background

Bund für
Umwelt und
Naturschutz
Deutschland

BUND
FRIENDS OF THE EARTH GERMANY

Fluorochemicals: Persistent, Dangerous, Avoidable

Table of contents

This project is financially supported by: BMU

The publisher is responsible for the content of this publication.

Federal Ministry for the Environment, Nature Conservation and Nuclear Safety

Umwelt Bundesamt

Abstract

PFAS are non-aromatic, organic chemicals in which the hydrogen atoms in the carbon chain are fully replaced ("per") or partly but almost entirely replaced ("poly") by fluorine atoms. At least 4,700 substances belong to this group of substances. All these chemicals have in common that their environmental degradability is fairly slow and very limited and therefore remain resistant for years to decades. PFAS – the best-known representatives are PFOA (perfluorooctanoic acid) and PFOS (perfluorooctane sulfonate) – have particular technical properties: for example, they are not only water-repellent but also oil- and dirt-repellent. They are used in a variety of applications, for example, in fabrics, food packaging, firefighting foams, lubricants and they are used as well as active ingredients in pesticides and pharmaceuticals. Some PFAS are known to be chronically toxic at extremely low concentrations, e.g., they affect the immune system and disrupt the thyroid function. For food, EFSA[1] has therefore published a scientific opinion on a safety threshold that the sum of four common PFAS should not exceed the dose of only 4.4 ng per kilogram of body weight per week. PFAS also pose a particular risk to the environment. Not only are they extremely persistent, but numerous representatives also accumulate in organisms (bioaccumulation) and/or are so mobile that they spread rapidly and are detected even in remote regions. PFOA and PFOS are therefore listed as persistent organic pollutants (POPs) in the Stockholm Convention and have been agreed for global elimination. Other representatives are legally restricted at the European level. However, the diversity of PFAS always allows for an evasion to other PFAS that are less intensively studied and therefore not yet regulated. The use of PFAS in the past did result in widespread contamination of waters and soils. For example, nearly at all civilian and military airfields we find serious legacy contamination because fluorochemicals were used in foam during firefighting exercises and operations. They resulted in groundwater contamination that often threatens drinking water supplies. Remediation is extremely difficult and often ineffective because PFAS are difficult to remove from water and soil. The extent of environmental contamination with PFAS can often only be estimated. The analytics required to monitor at very low concentrations are still under development and are not capable of capturing the diversity of PFAS used.

PFAS are "forever chemicals." Even when being incinerated for disposal, very high temperatures are required for these compounds to decompose completely. Therefore, drastic measures are necessary to prevent further increasing contamination of the natural environment. This background paper comprises recommendations and demands of BUND – Friends of the Earth Germany followed by the justification of these demands with an explanation of the properties, the applications and the occurrence of PFAS, a presentation of the regulations, the limit and guideline values as well as a presentation of the analytics of these chemicals. Furthermore, contaminated sites with PFAS and possibilities for their remediation as well as the existing need for research are mentioned.

[1] *European Food Safety Authority*

Recommendations and demands of BUND (Friends of the Earth) regarding PFAS

Fluorochemicals are organic chemicals in which all or part of the hydrogen atoms are replaced by fluorine atoms. As a result, the properties of the substances are significantly changed. This paper deals with a large class of per- and polyfluoroalkyl substances (PFAS), a group of substances consisting of over 4,700 chemicals[2] found in many products consumed on a daily basis

Phase-out of production and use – restrictions

- PFAS are a problem throughout the world. A global approach to the assessment and restriction/prohibition of PFAS is thus needed. The instrument currently available for this is the Stockholm Convention. This must be adapted and further developed in such a way that not only individual substances but the entire group of chemicals can be regulated. At the same time, waste containing PFAS must be strictly regulated within the framework of the Basel Convention. In the medium term, the Stockholm and Basel Conventions must be integrated into a Chemicals and Materials Framework Convention, which also regulates other substance policy agreements under its umbrella in a legally binding manner.
- At the EU level, the group approach set out in the Chemicals Strategy for Sustainability in accordance with the REACH Regulation must be implemented quickly and consistently. Previous experience has shown that bans or restrictions on individual PFAS have repeatedly led to replacement by other PFAS that have until then been less frequently used. However, it turns out that the entire group of substances is problematic, especially because of their persistence.
- The BUND calls for a complete phase-out of the production and use of PFAS by 2030. Phasing out consumer products (fabrics, paper, food packaging, impregnation sprays, cosmetics, ski waxes, etc.) is particularly urgent. The phase-out of these consumer products should be completed by 2025.
- A phase-out of technical applications (extinguishing agents, coatings/electroplating, use of fluoropolymers) by 2030 is desirable. Appropriate alternative procedures must be promoted and enforced through regulatory measures.
- The restrictions and prohibitions must also cover PFAS that are currently produced and marketed in low volumes or as mixtures.
- Essential uses, such as technical applications of polymers or medical applications, shall only be permitted where there are no suitable alternatives. Such uses must always be temporary. These exceptions are only permitted if they involve products with a long life span for special applications that are collected completely, seperated after use and subjected to orderly recovery or disposal. Applications in open environments such as in sprays, waxes or lubricants should not be considered exceptions.
- During the transitional period preceding a ban and for any necessary exceptions for special applications, labeling is required for all products (consumer products as well as professional products) as soon as these products contain PFAS.
- Suppliers are called upon to cease supplying products containing PFAS.
- In the meantime, national possibilities for restricting or labeling products containing PFAS must be applied to the fullest extent possible, for example, in food packaging.
- There is an urgent need for government and industrial research programs seeking alternatives to PFAS in order to achieve the goal of a complete phase-out by 2030.

[2] Other sources even speak of >9,000 chemicals, https://comptox.epa.gov/dashboard/chemical_lists/pfasmaster

- The tolerable weekly dose (TWI) of 4.4 ng/kg body weight published by EFSA for the sum of four individual substances PFOS, PFOA, PFHxS and PFNA must be consistently implemented in all areas with potential human exposure (food as well as drinking water, food packaging, the soil –> human pathway in the hazard assessment of soil pollution, insignificance thresholds for the assessment of pollution and contamination of groundwater).
- For other exposure-relevant individual compounds, values for a tolerable weekly intake (if possible as total intake) must also be worked out.
- The use of chemicals, for example, coolants which contribute to the contamination of environmental media with trifluoroacetic acid, should be severely restricted. In particular, the use of the refrigerant R1234yf in car air-conditioning systems should be discontinued.
- Approvals of medicinal products and pesticides containing active substances with trifluoromethyl groups must be reviewed and, if necessary, revoked.

