Identification

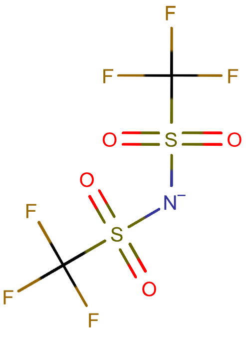
3. Quantification

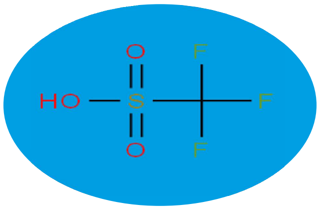
4. More Ionic Liquids?

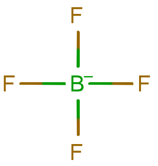
IONIC LIQUIDS

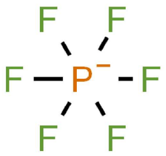
- Extensive literature research about ionic liquids – more than 600 potential candidates
- **Green** chemistry
- Are other novel PFAS among ionic liquids? (Yes, for sure)
- Are other fluorinated ionic liquids or ionic liquids in general discharged into the environment in significant quantities?



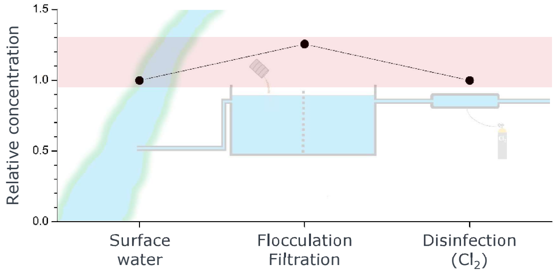


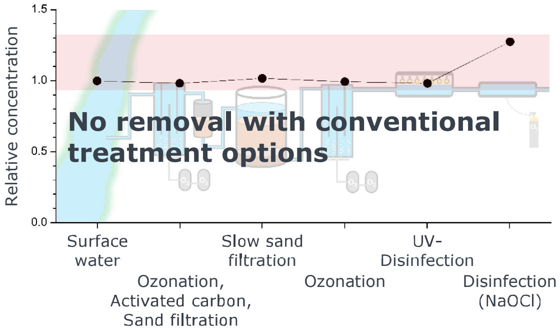




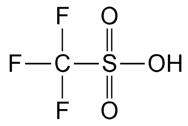


BEHAVIOR DURING DRINKING WATER PRODUCTION
TRIFLUOROMETHANESULFONIC ACID (TFMSA)



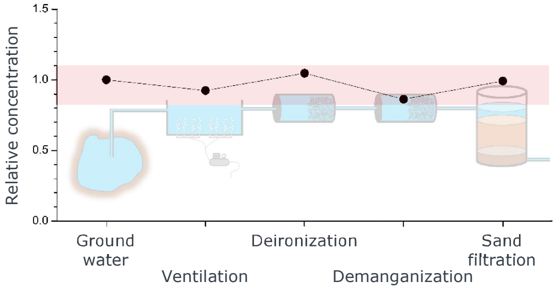


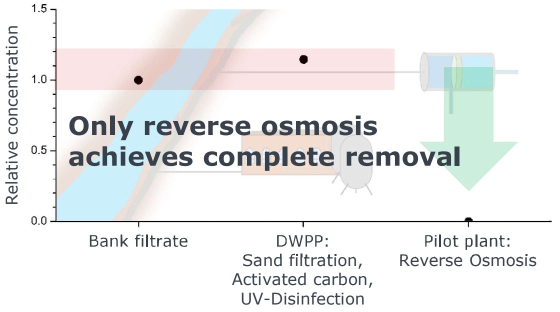
No removal with conventional treatment options



$\mathrm{F_3C{-}SO_2{-}OH}$

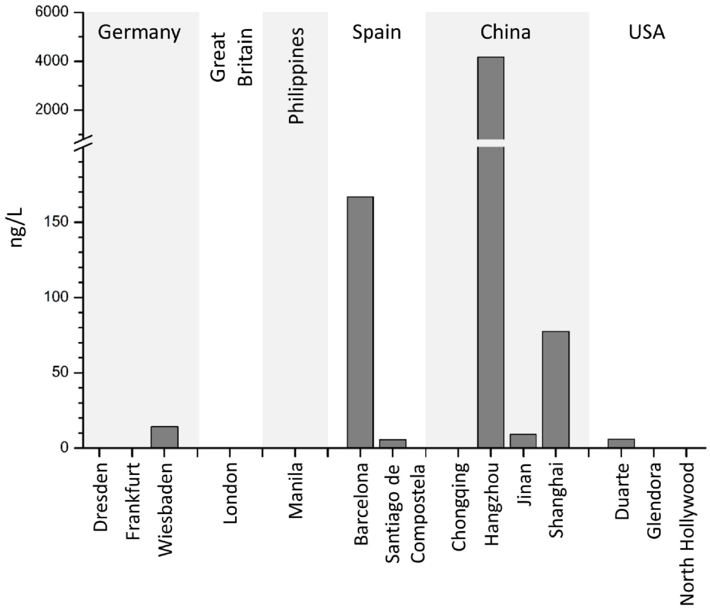
~10-50 ng/L





Only reverse osmosis achieves complete removal

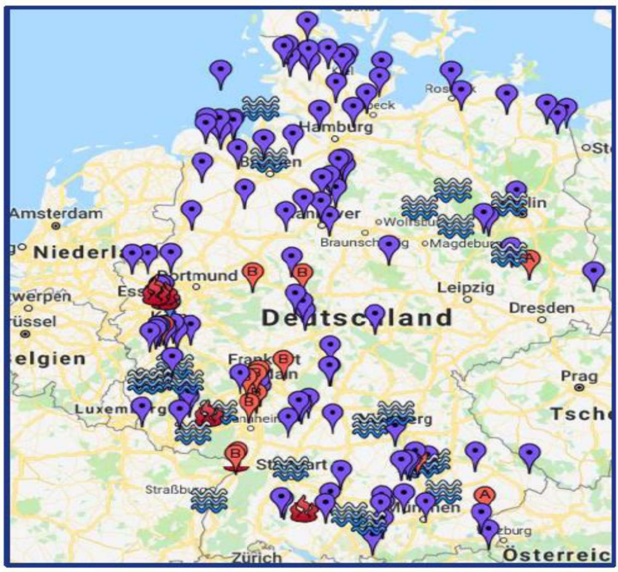
OCCURRENCE IN TAP WATER
TRIFLUOROMETHANESULFONIC ACID (TFMSA)



- 100-1,000 t/a (REACH)
- Used in various industrial processes
- ^{18}O-labeled standard was synthesized
- Concentrations in tap water mostly low ng/L range
- Tap water in Hangzhou contains ~4µg/L
- 1 European groundwater with ~10 µg/L
- Local hotspots may lead to elevated drinking water concentrations

PFAS HOT SPOTS IN GERMANY

Suspected and **c**ontaminated sites



- Unknown source
- **Use of AFFF fire fighting foam**
- **Training with AFFF fire fighting foam**
- Soil application
- Manufacturing site
- other industrial sites

https://www.stadtwerke-rastatt.de/pfc-schadensfalluebersicht

CONCLUSION 4.9.1

- Numerous potential sources of PFAA and PFSA incl. precursors
- Analytical methods extremely challenging dur to matrix
- First quantitative data about many hitherto scarcely investigated or unknown PFAS as PM-chemicals generated
- Some of these PFAS cannot be removed with conventional water treatment technologies – potentially applying reverse osmosis seems
- Local hotspots may lead to elevated drinking water concentrations when no efficient removal can be achieved (example TFMSA)
- Only a fraction of potential intentionally produced and even less transformation-derived PM-chemicals yet investigated

QUESTIONS 4.9.1 PFAS IN OTHER ENVIRONMENTAL MATRICES

Which PFAS from which source in non-environmental media are prone to enter the environment and how?

- Differences between fire-fighting foams, textiles, coating, etc…

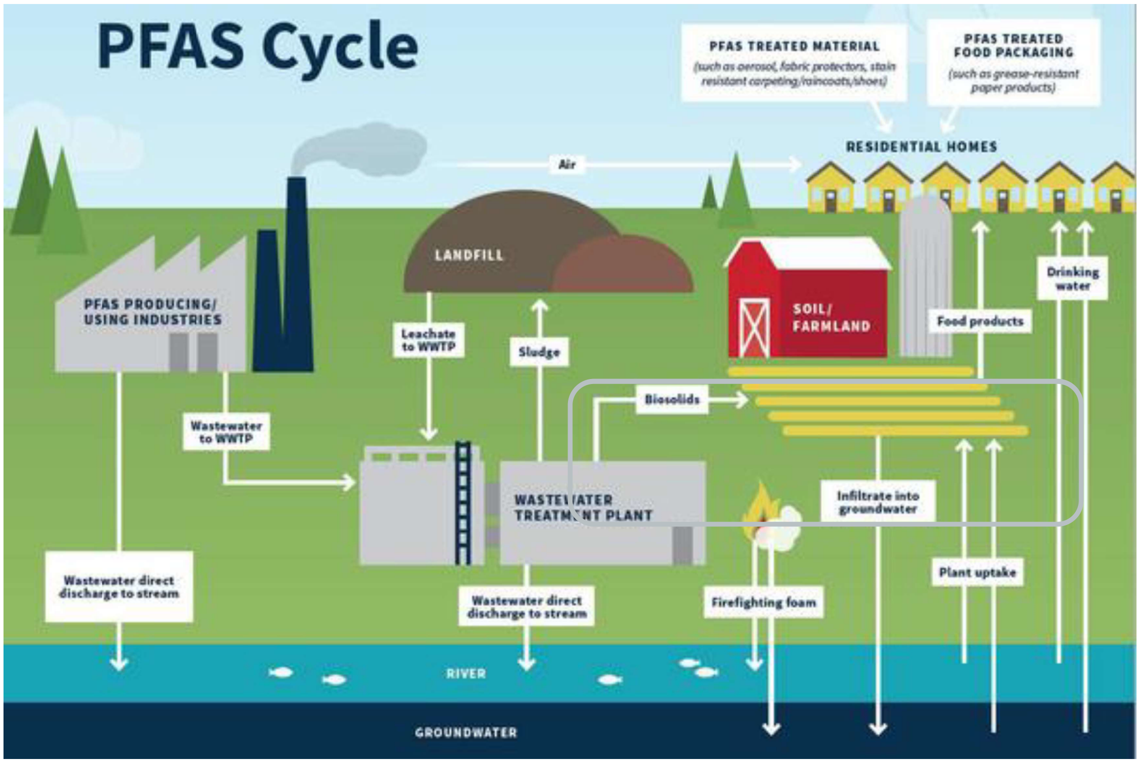
How can stakeholders (e.g. producers, society, ...) reduce risks?