Analytics and monitoring

- Monitoring (emissions from exhaust gas and exhaust air from industrial plants, pollution of environmental media, food, biota, humans) of the release, spread and effects of PFAS must be significantly intensified and expanded. This monitoring needs to be extended with regard to both the wide variety of the PFAS being monitored and the media examined. This is especially true since long-lasting PFAS will remain detectable in the environment for several decades even after a ban.
- All drinking water production units must be tested for PFAS every year. These tests should be carried out both in raw water and in processed drinking water. At least the 20 individual PFAS parameters of the EU Drinking Water Directive (EU 2020) as well as relevant polyfluorinated compounds with a detection limit of 1 ng/l must be analyzed. A corresponding requirement must also apply to all medicinal and mineral water sources.
- As the main intake of PFAS for newborns and infants is through breast milk, nursing mothers should be counseled and given the opportunity to have their breast milk tested for at least the four PFAS compounds (PFOS, PFOA, PFHxS, PFNA) considered by EFSA to be of particular relevance.
- For monitoring, further development and validation of analytical procedures is necessary:
  - Sum parameters such as AOF, which quantitatively cover as many PFAS as possible with high sensitivity, including polymers with fluorinated side chains
  - Extension and optimization of the extraction methodology for soil and other solid environmental media as well as for products and waste
  - Optimization and standardization of the TOP assay for aqueous and solid environmental media
  - Biological assays that detect as many PFAS as possible with sufficiently high sensitivity
  - Significant expansion of single-substance analysis and improvement of sensitivity
  - Development and validation of suitable sampling methods for exhaust gas and exhaust air that allow complete detection of at least the per- and polyfluorinated alkylcarboxylic and alkylsulphonic acids as well as the oxocarboxylic acids (ether carboxylic acids) and their decomposition products.
- A limited number of representative PFAS precursors should be defined which make it possible to apply valid analytical procedures to qualitatively and quantitatively detect the release of PFAS and their components in the exhaust gas of thermal plants such as in waste incineration even at low concentrations.

Contaminated sites and waste

- A special funding program amounting to at least € 150 million for the recording, risk assessment and remediation of PFAS-contaminated sites should be set up by the German government and the states.
- In order to treat the many sites contaminated with PFAS, efficient remediation technologies must be (further) developed.
- Suspected cases of firefighting foam being discharged into the environment must be systematically checked and subjected to a risk assessment.
- In the case of remediation, the polluter-pays principle must be applied consistently. This applies in particular to the (former) manufacturers of PFAS.
- Recycling of products containing PFAS should be avoided due to the risk of PFAS being carried over into secondary raw materials.
- Safe waste treatment technologies (e. g., for paper sludge) must be developed.
- Uniform criteria for the disposal of waste and soil containing PFAS need to be developed.
- Waste containing PFAS must be incinerated in plants where the temperatures involved lead to complete destruction of the fluorochemicals or the residual products are effectively removed from the exhaust gas stream.
- The destruction of PFAS in waste incineration plants and the elimination of PFAS and their derivatives from the exhaust gas stream of incineration plants need to be investigated in more detail. Based on this, processes for the incineration of waste that contains PFAS must be developed in order to ensure PFAS and resulting residual products are disposed of safely.
- The post-combustion of the exhaust gas stream of all plants for the reactivation of activated carbon must also take place at temperatures that lead to the complete destruction of fluorochemicals.

Information and research

- Manufacturers of PFAS must disclose chemical structures, methods of analysis and production and import volumes, even below 1 t/year. Standard substances must be made available or unrestricted access must be made possible. Annex VI of the REACH Regulation must require the provision of spectra and standard substances in order to enable analytical identification and quantification of the substances.
- Well-prepared information and avoidance and behavioral advice on how to deal with PFAS for consumers and retailers are necessary.
- Research on PFAS must be funded in particular through a BMBF joint research project with a financial endowment of at least € 100 million, for example, toxicology of short-chain PFAS, accumulation in crops, PFAS-free processes and products, treatment of drinking water, processes for remediation of contaminated sites.
- The rapidly increasing knowledge of the toxicology and epidemiology of PFAS and other chemical substances in the environment must be made part of the curriculum for training physicians.

Explanation and justification of recommendations and demands

1. Properties, occurrences, applications

What are PFAS

Fluorochemicals of the type PFAS (per- and polyfluorinated alkyl substances) have been synthetically produced since the 1950s. There is no natural source of these compounds.

PFAS are non-aromatic, organic chemicals in which the hydrogen atoms in the carbon chain are fully replaced (per) or partly but not completely replaced (poly) by fluorine atoms. Previously, this group of substances was referred to as PFCs (per- and polyfluorinated chemicals). The best known are perfluorinated alkyl alkylcarboxylic and alkylsulfonic acids such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS, see Fig. 1). Some newer PFAS contain an oxygen atom within the carbon chain (e. g., perfluoroether acids such as ADONA[3] or HFPO-DA[4]). In general, all chemicals with a CF2 group or CF3 group are PFAS (Kwiatkowski C. F. et al. 2020, REACH helpdesk 2021b). PFAS also include short-chain fluorocarbons and chlorofluorocarbons (HFCs and CFCs) as well as some bromine derivatives (halons), which damage the ozone layer and/or cause a strong greenhouse effect. The definition also covers fluorinated polymers in which the central carbon chain (as in polytetrafluoroethene, PTFE[5]) or the side chains (as also seen in fluorinated polyacrylates) are per- or polyfluorinated. Finally, partially fluorinated precursors that are slowly converted into perfluorinated molecules in the environment must also be taken into account (Held T. 2020). Suggestions are being made to categorize the very large number of several thousand PFAS into defined groups (Buck R. C. et al. 2021).

What are the technical characteristics of PFAS?

In many PFAS, there is a mostly polar functional group at one end of the carbon chain, such as an acid, alcohol or ester group. As a result, they have surface-active properties and behave similarly to wash-active substances (surfactants), which is why the term perfluorinated surfactants (PFS) used to be common for such PFAS. In contrast to other known surfactants, the strongly electronegative properties of the fluorine atoms mean that such PFAS are not only water-repellent, but also oil- and dirt-repellent. In addition, the high thermal and chemical stability of PFAS make their use possible in many different applications.

Why do PFAS pose a problem to the environment?

The most striking property of PFAS is their extreme persistence: Under naturally occurring conditions they are scarcely degradable. In the case of partially fluorinated chemicals, slow microbial conversion processes with degradation of the non-fluorinated molecular part are known, but the perfluorinated residue persists for a very long time. There is virtually no way to split multiple carbon fluorine bonds on a carbon atom under environmental conditions through biological or abiotic processes. That is why PFAS are called "forever chemicals." For this reason alone, extremely persistent substances pose a threat to the environment regardless of their other ecological or toxicological properties (BUND 2019).

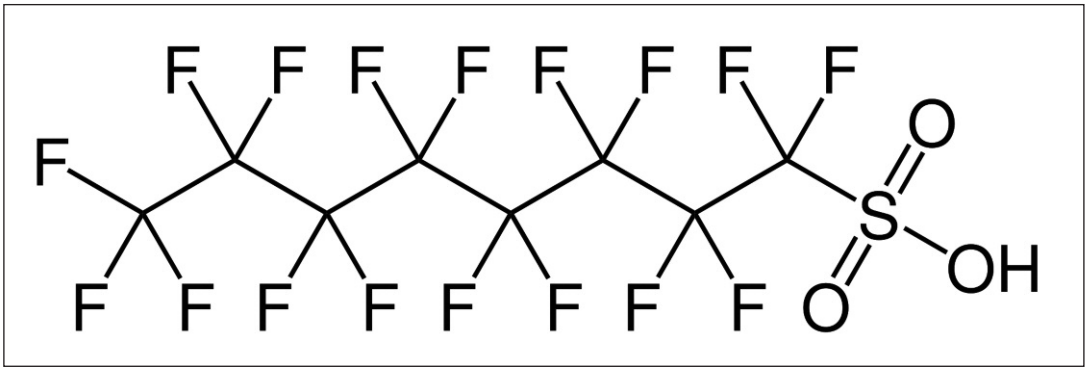

Fig. 1: Formula for the structure of perfluorooctanesulfonic acid (PFOS) © www.wikipedia.de

[3] ADONA: Ammonium salts of ammonium 4,8-dioxa-3H-perfluorononanoate (DONA)

[4] HFPO-DA: 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid

[5] Trade name Teflon

Since PFAS are hardly degraded, but at the same time new additional loads are perpetually being introduced into the environment, the amount detectable in the environment is continuously increasing. The fact that "forever chemicals" cannot be recovered if a harmful effect is detected is especially critical.

However, many PFAS are not only persistent, but also have other problematic ecological properties. Perfluorinated carboxylic and sulfonic acids with chain lengths of 6 to 14 carbon atoms are the most thoroughly investigated:

- PFAS can be absorbed from the soil, for example, by crops, with short-chain ones accumulating more than their long-chain counterparts (Stahl T. et al. 2009, Krippner J. et al. 2014, Krippner J. et al. 2015), as well as from rainfall runoff (Blaine A.C. et al. 2014). In this way, they can enter food chains and food nets.
- Many PFAS with C6-C14 chain lengths accumulate in organisms and along food chains and food webs. They bioaccumulate by binding to proteins in the blood, liver and kidneys. In fish, a bioconcentration factor of 2,800 was measured for PFOS (Umweltbundesamt 2011). They are only very slowly excreted again. Thus, the biological half-lives for PFOA, PFOS, PFNA[6] and PFHxS[7] in the human body range from two to nine years.
- PFAS are comparatively mobile when waterborne or airborne. Neutral PFAS such as fluorotelomer alcohols are comparatively volatile and contribute to indoor air pollution (Morales McDevitt M.E. et al. 2021). When PFAS are emitted into the air, they can be transported to Arctic and high mountain regions (Joerss H. et al. 2020). They are also transported over long distances when dissolved in water. In Hesse, 364 groundwater monitoring point inspections for 21 different PFAS were carried out annually from 2009 to 2016. PFAS could be detected at about 90 % of the measuring points (Gassmann M. et al. 2021). They penetrate the unsaturated soil zone and can then be transported by the groundwater over long distances. Short-chain anionic alkylcarboxylic and alkylsulfonic acids seep away more quickly, while longer-chain acids and especially cationic and zwitterionic representatives are more strongly bound to the soil particles.
- In aquatic organisms, perfluorinated alkylcarboxylic and alkylsulfonic acids can disrupt reproduction and development at low concentrations and also affect sexual and thyroid function (Lee J.W. et al. 2020). In fish and daphnia, effect concentrations of PFOS in the chronic test are below 1 mg/l (Gerst M. et al. 2008). Among freshwater organisms, mosquito larvae (Chironomides) react most sensitively with a LOEC[8] of only 2 µg/l (Umweltbundesamt 2011).
- Some publications report that the reproductive capacity and the behavior of important pollination insects such as honeybees (Sonter C. A. et al. 2021) and bumblebees (Mommaerts V. et al. 2011) can be negatively affected by PFOS.

The environmentally relevant properties of, for example, short-chain PFAS and fluorinated oxocarboxylic acids (ether carboxylic acids), on the other hand, are much less well known.

Why do PFAS pose a risk to human health?

Here, too, perfluorinated alkylcarboxylic and alkylsulfonic acids with chain lengths of 6 to 14 carbon atoms are the most thoroughly investigated. So far, only a few studies have been carried out on short-chain and other per- and polyfluorinated substances. Nevertheless, these compounds are advertised by the industry as "harmless alternatives" to PFOAs and PFOS. Numerous effects have been described (Sunderland E.M. et al. 2019, Fenton S. et al. 2021 – see Figure 2). From 2005 to 2013, a C8 Science Panel[9] investigated the effects of PFOA exposure on the population in the vicinity of a manufacturer in the US (C8 Science Panel 2020):

- The effects on the immune system are the most serious (Beans C. 2021): Epidemiological studies have shown that antibody buildup following vaccination of children is significantly reduced by exposure to PFAS (Grandjean P. et al. 2012, Abraham K. et al. 2020). Consequently, on the basis of two studies with human beings the European Food Safety

[6] PFNA: Perfluorononanoic acid
[7] PFHxSA: perfluorohexanesulfonic acid
[8] LOEC: Lowest observed effect concentration
[9] A group of scientists who compiled results for PFOA

Authority (EFSA) has set a very low group tolerable weekly intake (TWI) of only 4.4 billionths of a gram per kilogram (ng/kg) body weight for the sum of four PFAS (PFOS, PFOA, PFNA and PFHxS) (EFSA 2020).

- Furthermore, the formation of thyroid hormone is impaired even at comparatively low concentrations. For example, there is a causal relationship between PFHxS and PFOS exposure and disruption of thyroid function in mothers in the early stages of pregnancy (Xiao C. et al. 2020, Birru R.L. et al. 2021). Based on the effect on thyroid hormones, a biological test for PFAS has been developed (Annex A).
- There is clear evidence that PFOA leads to increased incidence of testicular and kidney cancer, for example, in a study that investigated the occurrence of cancer in relation to the distance from a single identifiable localized source (Vieira V.M. et al. 2013). Although the incidence of testicular cancer has increased significantly in recent decades and the prebirth effects of chemical substances in the environment are a possible cause, until now no longitudinal studies have investigated the results reported by Vieira et al. The carcinogenic effects of some PFAS may result from increased mutation rates in genetic material (mutagenesis) as well as from epigenetic effects.
- Studies in the US of adults and children who ingested drinking water contaminated with PFAS identified elevated blood lipid levels. Disorders of fat and sugar metabolism as well as obesity are among the consequences of PFAS exposure.
- Several studies indicate the existence of liver damage caused by PFAS (Salihovic S. 2018, Stratakis N. 2020). Some PFAS are liver-toxic and destroy liver cells. Pathologically altered metabolic pathways and products can lead to considerable liver damage (fatty liver, fibrosis, steatohepatitis) even in children (Jin R. 2020).
- Animal studies have demonstrated the kidney toxicity of PFAS (ATSDR 2018). Of all body tissues, the highest PFAS levels are found in the kidneys (Blake B.E. 2018). Although the kidneys are the main excretory organ for PFAS, about 99.9 % of PFAS are reabsorbed in the renal tubules. This also contributes to the non-degradability of the fluorochemicals and to their accumulation in the human body (bioaccumulation).
- The transmission of PFAS from mother to child dur-