- Directly and indirectly

What are the most pressing issues?

- Knowledge gaps (occurrence, mobility, chemistry, toxicity …)
- Regulation (thresholds, monitoring, standards, …)
- Application and barriers

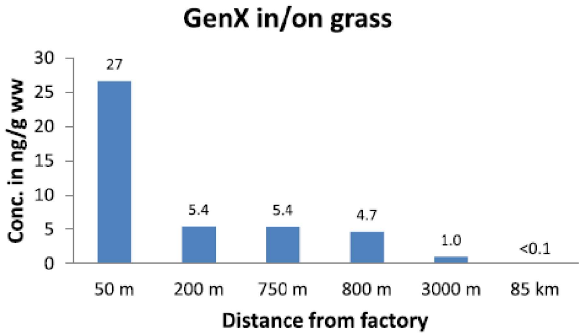
4.9.2. PFAS IN OTHER ENVIRONMENTAL MATRICES (E.G. SOIL, SEDIMENTS, MANURE)

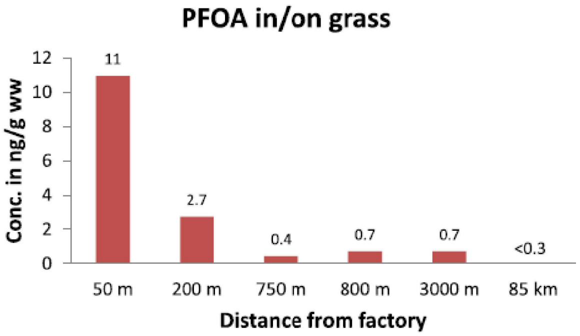


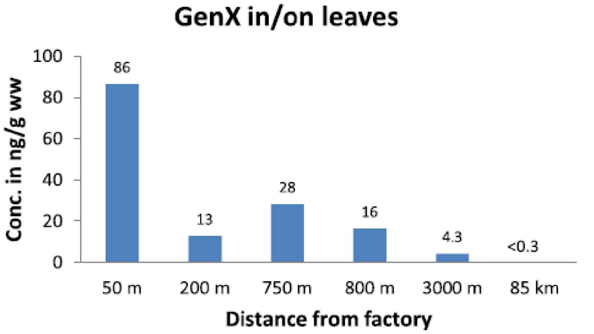
NRWA 2019

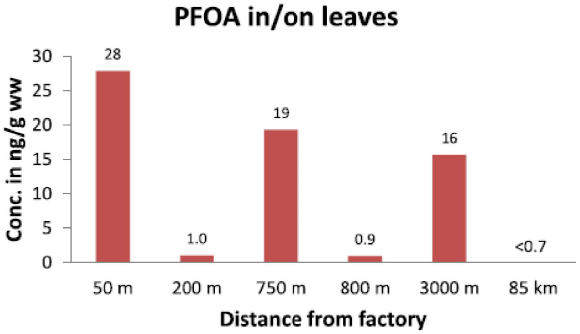
SOURCES CHEMICAL PRODUCTION

PFOA/GenX **in plants** near Dutch manufacturing site (*Brandsma et al. 2019*)



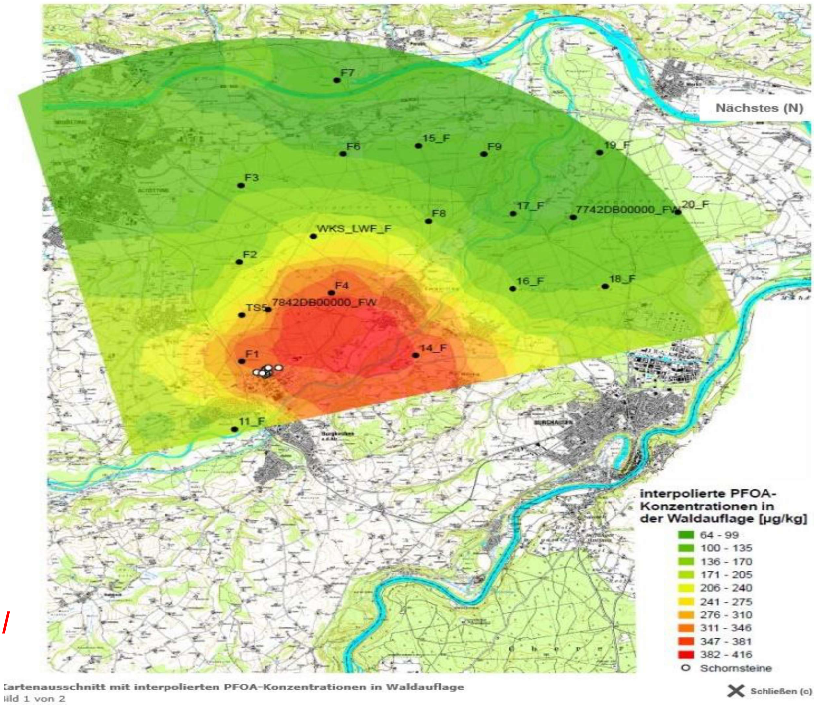






SOURCES CHEMICAL PRODUCTION

Interpolated PFOA-concentrations in **soil** (Gendorf, Germany).



Kartenausschnitt mit interpolierten PFOA-Konzentrationen in Waldauflage
ild 1 von 2

Further refs:
Gellrich, Knepper, Stahl

https://www.lfu.bayern.de/altlasten/pfoa_gendorf/bodenbelastungen/index.htm

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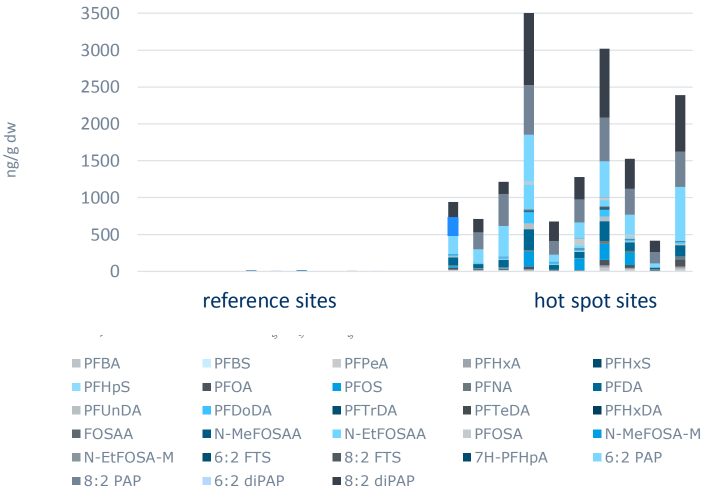
HOT SPOT SITE IN RASTATT, SOUTHERN GERMANY

Comparison of soil samples from the German environmental specimen bank
and from hot spot sites in Southern Germany, which are contaminated with PFAS from paper sludge.



Umweltskandal in Rastatt und Mannheim

Jetzt sind 747 Hektar mit PFC belastet

Von Thomas Faltin 12. Dezember 2017 · 14:43 Uhr

Im Norden Mannheims sind in diesem Jahr zahlreiche weitere Äcker entdeckt worden, auf die verunreinigte Papierschlämme ausgebracht worden sind. Die Stadtwerke Rastatt müssen Millionen von Euro investieren, um das Wasser zu schützen.

Rastatt/Mannheim – Es ist eine der größten Umweltverschmutzungen in der Geschichte Baden-Württembergs: Rund um Rastatt, Baden-Baden und Mannheim sind hunderte Hektar Fläche mit der Chemikalie PFC verseucht. Womöglich stammen die Stof-

Das Wasserwerk Rauental muss umgebaut und erweitert werden, um das belastete Trinkwasser reinigen zu können. Foto: Star Energiewerke

PFAS problem from paper waste biosolids in Southern Germany

COURTESY C.SCHULTE, WORKSHOP ON PFAS MONITORING IN WATER AND OTHER MEDIA

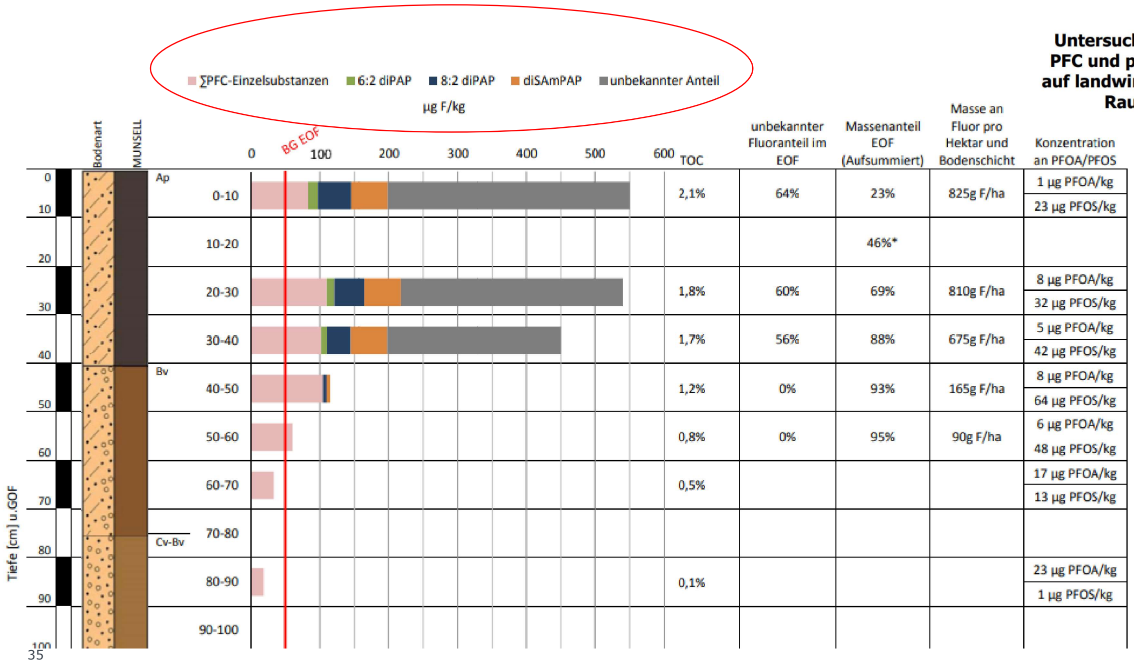
PFAS IN SOIL IN THE AREA OF RASTATT, BADEN-WÜRTEMBERG, GERMANY FOLLOWING CONTAMINATION BY SLUDGE (PRESUMABLY 2006-2008) FROM PAPER INDUSTRY; ANALYSIS DATA BY TZW, KARLSRUHE, GERMANY IN 2018

HOCHSCHULE FRESENIUS
UNIVERSITY OF APPLIED SCIENCES

LANDKREIS RASTATT

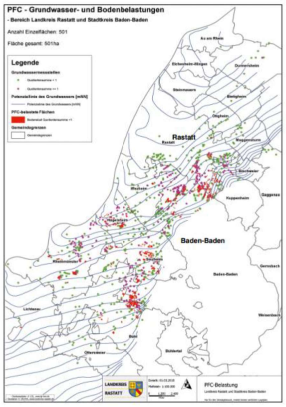
BERICHT

Untersuchung der Tiefenverlagerung von PFC und potentiellen Vorläufersubstanzen auf landwirtschaftlich genutzten Flächen im Raum Rastatt / Baden-Baden



Tiefe	TOC	unbekannter Fluoranteil im EOF	Massenanteil EOF (Aufsummiert)	Masse an Fluor pro Hektar und Bodenschicht	Konzentration an PFOA/PFOS
0-10	2,1%	64%	23%	825g F/ha	1 µg PFOA/kg 23 µg PFOS/kg
10-20			46%*		
20-30	1,8%	60%	69%	810g F/ha	8 µg PFOA/kg 32 µg PFOS/kg
30-40	1,7%	56%	88%	675g F/ha	5 µg PFOA/kg 42 µg PFOS/kg
40-50	1,2%	0%	93%	165g F/ha	8 µg PFOA/kg 64 µg PFOS/kg
50-60	0,8%	0%	95%	90g F/ha	6 µg PFOA/kg 48 µg PFOS/kg
60-70	0,5%				17 µg PFOA/kg 13 µg PFOS/kg
70-80					
80-90	0,1%				23 µg PFOA/kg 1 µg PFOS/kg
90-100					

https://www.landkreis-rastatt.de/site/kreis-rastatt/get/documents_E-429867916/kreis-rastatt/Objekte/03_Aktuelles/PFC/Bericht%20Tiefenverlagerung%20EOF_mitAnlagen_221018.pdf



OCCURRENCE SOIL/LANDFILLS

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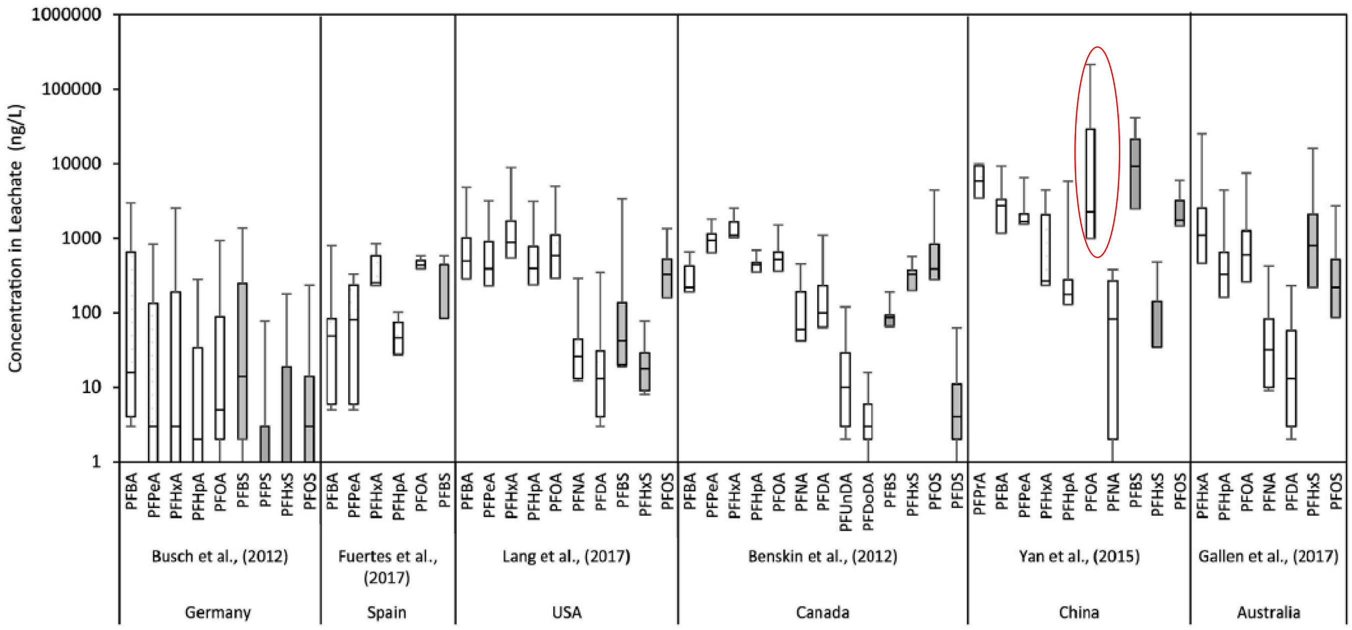
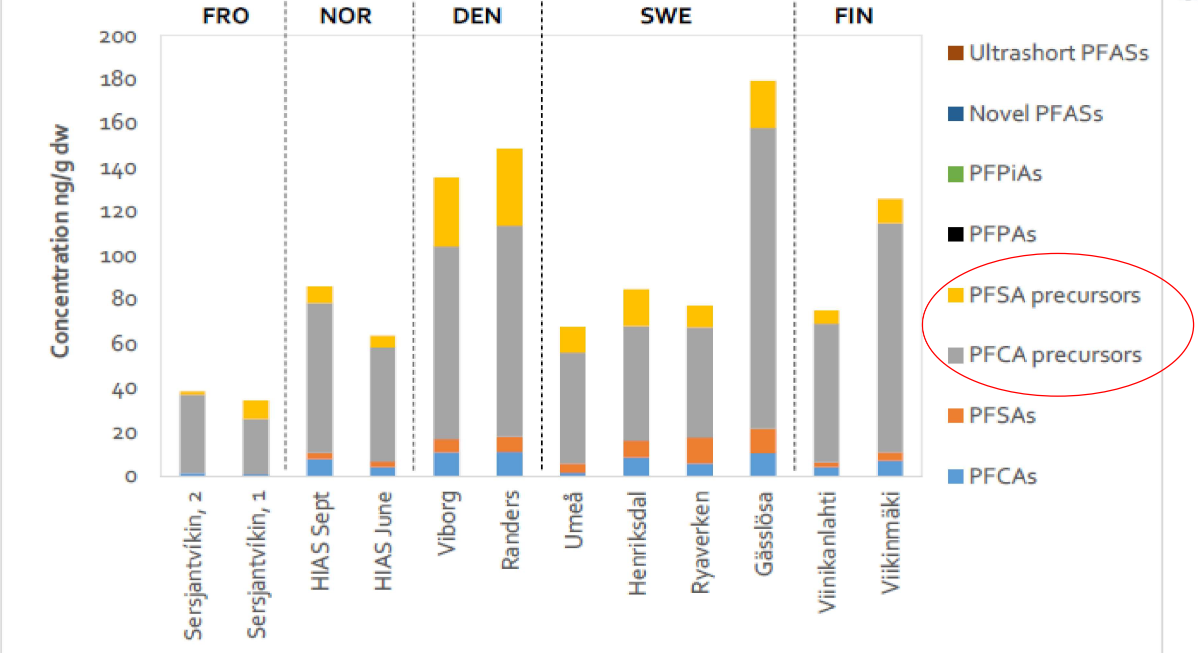
Landfills as source for PFAS in 6 countries (*Hamid et al. 2018*)