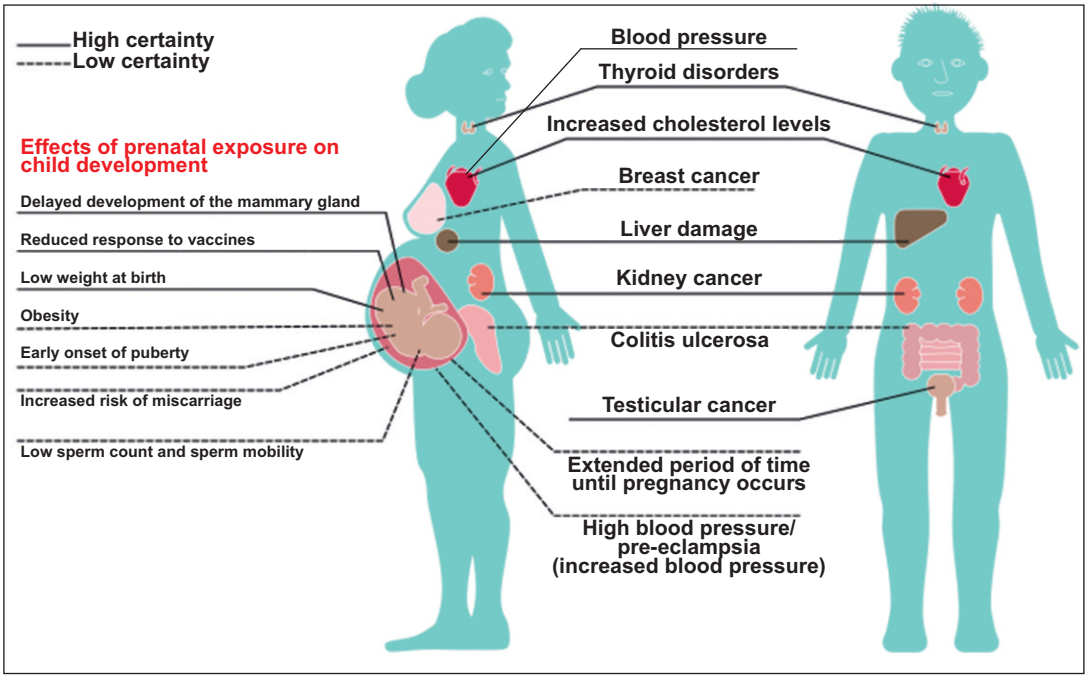

Fig. 2: Toxicological effects of PFAS on humans © https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7906952/

ing breastfeeding is also critical. Fromme H. et al. (2010) established a median value of 40 pg/ml for PFOS in mother's milk. In a US study, the breast milk of 50 women was examined for 39 PFAS (Zheng G. et al. 2021). The median values were 121 pg/ml for the sum of 39 PFAS and 30.4 pg/ml for PFOS. In newborn children the tolerable weekly dose (TWI) determined by the EFSA (see above) is thus exceeded by a factor of 10. Decreased immune competency is likely in many babies affected. Compared with other breast-milk studies, Zheng et al. concluded that concentrations of PFOA and PFOS that are already subject to regulation are decreasing; those of the short-chain and other longer-chain variants, on the other hand, are increasing significantly.

- Numerous publications indicate that PFAS can be toxic to reproduction. Both PFOA and PFOS are classified as toxic to reproduction. Fluorochemicals can suppress the formation of androgens (males hormones) (antiandrogenic effect) and thus negatively affect both penis and semen development (Rosenmai A.K. et al. 2013). The endocrine-disrupting effects of PFAS reduce both male and female fertility (Di Nisio A. et al. 2019, Di Nisio A. et al. 2020a).
- Particular attention should be paid to the effects on brain function. For example, Chen M.H. et al. (2013) reported delayed development of mobility (gross motoric skill) in two-year-old children after prenatal exposure to PFOS. There is also evidence of a relationship between prenatal exposure to fluorochemicals and disturbances of concentration (Forns J. et al. 2020), possibly as a result of a reduction of dopamine in the brain through PFOS and PFOAs (Foguth R.M. et al. 2019). Several epidemiological studies have shown impairment of intellectual performance, especially when there is prenatal exposure to PFAS (Gallo V. et al. 2013.)
- Several other health impairments are also described in the literature. For example, a connection between childhood caries and exposure to perfluorodecanoic acid (PFDA) is likely (Wiener C.A. et al. 2019). Bone loss (osteoporosis) has been caused by PFOA even in young men (Di Nisio A. et al. 2020b).

What are PFAS used for?

Their special technical characteristics lead to highly diverse uses of PFAS (Glüge J. et al. 2020, REACH helpdesk 2021a). The most important are:

- Some fluorocarbons are still widely used as propellants, refrigerants and extinguishing agents and in plastic foams (polystyrene and polyurethane).
- PFAS are used to impregnate fabrics and leather to make them water and dirt repellent. This applies in particular to outdoor and workwear as well as household fabrics such as carpets (Fig. 3). Impregnating sprays also often contain PFAS, including polyfluorinated silanes such as tridecafluorooctylsilanetriol[10], which according to REACH Annex XVII is restricted since January 2, 2021.
- The water and grease repellent properties of PFAS are useful for treating the surface of paper and printed products. This also applies to food packaging (including forms that are actually compostable) such as coffee cups, disposable tableware and pizza boxes, some of which contain high PFAS levels (Straková J. et al. 2021 – Fig. 3). Initial investigations from Hesse (Hessian State Laboratory) on water and ethanol extracts of coated food contact materials using the adsorbable organic fluorine (AOF) method (see Annex A) confirm these results. More than 100 µg/g were found in every third sample of paper (see von Abercron E. 2021). During paper recycling, PFAS can contaminate scrap paper.
- The surface-active properties of PFAS, for example PFOS, justify their use in firefighting foam (Fig. 3). Especially at airfields, fire extinguishing training exercises and operations with these substances which led to contamination of the soil and groundwater have taken place.
- PFAS in ski waxes increase slipperiness.
- In electroplating involving chrome plating with hexavalent chromium, Cr(VI), PFOS and its substitutes such as 6:2-FTS[11] as a wetting agent prevent the toxic chromate aerosols from rising and improve the runoff behavior of the pickling liquids from products.

[10] *3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its alkyl derivatives*

[11] *6:2 FTS: 6:2 Fluortelomer sulfonic acid, also known as H_4PFOS (H4-polyfluorooctanesulfonic acid)*

- Polytetrafluoroethene (PTFE) and other fluoropolymers such as perfluoropolyethers (PFPE) are used for coating pans and pots as well as other surfaces. As a result, adhesion of food or food residues is avoided and the products withstand high thermal and chemical loads. PFOA and substitutes such as ADONA and HFPO-DA serve as emulsifiers for the production of fluoropolymers.
- Cosmetics such as sunscreen and hair care products often contain PFAS to make them water-repellent (Whitehead H.D. et al. 2021).
- PFAS can be found in numerous construction products such as floor coverings, cables, coated woods, solar panels and glass (Green Science Policy Institute 2021).
- Some pesticides contain co-formulant PFAS as wetting agents, with PFOA now being replaced by other substances. About 30 active ingredients contain trifluoromethyl (CF3) groups (e. g., fluridone, flufenacet), which contribute to the spread of trifluoroacetic acid (TFA) after transformation in the environment (see below). This also applies to a number of active pharmaceutical ingredients (e. g., flecainide, sitagliptin). Meanwhile, about 30 % of the newly approved active substances in medicinal products are fluoroorganic compounds (Müller M. 2021).

Most applications can be replaced by suitable fluorine-free alternatives.

Fig. 3: PFAS in firefighting foams make effective firefighting possible – outdoor jackets are often impregnated with PFAS – PFAS make food packaging grease-repellent © iStockphoto

What happens to waste that contains PFAS?
The high stability of the C-F bond also makes PFAS a problem in waste disposal:

Consumer products containing PFAS are predominantly disposed of as municipal waste and are either incinerated or deposited in landfill. State-of-the-art landfill avoids contamination of groundwater. Leachate is often treated, for example, by reverse osmosis, before it is discharged into the sewage system. No biodegradation of PFAS takes place in sewage treatment plants; a portion is absorbed into sewage sludge and, if it is not incinerated, is spread on farmland (Reach Helpdesk 2021a).

So far, there is little and conflicting data on the conditions under which PFAS are fully mineralized during combustion (U.S. EPA 2020). It is possible that at least 1,100 °C for 2 seconds is sufficient for the complete decomposition of most PFAS during combustion (Yamada T. et al. 2005, UNEP-POPs 2021, Umweltbundesamt 2020d). There are indications that fluororganics are largely converted to inorganic fluoride by state-of-the-art municipal waste incineration (minimum combustion temperature 850 °C) (Aleksandrov K. et al. 2019). On the other hand, the mineralization of tetrafluoromethane (CF4), whose thermal decomposition is particularly difficult, requires a combustion temperature of over 1,400 °C (Tsang W. et al., 1998).

Germany's 17th Federal Immission Control Ordinance (BImSchV) prescribes a minimum combustion temperature of 850 °C. A minimum combustion temperature of 1,100 °C is only required for the incineration of hazardous waste with halogen content of at least 1 %. For many products containing PSASs and in municipal waste, the fluorine content is significantly lower than 1 %. Plants for incinerating municipal waste are operated mostly at temperatures above the minimum of 850 °C, but under 1,100 °C. PFAS decompose into short-chain decomposition products and hydrofluoric acid (HF), which are disposed of with other acidic components of the raw exhaust fumes with the help of alkaline substances. Any unburned PFAS and their derivatives should be fixed by adsorption (e. g., to activated carbon, coke or lime) and removed from the raw exhaust gas. However, there is still a lack of sufficient valid data on the effectiveness of this elimination of PFAS and its decomposition products from raw exhaust gas (U.S. EPA 2020). Presumably, in cement kilns in which alkaline conditions for neutralizing hydrofluoric acid (HF) prevail, temperatures are achieved that are sufficiently high (up to 1,400 °C) to almost completely destroy the PFAS, but here, too, validated studies are lacking.

Product streams in which waste is separately collected with subsequent recycling, are problematic, for example, paper, which is used in many types of food packaging, and with fabrics. During recycling, the PFAS are carried into the secondary products and contaminate them.

Where are PFAS found in humans and the environment?
The numerous uses of PFAS also lead to a variety of inputs into the environment and to human exposure. Wang Z. et al. (2014a, 2014b) published global emission inventories for perfluorocarboxylic acids and were able to quantify a variety of different input pathways. Washington J.W. et al. (2015) investigated the hydrolysis of side chain polymers (polyacrylates with fluorotelomer alcohols as side chains) in soil and water. The half-lives cover a range of 10 to 100 years. Due to high production volumes, this contributes significantly to background pollution with PFAS in the environment (oceans and terrestrial ecosystems) (Washington J.W. et al. 2019).

PFAS enter surface water via wastewater (von Abercron E. et al. 2019). In sewage treatment plants, they are partially bound to sewage sludge (Stahl T. et al. 2018), which leads to soil and groundwater pollution when the sewage sludge is used in farming. Abrasion of polymeric PFAS can also be found here, combined with microplastics from other polymers. If groundwater or surface water is used as drinking water, this may also contain PFAS if the protective barriers of drinking water treatment are overcome due to the properties of this special group of substances. These barriers are

eliminated when contaminated groundwater or surface water is directly used for agricultural irrigation, in home gardens or for fishponds and PFAS then accumulate in soils, crops or fish (Blaine A. C. et al. 2014, Bethke H. & Budde J. 2020).

Some PFAS are relatively volatile, which is why relevant quantities can be detected indoors as a result of outgassing from products such as carpets. Air measurements have even shown that, in addition to food, indoor air is a relevant exposure pathway for PFAS. In particular, fluorotelomer alcohols such as FTOH 6:2 and FTOH 8:2 are so volatile that they are detected in relevant concentrations (Morales McDevitt M. E. et al. 2021). In the vicinity of production sites, soil contamination across a wide area can be detected via the air pathway. Air measurements far away from emission sources demonstrate the global problem posed by this group of substances (Rauert C. et al. 2018).
PFAS levels are now being determined in numerous environmental media, in organisms, in food and in humans as part of monitoring programs (Kotthoff M. et al. 2020). In soils, longer-chain PFAS are more tightly bound than short-chain compounds (Krippner J. et al. 2014). The latter thus also enter the groundwater more quickly. The concentrations of PFOS and PFOA in most environmental media (as well as in breast milk, see above) have decreased in the past 10 to 20 years, as these two substances are already regulated by chemical law. By contrast, the concentrations of other PFAS that have been subjected to less study and are used as substitutes are increasing (Falk et al. 2019). Some PFAS which are now widespread are not yet included in the monitoring programs. By means of the TOP assay (see Annex A), which also detects unknown precursor substances, it can be demonstrated that the concentrations of sum determinations in sediments and bream are often a multiple of the values of individual determinations (Göckener B. et al. 2020a, 2021). The transfer of toxic substances in food can also be seen in research on the eggs of hens given chicken feed from a contaminated region (Göckener B. et al. 2020c, Kowalczyk J. et al. 2020).
Data from the Federal Environmental Specimen Bank (UPB)[12] clearly show the increase in PFAS contamination over the past 25 years (Fig. 4). The bioaccumulation, such as of PFOS, is also clearly evident in the

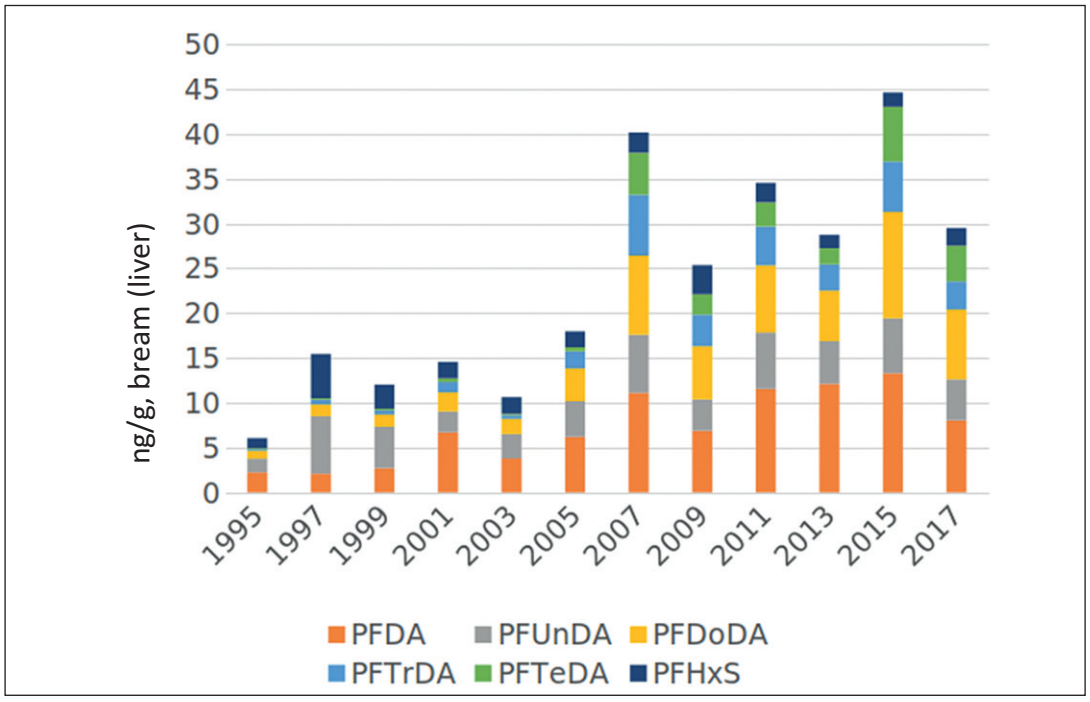

Fig. 4: Increase in the concentration of longer-chain perfluoroalkylcarboxylic acids in the liver of bream © Umweltprobenbank 2020

food chain (Table 1): If bream have a contamination level of 1 ng/g fresh mass in their muscles, average concentrations of 100 ng/g can be found in their livers. As in warm-blooded animals (Stahl T. et al. 2011), the liver is apparently also a target organ for the accumulation of PFAS in fish (Falk S. et al. 2014). In fillets of fish from Lake Constance (perch, whitefish, tench) values between 1.8 and 30 ng/g fresh mass were found for the total of PFOS, PFOA, PFHxS and PFNA (CVUA Freiburg 2021). Based on the EFSA-based TWI of 4.4 ng/kg body weight for these four PFAS (see above), an adult weighting 70 kg already attains the TWI with a single serving of 200 g of these fillets. He even exceeds it by a factor of about 20 with the higher values. In Bremen and Lower Saxony, PFOS concentrations of 1,000 and 2,000 ng/g, respectively, were measured in individual fish (Bethke H. & Budde J. 2020). About 35 ng/g are found in eggs of the silver gull, and other animals that feed on fish, such as sea eagles, seals and otters, even display loads of up to 6,200 ng/g in the liver, according to studies with individual animals by the University of Athens (Koschorreck J. et al. 2020, Umweltbundesamt 2021c). Examples of measured values can be found in Table 1.