OCCURRENCE SEWAGE SLUDGE



Sewage sludge in 5 Nordic European countries as source for PFAS *(Kärrman et al. 2019)*

OCCURRENCE IN SLUDGE SAMPLES FROM MUNICIPAL AND INDUSTRIAL WASTE WATER TREATMENT PLANTS

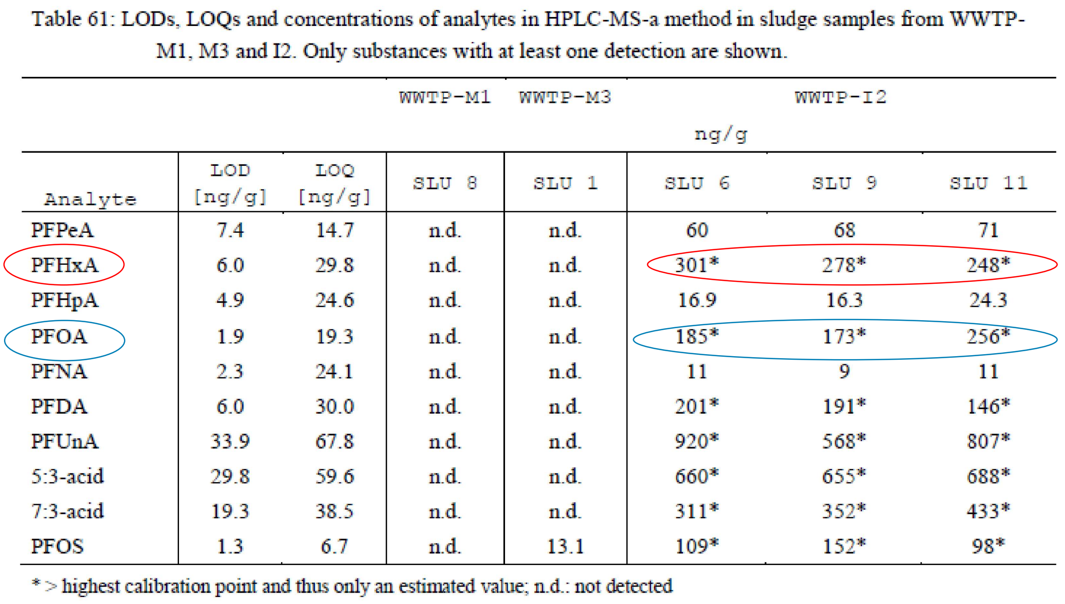


Table 61: LODs, LOQs and concentrations of analytes in HPLC-MS-a method in sludge samples from WWTP-M1, M3 and I2. Only substances with at least one detection are shown.

			WWTP-M1	WWTP-M3	WWTP-I2		
			ng/g				
Analyte	LOD [ng/g]	LOQ [ng/g]	SLU 8	SLU 1	SLU 6	SLU 9	SLU 11
PFPeA	7.4	14.7	n.d.	n.d.	60	68	71
PFHxA	6.0	29.8	n.d.	n.d.	301*	278*	248*
PFHpA	4.9	24.6	n.d.	n.d.	16.9	16.3	24.3
PFOA	1.9	19.3	n.d.	n.d.	185*	173*	256*
PFNA	2.3	24.1	n.d.	n.d.	11	9	11
PFDA	6.0	30.0	n.d.	n.d.	201*	191*	146*
PFUnA	33.9	67.8	n.d.	n.d.	920*	568*	807*
5:3-acid	29.8	59.6	n.d.	n.d.	660*	655*	688*
7:3-acid	19.3	38.5	n.d.	n.d.	311*	352*	433*
PFOS	1.3	6.7	n.d.	13.1	109*	152*	98*

* > highest calibration point and thus only an estimated value; n.d.: not detected

UBA, Germany, Final Report (Project No. (FKZ) *3712 65 415/01*);
Investigations on the presence and behavior of precursors to perfluoroalkyl substances in the environment as a preparation of regulatory measures ; Hochschule Fresenius, University of Amsterdam, 2015

OCCURRENCE SEWAGE SLUDGE AND BIOSOLIDS

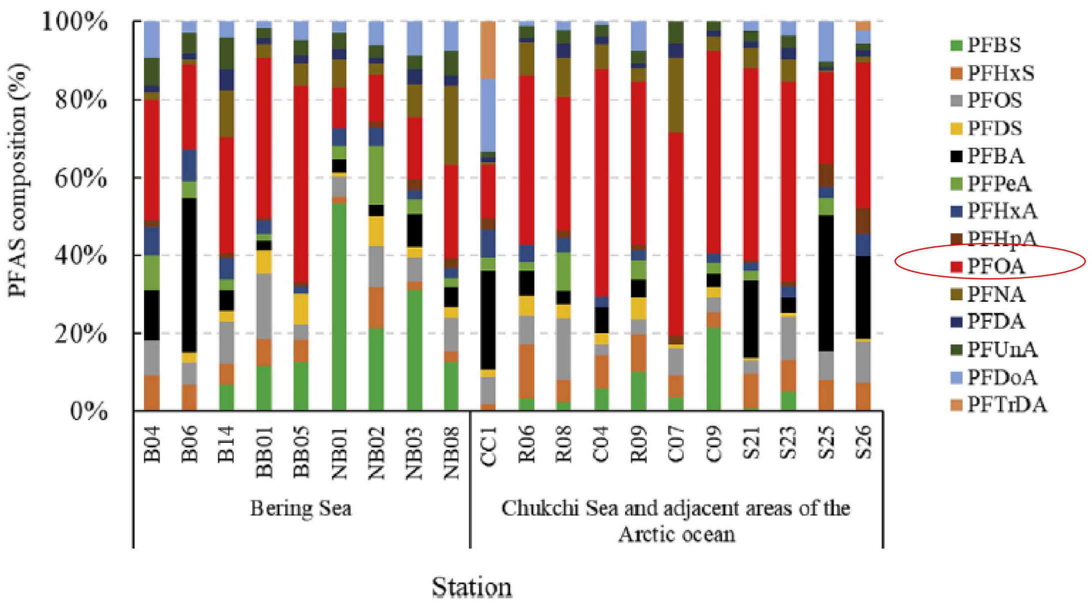
Further references:

Municipal sewage sludge in 20 Chinese provinces as source for PFAS (*Wang et al. 2019*)

The 2001 U.S. EPA National Sewage Sludge Survey suggested that the load of PFASs in the US biosolids was 2749–3450 kg/a based on the 13 PFASs measured. Of this total US load, an estimated 1375–2070 kg/a was applied for agriculture […] (*Sunderland et al. 2019*)

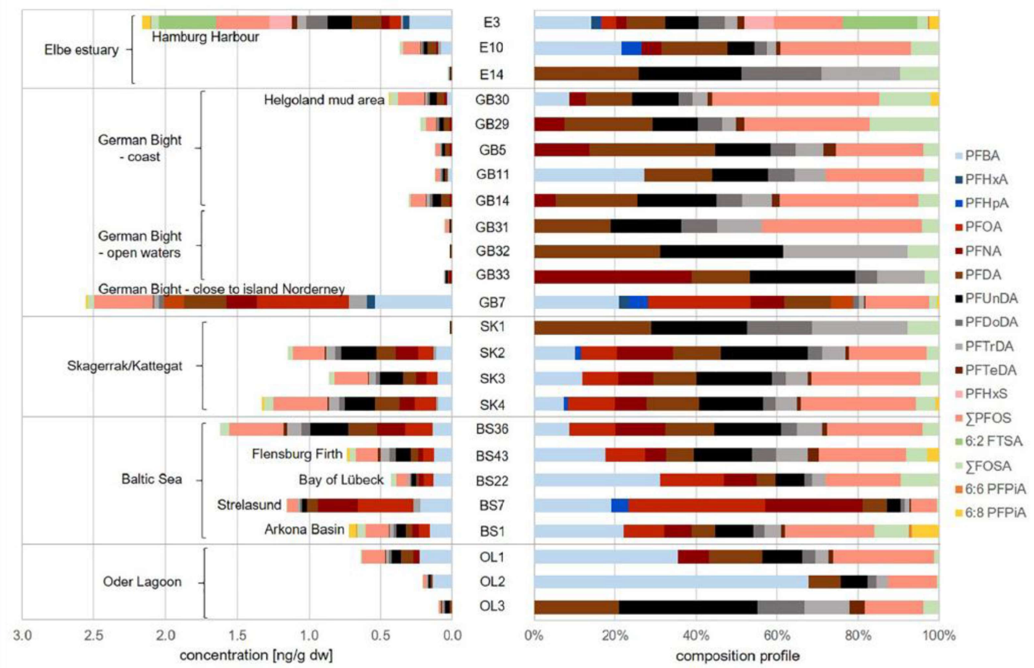
OCCURRENCE SURFACE SEDIMENTS

Spatial distribution and composition of individual PFAS in surface sediments of the Bering Sea, Chukchi Sea and adjacent Arctic Ocean (*Kahkashan et al. 2019*)



OCCURRENCE SURFACE SEDIMENTS

Concentrations [ng/g dw] and composition profiles of individual PFASs in surface sediment samples of Northern an Baltic Sea (*Joerss et al. 2019*)



4.9.2. PFAS IN OTHER ENVIRONMENTAL MATRICES (SOIL, SEDIMENTS, MANURE……..)

Which are the dominant entry pathways of PFAS into the **non-aquatic environment**, their associated risks and potential measures?

- Relevant source for PFAS in groundwater and drinking water
- *PM chemicals problematic; storage potential of precursors INCLUDING fluorinated polymers!*

How do we identify hot spots and manage risks?

- Not only as source control after contamination of groundwater
- *Monitor PFAS producing industrial sites (s. GenX) and surrounding area (air, soil, water cycle); including target, non-target and sum parameters in defined frequency*

What are the most pressing issues?

- Knowledge gaps (occurrence, mobility, chemistry, …) analysis; fate; polymeric precursors; illegal dump sites (sludge use…
- Regulation (thresholds, monitoring, standards, …)
- Application and barriers
- costs…(analysis, remediation, information to public…

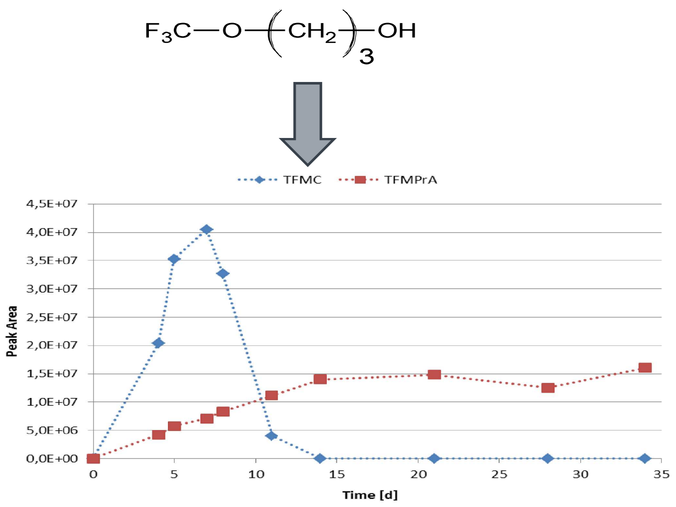
4.9.3. ALTERNATIVE SOLUTIONS (E.G. PFAS FREE PRODUCTS, SUBSTITUTION,)

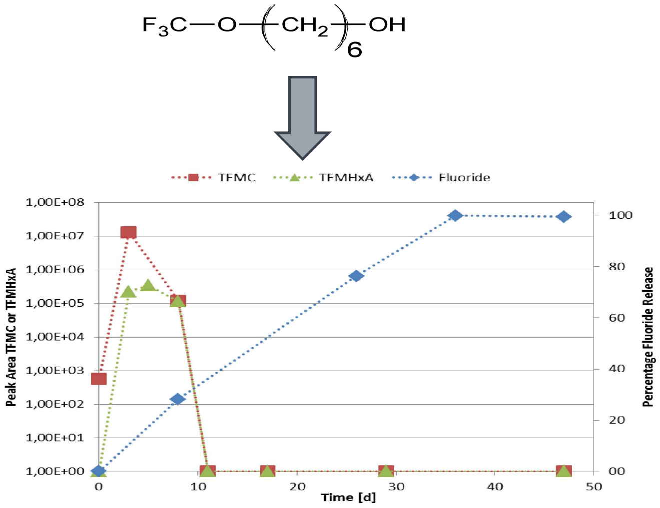
Goals:

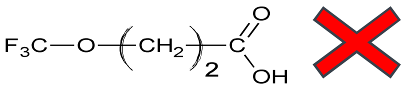
- Requested properties, eg. reduction of surface tension must be fulfilled
- Eficiency, e.g. concetration
- (Bio)degradation….even mineralisation? Or closed loop systems?
- Avoidance of PM chemicals (possible?)
- Toxicity of e.g. transformationproducts (e.g. fluoro phosgene..)

A few examples shown now…

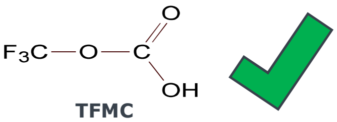
BIOTRANSFORMATION OF TRIFLUOROMETHOXY DERIVATIVES



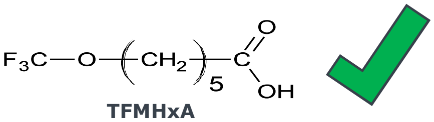




TFMPrA



TFMC



TFMHxA

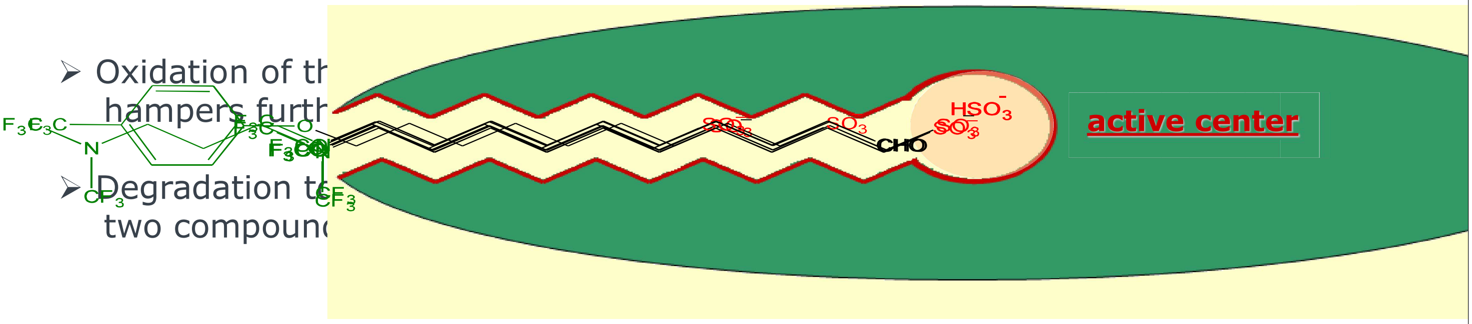
DEGRADATION PATHWYS OF TRIFLUORMETHOXYSULFONATES

- There are two different primary degradation steps: desulfonation and alkyl chain oxidation

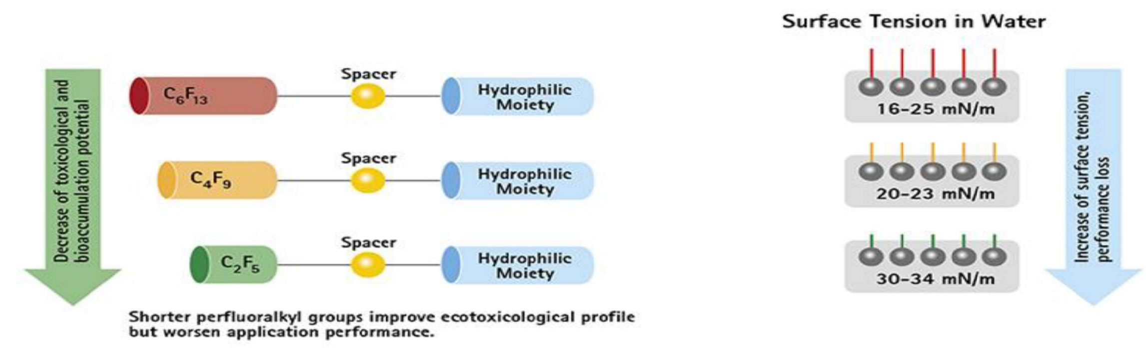
- Desulfonation as a primary degradation step depends on the alkyl chain length

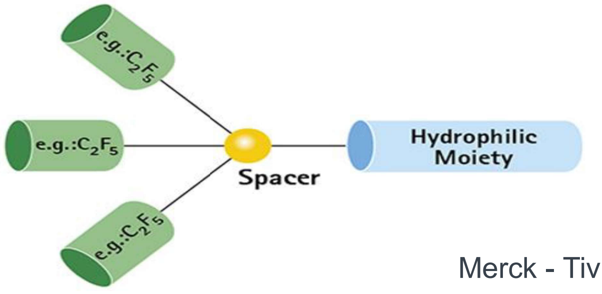
- Oxidation of th
  hampers furth

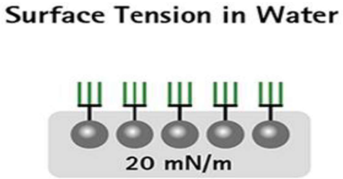
- Degradation t
  two compoun



IDEA OF BRIDIGING VARIOUS SHORT CHAIN PFAS IN ORDER TO ACHIEVE SIMILAR SURFACE TENSION REDUCTION AS PFOA







Merck - Tivida® FL 2300-30 – The New High Speed Fluorosurfactant

DWR GEAR PRODUCER JACK WOLFSKIN

Goal 2015: To achieve PFAS – free textiles until 2020 (achieved)….(www. Jack wolfskin.de)

JACK WOLFSKIN INTERVIEW STEFAN POSNER

PFC-free alternatives are supposedly performing less good than PFC-containing DWR finishes. What are the issues, and what are the reasons? Where is research at with regards to solving these challenges?

Highly fluorinated side chain polymers have unique oleophobic and hydrophobic properties, which provide extremely low surface tension and consequently oil repellent properties. This cannot be achieved with other groups of chemicals. If socalled non fluorinated alternative polymers are used, they may achieve water repellent properties but not oil repellent properties due to their higher surface energy. Some of the main alternative DWR chemistries are siloxane-based or hydrocarbon-based polymers. There are also hyperbranched hydrophobic polymers (dendritic, i.e., highly branched polymers) and specifically adjusted comb polymers that will act as active components1 . Less common are fluorinated siloxane structures of which we know almost nothing. There is also research on plasma technology that may be an alternative to modify textiles surfaces to DWR properties (www.supfes.eu). Conclusively the only way forward from a scientific perspective to maintain oil repellent properties are to invent and apply new structures of fluoro chemistry, that can provide the same oil repellent performance as the current PFAS chemistry and that these new structures are scientifically shown to be less harmful to the environment and humans than the current PFAS chemistry. These efforts are still emerging and not in any way close to either pilot or full scale production as far as recent studies in these matters are concerned.