Type of sample	PFOS concentration (ng/g wet weight)
Bream (filet)	1
Bream (liver)	100
Herring gull (eggs)	35
Sea eagle (liver)	625
Seal (liver)	693
Otter (liver)	6,182

Table 1: PFOS concentrations in biota samples from German's Federal Environmental Sample Database

[12] *https://www.umweltprobenbank.de*

In humans, who absorb PFAS mainly through food (including drinking water) and through indoor air, the concentrations of PFOA and PFOS in blood plasma have decreased in recent years; other PFAS such as PFHxS are now generally showing an upward trend (Göckener B. et al. 2020b). In a study of 1,109 blood samples from children and adolescents, 2.49 ng/ml of PFOS and 1.12 ng/ml of PFOA (geometric mean values) were detected, although the two substances were already subject to strict regulation at the time the adolescents were born (Duffek A. et al. 2020).

Not only directly used PFAS can be found in the environment and human samples, but also ones derived from abiotic or microbial conversion of polyfluorinated chemicals. For example, in 6:2 FTS and fluorotelomer alcohols, the non-fluorinated parts of the molecule are converted. Perfluorinated carboxylic acids are produced as derivative products (Held T. 2020).
Trifluoroacetic acid occupies a special position:

Trifluoroacetic acid (TFA) – the smallest perfluorocarboxylic acid

Trifluoroacetic acid is a strong acid used in biotechnology and chemical synthesis. The pollution of the river Neckar following the establishment of a chemical company in Bad Wimpfen attracted attention a few years ago. But TFA is not just a regional problem. It is found everywhere: in precipitation, surface water, groundwater, soil and in the air. Even in isolated bodies of water, in mountainous regions and in the world's oceans, concentrations of 100 to 600 ng/l (Scheurer et al. 2017; ECHA 2020; Rippen 2021, Umweltbundesamt 2021) are being detected. In addition to occurring (to a small extent) naturally in deep-sea vents in the oceans, TFA is produced by thermal decomposition of PTFE and by degradation processes in chemicals containing a CF3 group. Some active pharmaceutical ingredients, pesticides in particular, appear to play an important role in local and regional groundwater pollution (Banning H. 2021). However, TFA especially is formed from hydrofluorocarbons such as 1,1,1,2-tetrafluoroethane (R-134a) and 2,3,3,3-tetrafluoropropene (R-1234yf). The latter in particular contributes significantly to the increasing concentrations of TFA in the environment. R-1234yf is a common substitute for fully halogenated CFCs, which can damage the ozone layer and/or worsen the greenhouse effect. It has a relatively low greenhouse potential and decomposes rapidly in the atmosphere with trifluoroacetic acid (TFA) as final product (Deutsche Umwelthilfe 2020).

TFA is also a "forever chemical." It cannot be retrieved from water by means of treatment processes. Meanwhile, increasing serum concentrations in the blood of humans are being detected (Yishuang D. 2020). Germany's Federal Environment Protection Agency (UBA) has set a drinking water guideline value of 60 µg/l (Umweltbundesamt 2020a). Although the harmful effects of TFA that are known today are limited, urgent action is needed to prevent further inputs into the environment. Such action might include a ban on the use of R-1234yf in car air-conditioning systems; these can also be operated with CO_2. Modeling by the UBA has shown that the TFA load via precipitation in Germany will increase tenfold to 4 kg per km^2 annually by 2050 (Umweltbundesamt 2021b).

2. Regulations and threshold values

The burden on humans and the environment has reached a level that requires urgent action. The Nordic Council of Ministers' publication estimating the health and environmental costs to society associated with PFAS exposure shows that the annual health costs caused by PFAS are estimated at €52 to €84 billion in the European Economic Area alone. Inaction will thus be more expensive in the medium term (Nordic Council of Ministers 2019).

The global level

The production and use of most HFCs, CFCs and halons are now banned or severely restricted globally by the Montreal Protocol. The international treaties have been adopted into European law by EU Regulations 1005/2009 and 517/2014.

PFAS are persistent chemicals. In addition, if they are bioaccumulating and toxic and detected worldwide in remote regions, they meet the criteria for persistent organic pollutants (POPs) under the Stockholm Convention. This lists substances whose production and use is banned or at least severely restricted internationally. The two main representatives PFOS and PFOA and their precursors are among them. Only a few applications (e.g., PFOA for working clothes in the occupational and medicinal sector) are still permitted for a limited period of time. Inclusion of PFHxS in the POP list is currently being prepared. The provisions of the Stockholm Convention are binding European law based on EU Regulation 2019/1021 (POPs Regulation).

The Stockholm Convention regulates only individual substances and their precursors, not groups of substances, as is now provided for at the EU level (see below). It also does not deal with product-related regulations and legal requirements for material streams. Mobility in the water cycle is also not taken into account when identifying POPs.

The Basel Convention, which regulates the cross-border shipments of hazardous waste, is also relevant. In this Convention, rules for the treatment of waste containing POP waste are laid down.

As part of the Strategic Approach to International Chemicals Management (SAICM), a United Nations forum for identifying goals for the sustainable management of chemicals, PFAS are among the eight issues of concern identified so far. At the Second International Conference on Chemicals Management (ICCM2) in 2009, Resolution II/5 called for the development of regulatory approaches to reduce emissions

Important international conventions on the regulation of PFAS

The Basel Convention of 1989, http://www.basel.int/, regulates the control of cross-border shipments of hazardous waste and their disposal.

The Stockholm Convention of 2001, https://www.pops.int/, prohibits or restricts the production and use of some persistent organic pollutants (POPs) and also minimizes the unintended formation of POPs (such as polychlorinated dibenzodioxins and furans, PCCD/F) as by-products in technical and thermal processes. Further substances are continuously being identified and included as POPs; currently 30 substances are subject to regulation.

The Montreal Protocol of 1987, https://www.unido.org/our-focus-safeguarding-environment-implementation-multilateral-environmental-agreements/montreal-protocol/ prohibits ozone-depleting substances such as chlorofluorocarbons (CFCs). With the Kigali Resolution in October of 2016 to reduce the consumption of climate-damaging hydrofluorocarbons (HFCs) worldwide, the Montreal Protocol was extended to cover a new group of substances.

of perfluorinated chemicals with the aim of global elimination of these substances (UNEP-SAICM 2018). SAICM is supported by the OECD, which maintains an information portal and a global database on PFAS (OECD). More than 4,700 CAS numbers (Chemical Abstract Service Registry Number) have so far been assigned to PFAS. Complete coverage is prevented by lack of transparency concerning production quantities and PFAS use, as well as suitable analytical procedures in supervisory authorities. However, there is much evidence to indicate that global production is constantly increasing. One indicator is the number of patent applications in the US which include the prefix "perfluor": This figure has now reached 400 per month (IPEN 2019).