JACK WOLFSKIN INTERVIEW STEFAN POSNER

Does any scientific data exist how PFC-free alternative DWR finishes compare to those containing PFCs with regard to their hazardousness for human health and the environment?

There are a number of recent scientific and governmental studiest hat describe the hazard characteristics of both fluorinated and non-fluorinated DWR chemistries. Though there is scarce hazard data for some of these alternatives there is no way possible to conclude that non fluorinated alternatives are “better” than highly fluorinated DWR chemicals in a general way. As always these matters have to be assessed on every individual DWR chemistry and their specific precursors.

JACK WOLFSKIN INTERVIEW STEFAN POSNER

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FURTHER APPROACHES

Problem microplastic….e.g. PET, polyurethanes, polyester…PMMA, ….

Recycling so far still a problem…

Alternative: Wool, polycarbon acids…

Are siloxanes a (safe) alternative ?

3.3 ALTERNATIVE SOLUTIONS (E.G. PFAS FREE PRODUCTS, SUBSTITUTION, RELINQUISHMENT)

Which PFAS alternatives exist, which are being developed, which are substantially being used, and which PFAS are currently indispensable?

- Can we rank PFAS according to their need for substitution (e.g. amount used and known toxicity)?

What is necessary for producers using PFAS to switch to PFAS free materials?

- Which PFAS free materials can be recommended from an environmental point of view?

What are the most pressing issues?

- Knowledge gaps (occurrence, mobility, chemistry, governance …)
- Regulation (thresholds, monitoring, standards, …)
- Application and barriers
- …

RELEVANT PUBLICATIONS

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BOOKS & Book chapter

- Knepper TP and Lange FT (Eds.) Polyfluorinated Chemicals and Transformation Products, Series: The Handbook of Environmental Chemistry, D Barceló , AG Kostianoy (Series Eds.) Springer 17 (2012) 24
- Frömel T, Knepper TP: Mass Spectrometric Approaches to Reveal Biotransformation Products from Per- and Polyfluorinated Chemicals. In Polyfluorinated Chemicals and Transformation Products, TP Knepper and FT Lange (Eds.) The Handbook of Environmental Chemistry, D Barceló, AG Kostianoy (Series Eds.) Springer, 17:41-61 (2012) https://doi.org/10.1007/978-3-642-21872-9_3
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RELEVANT PUBLICATIONS

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Neuwald, I., Zahn,D., Knepper TP: Are (fluorinated) ionic liquids relevant environmental contaminants? High-resolution mass spectrometric screening for per- and polyfluoroalkyl substances in environmental water samples led to the detection of a fluorinated ionic liquid; J. Anal Bioanal Chem., in revision

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Llorca M, Farré M, Sànchez-Melsió A, Villagrasa M, Knepper TP, Barceló D: Perfluoroalkyl phosphonic acids adsorption behaviour and degradation by wastewater organisms Sci. Total Environ. 636:273–281 (2018) https://doi.org/10.1016/j.scitotenv.2018.04.271

Gremmel C, Frömel T, Knepper TP: HPLC–MS/MS methods for the determination of 52 perfluoroalkyl and polyfluoroalkyl substances in aqueous samples. Anal Bioanal Chem 409:1643–1655 (2017) https://doi.org/10.1007/s00216-016-0110-z

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PFAS IN NON-ENVIRONMENTAL MEDIA

- ❑ **Non target analyses are useful for detecting unknown substances, but challenging to perform**
- ❑ **Impregnation sprays difficult to measure unreacted monomers, they may react further**
- ❑ **Watch list should be made specific for product categories/matrices**
- ❑ **We need standardized methods for sample prep and analysis (eg microplastics)**
- ❑ **Regulation based on risk assessment versus analytical LOQ ?**
  - ❑ **Too many PFAS to do single product RA**
  - ❑ **Approach needed for PFAS family**
  - ❑ **Information from industry on products and volumes is needed, but how to achieve this?**

PFAS IN NON-ENVIRONMENTAL MEDIA

- Prioritize regulation/substitution of PFAS in open applications (eg FFF)
- Aim for closed loops eg for ionic liquids in batteries and how to manage end of life?
- Product labels may help to increase awareness from consumers, but beware of overload and integrate in other labels eg one ECO-label
- Public procurement
- Enough information available for restricting use, but
  - Method needed for monitoring of restrictions
  - Chemical standards need to be available for PFAS of concern in specific materials eg leather

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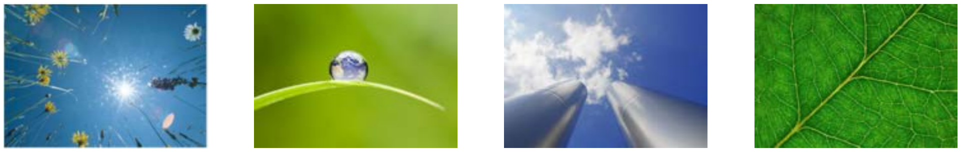
PFAS IN OTHER ENVIRONMENTAL MATRICES (E.G. SOIL, MANURE)

- Transport via air can be important
  - Wastewater treatment plants, incineration of household waste and sewage sludge, landfills and production sites
  - Incineration needs to be studied more (eg 1400 °C) and regulated
- Point sources need to be known and monitored
  - Harmonized EU inventory needed of PFAS contamination
- Zero emission goals for industry (feasible?)
- Essential uses need to be identified
  - By whom?
  - Should not be done from market perspective, but society perspective
- Innovation needed for cleanup technologies
- Biosludge application regulation exists, but PFAS limits are not included
- Industrial emissions directive can be useful for issuing environmental permits … BREFS should include PFAS

ALTERNATIVE SOLUTIONS (E.G. PFAS FREE PRODUCTS, SUBSTITUTION)

- ❑ **Substitution of reagents in production process is difficult for high performance F-polymers**
- ❑ **How to phase out non essential applications?**
  - ❑ **Economic factors versus public health/environment**
  - ❑ **Essential use can change with time**
- ❑ **Innovation needed for alternatives for PFAS**
- ❑ **Evolution to shorter chain alternatives … industry should consider risks**
- ❑ **Better communication necessary between different stakeholders**
- ❑ **We do not need all these high performance applications (eg cosmetics)**

Annex II.6 – Parallel sessions, guiding questions



WORKSHOP AND WORKSHOP REPORT ON PFAS MONITORING

PARALLEL SESSION I: CHARACTERISATION OF PFAS IN GROUNDWATER, SURFACE WATER & DRINKING WATER

Moderators: Frederic Béen (KWR), Stefan Voorspoels (VITO)
Raporteurs: Ulrich Borchers (IWW), Paul Campling (VITO)

ENV.C.2/2016/FRA/0032

PFAS IN GROUNDWATER, SURFACE WATER & DRINKING WATER

1.1 SAMPLING TECHNIQUES AND PROTOCOLS

- Sampling procedure is a very important part of the analytical approach and has therefore to be defined properly
  - Validation of procedures necessary
  - Some guidance can be found in the ISO 5667-3
  - Tubing, Sample bottles, stabilization, transport time and storage time have to be fixed and **validated**
  - Losses of PFAS possible and degradation of precursors has to be considered
- It is crucial that the client and the lab define the goals of analysis prior to the campaign starts
- For sampling the existing sampling standards have to be considered when being an accredited lab (ISO 17025)

1.1 SAMPLING TECHNIQUES AND PROTOCOLS

- Passive sampling not suitable for surveillance monitoring but very helpful for investigative monitoring
  - No experience with passive sampling for PFAS in waters in participating labs present at the workshop
    - iFlux Belgium develops a kind of passive samplers for water (**Water flux cartridges)** **(**information without any proove of suitability!) www.ifluxsampling.com
  - ISO guidelines for passive sampling available
    - **ISO 5667-23:2011-03** Water quality - Sampling - Part 23: Guidance on passive sampling in surface waters
  - Alternative approaches like DGT available but on the stage of academia/research

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European Commission

Biermann presentation: Draft PFAS Parameter Annex I

'Sum of PFASs 0.1 µg/l	**'PFASs Total' 0.5 µg/l**
'Sum of PFASs' means the sum of all per- and polyfluoroalkyl substances considered a concern for drinking water ***listed in Annex III***. This is a subset of PFAS substances that contain a perfluoroalkyl moiety with three or more carbons (i.e. –CnF2n–, n ≥ 3) or a perfluoroalkylether moiety with two or more carbons (i.e. –CnF2nOCmF2m–, n and m ≥ 1).	'PFASs Total' means the totality of per- and polyfluoroalkyl substances. • **This value shall only apply once technical guidelines for monitoring this parameter are developed.** • **Member States may then decide to use either one or two of the parameters 'PFAS Total' or 'Sum of PFAS'** (wording under review!)

Biermann presentation:
PFAS Substances List Annex III

Perfluorobutane sulfonic acid (PFBS)	Perfluorobutanoic acid (PFBA)
Perfluoropentane sulfonic acid (PFPS)	Perfluoropentanoic acid (PFPA)
Perfluorohexanesulfonic acid (PFHxS)	Perfluorohexanoic acid (PFHxA)
Perfluoroheptane sulfonic acid (PFHpS)	Perfluoroheptanoic acid (PFHpA)
Perfluorooctanesulfonic acid (PFOS)	Perfluorooctanoic acid (PFOA)
Perfluorononane sulfonic acid (PFNS)	Perfluorononanoic acid (PFNA)
Perfluorodecane sulfonic acid (PFDS)	Perfluorodecanoic acid (PFDA)
Perfluoroundecane sulfonic acid	Perfluoroundecanoic acid (PFUnDA)
Perfluorododecane sulfonic acid	Perfluorododecanoic acid (PFDoDA)
Perfluorotridecane sulfonic acid	Perfluorotridecanoic acid (PFTrDA)

PFAS IN GROUNDWATER, SURFACE WATER & DRINKING WATER

1.2 ANALYTICAL METHODS AND TARGET PARAMETERS

- Target analysis for all PFAS in general possible according to existing ISO standards
  - **ISO 21675** – PFAS in unfiltered water, incl. isomer (PFOA, PFOS) quantification and normative method if suspended material > 2 g/L
  - (ISO 25101 – PFOS and PFOA in unfiltered water)
- A revision of existing ISO standards may be necessary to implement all requirements for the list of substances mentioned in the DWD
  - To check whether performance and all other requirements are according to the need of DWD
- TOPA may be helpful or a necessary pre-treatment step if also precursors of PFAS shall be included
  - But **definitions in the legal text of DWD should be more precise/detailed** (PFAS or PFAS + precursors?)
  - Costs after application of TOPA are double as high in comparison to normal analysis

PFAS IN GROUNDWATER, SURFACE WATER & DRINKING WATER

1.2 ANALYTICAL METHODS AND TARGET PARAMETERS

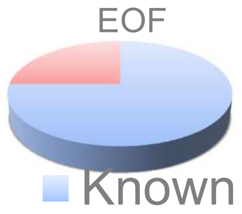
- How do we define a uniform **“total PFAS content”** (DWD= 'PFASs Total' limit 0.5 µg/l) in the analytical chemical context?
- **Definition not available or not precise enough** at the time being.
- That’s a matter for developing further guideline (also in the field of legislation = DWD) → scientific input needed
- Total PFAS ('PFASs Total‘) is really a matter of a consensus (need a proper standardised method)
  - EOF (assumption: not suitable for DW due to lack of sensitivity)
  - AOF (assumption: not suitable for DW due to lack of sensitivity)
  - PIGE (interesting approach, But result is also a kind of AOF instead of TOF)
    - PIGE = Particle Induced Gamma-ray Emission Spectroscopy (Graham Peaslee)
- At the time being: sensitivity is too low and selectivity is not really clear and/or not defined for DWD purposes
  - It has to be considered that total methods end up with a fluoride concentration instead of a concentration for PFAS
  - Not comparable with a mass concentration of PFAS
  - But same limit values for Drinking Water (**inconsistency**)

PFAS IN GROUNDWATER, SURFACE WATER & DRINKING WATER

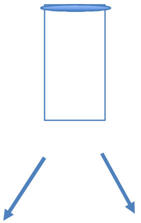
1.2 ANALYTICAL METHODS AND TARGET PARAMETERS

- Are non-specific methods for the determination of organically bound fluorine (EOF, AOF, …) a preferable approach for the monitoring of PFAS?
- Target analysis of PFAS is preferable as it gives
  - More information on the congeners present in a sample
  - More information on the toxicity/effect of a sample
  - A better correlation to the limit value “Sum of PFAS” mentioned in the DWD draft
- Drawback:
  - It’s not possible to calculate (derive) a total PFAS sum by target analysis as the majority of possible congeners will theoretically not be included in the analysis (single method or set of methods)

Concept of mass balance



Mass balance = C_F target / C_F EOF



Fluoride measured after combustion 1100° C

Target PFAS by LC-MS/MS converted to fluoride

Not recovery corrected

1.2 ANALYTICAL METHODS AND TARGET PARAMETERS

- Suspect screening and NT screening (HRMS)
  - Very much at the beginning of setting up data bases and methods
  - Still challenging to extract the relevant data from the “big data” generated
  - Data mining and reduction important

Summary Analysis

	Target analysis of PFAAs and selected precursors	**Total oxidizable precursor assay (TOPA)**	**Extractable organic fluorine (EOF)**	**Non-target or suspect screening of PFAS**
Qualitative	High	Indicates precursor origins	No	Confidence level varies
Quantitative	High	PFCA oxidation products by LC-MS	Fluoride Lower sensitivity than LC-MS	No, or semi-quantitative
Quality control	Interlab studies, CRM´s	Positive control(s) of precursor compounds pH monitoring	Removal of inorganic F Background control Positive control	Sensitivity Multiple ionisation modes

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1.3 GROUNDWATER REMEDIATION STANDARDS – PARAMETRIC VALUES

- Elisa Vargas:
  - More information available via CIRCA DB (EC) from the work of WFD and GWD working groups
- Germany:
  - guidance values for groundwater (7 substances) according to drinking water values

PFAS IN GROUNDWATER, SURFACE WATER & DRINKING WATER

1.4 LATEST DEVELOPMENTS (I)

Europe (19.12.2019)

- Recent update of the EU drinking water directive (cf. Tobias Biermann)
- Sum of PFAS: 0.1 µg/L (i.e., for 20 compounds)
- PFAS total: limit for all 4700 compounds will be set by the European Parliament and Council
  - Commission is to develop a method for measuring all PFAS

PFAS IN GROUNDWATER, SURFACE WATER & DRINKING WATER

1.4 LATEST DEVELOPMENTS (II)

US EPA (19.12.2019)

- Interim recommendations to address **groundwater** contaminated with PFOA and PFOS
- Screening levels for PFOA and PFOS individually at *40 ng/L*
- Preliminary remediation goals (PRG) for PFOA and PFOS (individually or combined) set to *70 ng/L*
  - Responsible parties are to address levels of PFOA and/PFOS in drinking water > 70 ng/L

PFAS IN GROUNDWATER, SURFACE WATER & DRINKING WATER

1.5 PARAMETRIC VALUES

The Netherlands

PFOA

Threshold groundwater	Parametric value (µg/L)
Direct use of groundwater for drinking water production (upper)	0.39**
Direct use of groundwater for drinking water production (lower)	NA
Drinking water	0.0875
Human risk, ”living with garden”	130[#]
Human risk, ”living with kitchen garden”	12[#]

Lijzen et al. 2018 (RIVM)

PFAS IN GROUNDWATER, SURFACE WATER & DRINKING WATER

1.5 PARAMETRIC VALUES

The Netherlands

PFOS

Threshold	Parametric value groundwater (µg/L)
Groundwater (upper)	4.7 *
Groundwater (lower)	0.23 x 10^{-3} **
Human risk, ”living with garden”	310[#]

Wintersen et al. 2016 (RIVM)

PFAS IN GROUNDWATER, SURFACE WATER & DRINKING WATER

1.5 PARAMETRIC VALUES

Germany

Source:

- Umwelt Bundesamt
- Bund-Länder Arbeitsgemeinschaften Wasser (LAWA) und Boden (LABO)

Compound	Drinking water guidance value [µg/L]	Groundwater no effect levels [µg/L]
PFBA	10	10
PFPeA	-	
PFHxA	6	6
PFHpA	-	
PFOA	0.1	0.1
PFNA	0.06	0.06
PFDA	-	
PFBS	6	6
PFHxS	0.1	0.1
PFHpS	-	
PFOS	0.1	0.1
H4PFOS	-	
PFOSA	-	

PFAS IN GROUNDWATER, SURFACE WATER & DRINKING WATER

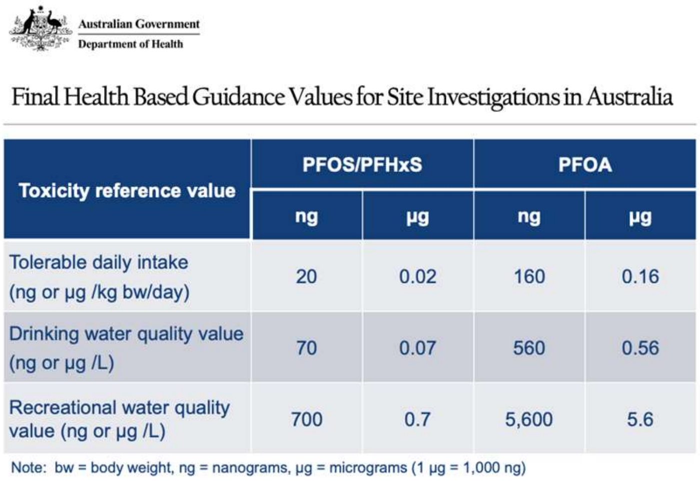
1.5 PARAMETRIC VALUES

Australia

Source: Dr Tony Hobbs

Australian Government

Deputy Chief Medical Officer



Australian Government
Department of Health

Final Health Based Guidance Values for Site Investigations in Australia

Toxicity reference value	PFOS/PFHxS		PFOA	
	ng	µg	ng	µg
Tolerable daily intake (ng or µg /kg bw/day)	20	0.02	160	0.16
Drinking water quality value (ng or µg /L)	70	0.07	560	0.56
Recreational water quality value (ng or µg /L)	700	0.7	5,600	5.6

Note: bw = body weight, ng = nanograms, µg = micrograms (1 µg = 1,000 ng)