PFAS are a problem not only in Europe, but also worldwide. For example, the states of Vermont (National Law Review 2021) and Maine (Chemical Watch 2021) in the US banned or severely restricted the manufacture and use of consumer products containing PFAS in 2021.

The European level

The European chemicals regulation REACH No. 1907/2006 (Registration, Evaluation, Authorization and Restriction of Chemicals) includes several PFAS in the list of potential substances of very high concern (SVHC) because they are PBT (persistent, bioaccumulating, toxic) or PMT (persistent, mobile, toxic) substances:[13] PFOA, PFOS, PFHxS, the perfluorocarboxylic acids C9–C14, HFPO-DA and PFBS.[14] In the future, use of these substances will require authorization, which will only be granted for a limited period of time if no suitable alternatives are available. PFOA and PFOS are already strictly regulated in the EU POPs Regulation. Furthermore, restriction of the spray application of a polyfluorinated silane[15] and several uses of perfluorohexanoic acid (PFHxA) are planned. Given the overwhelming persistence of all PFAS, the EU intends to regulate the entire substance group in its Chemicals Strategy for Sustainability published in October 2020 (EU COM 2020). Five countries (Germany, Denmark, Norway, Sweden and the Netherlands) are currently preparing an EU-wide restriction proposal (BMU 2021a). This should include all PFAS, including polymers, because these make a significant contribution to global background pollution (Washington J.W. et al. 2019). In this way, the call by numerous international scientists in the Zurich Statement for regulation of all PFAS as a group of substances will also be met, in order to avoid recourse to probably similarly dangerous PFAS that have been the subject of less research (Ritscher A. et al. 2018).

It will not be possible to find fluorine-free alternatives for all applications of PFAS in the short term. Consequently, so-called "essential uses" of PFAS need to be identified (Cousins I.T. et al. 2019). Based on the model of the Montreal Protocol, "essential" means that use is necessary for the health, safety and functioning of society and that there are no technically and economically feasible alternatives. Under no circumstances should this lead to the continuation of previous practices. For example, there are suitable fluorine-free firefighting foams (Wood Environment 2020) and impregnating agents for water-repellent textiles (Wood Environment 2019), although suitable fabrics have yet to be developed for protective clothing in the medical sector. There are other alternatives that can replace the use of PFAS in chrome plating and plastic staining (Umweltbundesamt 2020b). For example, the use of chromium(III) instead of chromium (VI) means that no PFAS are required. In the case of products for consumers such as clothing or cosmetics, labeling should be obligatory as long as they continue to be sold. There is an urgent need for the state and industry to set up research programs to develop suitable and safe alternatives for any remaining PFAS applications and to close existing data gaps.

The national level

Since the restriction or prohibition of the use of chemicals is predominantly regulated at the European level, regulatory leeway of EU member states is limited. They are limited to issues on which the EU has not (yet) taken action. These include several limit and guideline values (pp. 19–21); individual usage restrictions are also possible. For example, Denmark has largely banned the use of PFAS in food contact materials and set an

[13] Mobility in the water cycle is a characteristic which gives rise to an equivalent level of concern. This criterion was applied to short-chain PFAS.

[14] PFBS: Perfluorobutane sulfonic acid; PFOA and PFOS are listed in the EU POPs Regulation 2019/1021 for legal reasons.

[15] 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its alkyl derivatives

indicator value of 20 mg fluorine/kg in packaging material (Ministry of Environment and Food 2020).

Threshold and guideline values for PFAS: Significant reductions following reevaluation

The European Food Safety Authority (EFSA) has calculated a tolerable weekly dose (TWI) for the intake of PFAS from food in 2020 (EFSA 2020). In doing so it took into account that in the examination of food the highest levels were found in meat and meat products, eggs and egg products, fish and fish products, and fruit and fruit products. Consequently, only 4.4 ng/kg body weight may be absorbed per week through food. This tolerable weekly intake (TWI) applies to the sum of PFOA, PFOS, PFHxS and PFNA, which together currently make up about 90 % of human exposure[16] [17]. The Federal Institute for Risk Assessment (BfR) established that the long-term intake of PFAS in food exceeds the health-based limit in about 50 % of adults and young people (BfR 2021). This was preceded by much higher limits set in the years previous to this. For example, the guideline value for PFOA in 2008 was still 1,500 ng/kg body weight per day (Fig. 5). This development shows that the usual system of minimizing uncertainty through safety measures in cases where data were incomplete failed to work, at least in this case.

EFSA's low TWI for food shows that several other limits designed to prevent excessive human exposure are currently too high and need to be revised. This applies, for example, to the drinking water guideline and orientation values for 13 PFAS set by the German Umweltbundesamt (Federal Environment Agency) after consulting the Drinking Water Commission in 2016, such as 0.1 µg/l for PFOA and PFOS (Umweltbundesamt 2016). This determination was based on the assumption of a tolerable daily intake of 30 ng/kg body weight. EFSA calculated that 10 % of human intake is through drinking water. Even the new limit value of 0.1 µg/l for the sum of 20 individual substances[18] in the new EU Drinking Water Directive 2020/2184 (EU 2020) is unlikely to be maintained. The preliminary finding that probably just over 10 % of drinking water in Germany exceeds this value (Borchers U. 2021) illustrates the problem posed by PFAS regarding the purity

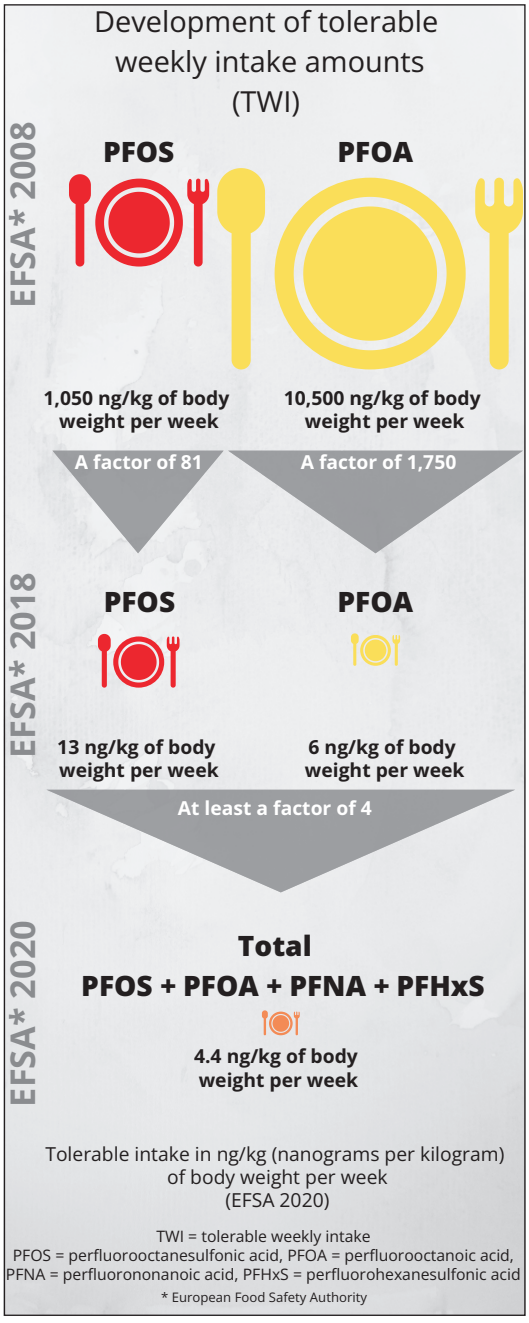

Fig. 5: With increasing knowledge about the harmful effects of PFAS, the values for the tolerable weekly intake (TWI) have become smaller © authors' own presentation based on Kowalczyk, German Federal Institute for Risk Assessment (BfR)

[16] A so-called benchmark dose (BMDL10) of 17.5 ng of the sum of PFOA, PFNA, PFHxS and PFOS per ml of serum for a one-year-old child has been derived from human studies. For a nursing mother (one year), this value corresponds to a daily intake of 0.63 ng/kg body weight of the PFAS sum, or 4.4 ng/kg body weight per week.