CONTACT & INFORMATION

UBA

Philipp HOHENBLUM

philipp.hohenblum@umweltbundesamt.at

IWW

Tim AUS DER BEEK, Ulrich BORCHERS

t.ausderbeek@iww-online.de; u.borchers@iww-online.de

KWR

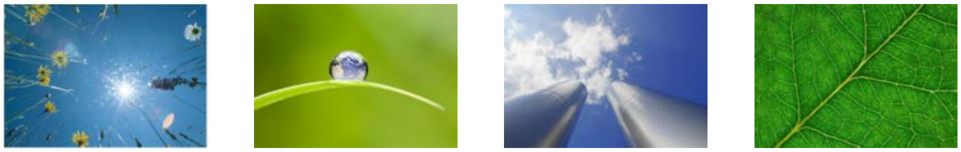
Frederic BEEN, Pim DE VOOGT

Frederic.Been@kwrwater.nl; Pim.de.Voogt@kwrwater.nl

VITO

Paul CAMPLING, Ilse VAN KEER

paul.campling@vito.be; ilse,vankeer@vito.be



WORKSHOP AND WORKSHOP REPORT ON PFAS MONITORING

PARALLEL SESSION II: CHARACTERISATION OF PFAS IN FOOD, CROPS, FEED (INCLUDING PACKING MATERIAL)

Moderator: Pim De Voogt (KWR)
Rapporteurs: Jan Bronders, Kaat Touchant (VITO)

ENV.C.2/2016/FRA/0032

PFAS IN FOOD, CROPS, FEED AND PACKAGING MATERIALS

- Sampling (sample collection) techniques and protocol
- Analytical methods and target parameters
  (PFAS total, PFAS sum, individual components)
- Reference samples
- New insights into BCF & MRL

PFAS IN FOOD, CROPS, FEED AND PACKAGING MATERIALS

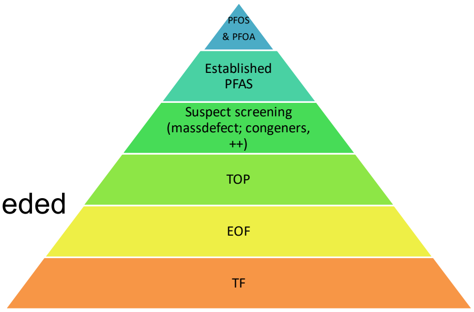
2.1 SAMPLING (SAMPLE COLLECTION) TECHNIQUES AND PROTOCOLS

We propose to collect the following sample types:

- Raw items randomly selected in supermarkets (Total Diet Study)
- Composite food (Ready to eat/cook food items):
- Cauldrons (whole meals, parallel sampling)
- Food packaging
- Data bases with data for individual food items collected from scientific reports
  - International, e.g. EFSA, IPCHEM
  - More data of all sample types are needed – including origin of food items
  - EU countries with no lab facilities should use labs in other countries (reference lab)
- Packaging materials – replacing plastic with coated paper material is creating new problem
- We do need (more) migration studies

PFAS IN FOOD, CROPS, FEED AND PACKAGING MATERIALS

2.2 ANALYTICAL METHODS AND TARGET PARAMETERS (PFAS TOTAL, PFAS SUM, INDIVIDUAL COMPONENTS)



- Analytical methods for individual PFAS are in place and sufficiently sensitive for food/feed analysis
- However the food matrix is different from soil and water; no standard methods are available yet
- Standardized method for TOP and appropriate QA/QC needed
- Individual component approach **AND** TOP
- Total PFAS before or after applying TOP? Both
- For packaging materials further information must be obtained about the applicability of TOP

PFAS IN FOOD, CROPS, FEED AND PACKAGING MATERIALS

2.3 REFERENCE MATERIALS

- What reference materials exist:
  - limited set by IRMM (fresh fish; drinking water)
  - EURL avails of flour; limited availability; not certified for PFAS
- Reference materials needed:
  - meat
  - eggs
  - milk (powder)
  - vegetables

with more certified values for a larger set of individual PFAS and for TOP

PFAS IN FOOD, CROPS, FEED AND PACKAGING MATERIALS

2.4 NEW INSIGHTS INTO BCF AND MRL

- Short chain PFAS tend to accumulate in crops and above ground vegetables
- Long chain PFAS accumulate in fish and meat and below ground vegetables
- Limited information about accumulation in food items (eg. cow’s milk and vegetables)
- MRLs will be assessed for individual PFAS only (for the time being); not for TOP
- MRLs will be defined for each food item separately based on occurrence levels
- Expected MRL levels can be achieved with current analytical methods

2.5 REDUCTION MEASURES

- EFSA (2018): considerable proportions of the European population exceed the newly established tolerable weekly intakes of both PFOS (13 ng/kg bw/wk) and PFOA (6 ng/ bw/wk)
- Possibilities for reduction of human exposure on short notice:
  - ban on use in packaging material (Denmark)
  - not importing food/feed with high levels; requires MRLs for food and frequent monitoring
  - consumption advice on selected highly contaminated food items

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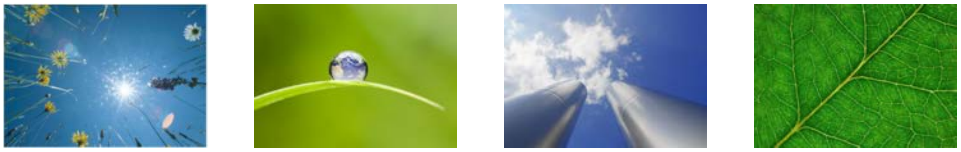
CONTACT & INFORMATION

UBA
Philipp HOHENBLUM
philipp.hohenblum@umweltbundesamt.at
IWW
Tim AUS DER BEEK, Ulrich BORCHERS
t.ausderbeek@iww-online.de; u.borchers@iww-online.de
KWR
Frederic BEEN, Pim DE VOOGT
Frederic.Been@kwrwater.nl; Pim.de.Voogt@kwrwater.nl
VITO
Paul CAMPLING, Ilse VAN KEER
paul.campling@vito.be; ilse,vankeer@vito.be

Parallel Session II – Workshop and workshop report on PFAS Monitoring
Borschette Conference Centre, Etterbeck ● 2020-01-14



WORKSHOP AND WORKSHOP REPORT ON PFAS MONITORING - PARALLEL SESSION III:

CHARACTERISATION OF PFAS IN OTHER MATRICES / MEDIA - ALTERNATIVES SUBSTITUTES FOR PFAS (14/01/2020)

Moderator: Tim aus der Beek (IWW)
Rapporteurs: Johan Gemoets (VITO), Cora Schmidt (IWW)

ENV.C.2/2016/FRA/0032

PFAS IN OTHER MATRICES / MEDIA - ALTERNATIVES SUBSTITUTES FOR PFAS

3.1 PFAS IN NON-ENVIRONMENTAL MEDIA

- Non target analyses are useful for detecting unknown substances, but challenging to perform
- Impregnation sprays difficult to measure unreacted monomers, they may react further
- Watch list should be made specific for product categories/matrices
- We need standardized methods for sample prep and analysis (eg microplastics)

- Regulation based on risk assessment versus analytical LOQ ?
  - Too many PFAS to do single product RA
  - Approach needed for PFAS family
  - Information from industry on products and volumes is needed, but how to achieve this?

PFAS IN OTHER MATRICES / MEDIA - ALTERNATIVES SUBSTITUTES FOR PFAS

- Prioritize regulation/substitution of PFAS in open applications (eg FFF)
- Aim for closed loops eg for ionic liquids in batteries and how to manage end of life?
- Product labels may help to increase awareness from consumers, but beware of overload and integrate in other labels eg one ECO-label
- Public procurement
  - Enough information available for restricting use, but
  - Method needed for monitoring of restrictions
  - Chemical standards need to be available for PFAS of concern in specific materials eg. leather

IWW KWR vito ENVIRONMENT AGENCY AUSTRIA umweltbundesamt

PFAS IN OTHER MATRICES / MEDIA - ALTERNATIVES SUBSTITUTES FOR PFAS

3.2 PFAS IN OTHER ENVIRONMENTAL MATRICES (E.G. SOIL, MANURE)

- Transport via air can be important
  - Wastewater treatment plants, incineration of household waste and sewage sludge, landfills and production sites
  - Incineration needs to be studied more (eg 1400 °C) and regulated
- Point sources need to be known and monitored
  - Harmonized EU inventory needed of PFAS contamination
- Zero emission goals for industry (feasible?)
- Essential uses need to be identified
  - By whom?
  - Should not be done from market perspective, but society perspective

IWW KWR vito ENVIRONMENT AGENCY AUSTRIA umweltbundesamt

PFAS IN OTHER MATRICES / MEDIA - ALTERNATIVES SUBSTITUTES FOR PFAS

- Innovation needed for cleanup technologies
- Biosludge application regulation exists, but PFAS limits are not included
- Industrial emissions directive can be useful for issuing environmental permits … BREFS should include PFAS

PFAS IN OTHER MATRICES / MEDIA - ALTERNATIVES SUBSTITUTES FOR PFAS

3.3 ALTERNATIVE SOLUTIONS (E.G. PFAS FREE PRODUCTS, SUBSTITUTION)

- Substitution of reagents in production process is difficult for high performance F-polymers
- How to phase out non essential applications?
  - Economic factors versus public health/environment
  - Essential use can change with time
- Innovation needed for alternatives for PFAS
- Evolution to shorter chain alternatives … industry should consider risks
- Better communication necessary between different stakeholders
- We do not need all these high performance applications (eg cosmetics)

CONTACT & INFORMATION

UBA

Philipp HOHENBLUM

philipp.hohenblum@umweltbundesamt.at

IWW

Tim AUS DER BEEK, Ulrich BORCHERS

t.ausderbeek@iww-online.de; u.borchers@iww-online.de

KWR

Frederic BEEN, Pim DE VOOGT

Frederic.Been@kwrwater.nl; Pim.de.Voogt@kwrwater.nl

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