[17] The reference value is the sum of PFAS analyzed in human studies

[18] Perfluoroalkylcarboxylic and sulfonic acids C4–C13

of drinking water. A limit of 2.2 ng/l for the sum of the individual substances evaluated by EFSA is under discussion (BBU 2021, Gierig M. 2021).

Critical values set by the Human Biomonitoring Commission should also be coordinated with the TWI value of the EFSA: The human biomonitoring value (HBM I), below which no threat to health can be anticipated, is currently 2 ng PFOA or 5 ng PFOS per ml of blood plasma. When a HBM-II value of 10 ng PFOA or 20 ng PFOS per ml of blood plasma is exceeded, consequences for health are possible. The values refer to individual substances and therefore do not take into account combination effects. Calculation of sum parameters would be useful.

The blood plasma of 21.1 % of children whose blood plasma was examined for PFOA in the current German Environmental Study on the Health of Children and Adolescents exceeded the HBM-I value of 2 ng/ml. The HBM-I value of 5 ng/ml blood plasma for PFOS was exceeded with 7.3 % of study participants (Duffek A. et al. 2020).

Given that many food contact materials are impregnated with PFAS, there is urgent need for precautionary bans or limits based on EFSA's assessment (Straková J. et al. 2021, Schaider L. A. et al. 2017). The EU Commission intends to revise the regulation for food contact materials in this regard.

EFSA's TWI also requires the verification of existing limit, test, guiding and threshold values for various media:

- Sewage sludge: Sewage sludge: 100 µg per kg of dry matter for the sum of PFOA and PFOS is the limit specified in the Sewage Sludge Ordinance for application to arable land.
- Groundwater: The German Working Group on water issues of the Federal States and the Federal Government (LAWA) set thresholds for seven individual perfluorinated substances, including 0.1 µg/l for PFOA (LAWA 2017). As part of the amended EU Groundwater Directive, threshold values for 10 individual substances are proposed.
- Surface water: The environmental quality standard (EQS) for PFOS of 9.1 µg per kg wet weight for fish or bivalve mollusks is also based on the protection of human health. For freshwater, the EQS for bioaccumulation is 0.65 ng/l (Umweltbundesamt 2011). Further EQSs for other PFAS are planned. In this context, initial work at the EU level on specifying environmental quality standards for the total concentration of 24 PFAS is interesting and welcome (JRC 2021). To do this, the relative potency factors (RTF) of the individual PFAS are used as a basis, similarly to current practice with toxic equivalence factors (TEF) for polychlorinated dioxins and furans (Bil W. et al. 2021).
- Soil: In the new version of the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) (Bundesrat 2021), the adoption of the insignificance thresholds as test values[19] was adopted for the soil –> groundwater pathway. The pathways soil –> plant and soil –> humans (children's playgrounds!) are not specified in the new version, especially since this runs up against analytic limits. According to estimates by Germany's Federal Environment Agency, until now the assessment of soil contamination with regard to the soil –> humans pathway (direct contact) has not been relevant (BMU 2020). In view of the new TWI value, however, this estimate should be checked again.

Overall, the values appear inconsistent. Sometimes they refer to certain individual substances (especially PFOA and PFOS), but at other times it is a sum value of up to 20 individual substances that must be monitored. No uniform basis for evaluation is recognizable. A change is urgently needed for the use of sum values regarding widely used PFAS, including the perfluoroether acids such as ADONA and HFPO-DA, which are being used as PFOA substitutes to a greater and greater extent. Even if sufficient toxicological and/or monitoring data are not yet available for some indi-

[19] *Test values for organic substances for the soil –> groundwater pathway at the point of sampling and in the leachate at the site of assessment*

vidual substances, they should be included in order to prevent inappropriate substitution within the wide range of different PFAS.

Monitoring of the numerous limit and guideline values is also a challenge for analytics. PFAS cannot yet be determined with the required sensitivity for all common individual PFAS substances in all environmental media, biota, human samples and products. The various sum parameters also require further optimization. Methods of analysis are currently developing rapidly (see Chapter 3).

Transparency and communication are necessary

Effective and efficient monitoring of legal requirements is only possible if the authorities who are responsible have sufficient information on the uses of the various PFAS, their production and import volumes, and the possibility of analytical monitoring. This is not the case with PFAS. There is no overview of the market for substances that replace PFOS and PFOA, which are not regulated. Very often it is shorter-chain alkylcarboxylic and alkylsulfonic acids or fluorinated oxocarboxylic acids such as HFPO-DA that "accidentally" stand out in the analysis of environmental samples and biota. In one sensational case, one manufacturer even complained that an analytical laboratory offered an analytical standard for the substance C_6O_4[20], a perfluoroether carboxylic acid marketed as a substitute for PFOA (Consumer Reports 2021). Manufacturers and importers must be required to provide chemical structures, analytical methods and analytical standards and to disclose the areas and quantities of use of their PFAS products. To this end, Annex VI of the REACH Regulation, in particular, must require the provision of spectra and standard substances in order to enable analytical identification and quantification of the substances.

Manufacturers should also be obliged to provide consumers and retailers with information and behavioral advice on the safe handling of PFAS and products containing them.

[20] *Perfluoro{acetic acid, 2-[(5-methoxy-1,3-dioxolan-4-yl)oxy]}, ammonium salt*

3. Analysis and monitoring

After substantial progress over the past 20 years, the accurate, joint analytical determination of more than 30 PFAS individual substances in various (environmental) media is now routinely possible with in part good sensitivity. For many PFAS (e.g., polymers, oxocarboxylic acids), however, suitable analytical methods are not yet available or are only available for research, so that monitoring data is at best available in individual cases and these are often not comparable (Humer M. & Scheffknecht C. 2021). Sum parameters such as AOF (adsorbable organic fluorine), EOF (extractable organic fluorine) and TOP (total oxidizable precursor) assay also detect PFAS to varying degrees and with varying sensitivity that are not accessible to single-substance analysis. The conventional method for extraction from soils and other solid media covers important PFAS substance groups only incompletely, and so far this has severely restricted the determination of sum parameters. For the detection of polymers with fluorinated side chains in products, waste and recycled materials, only TOF (total organic fluorine) is currently suitable as a sum parameter. There are no appropriate sampling procedures for determining PFAS in exhaust gases and exhaust air from incinerators and industrial plants, with the result that there is almost no data on this important area (see Annex A: "Analysis of per- and polyfluorinated alkyl substances").

4. Contaminated Sites

Firefighting foam that form an aqueous film – AFFF foams – contain PFAS, usually with a high proportion of PFOS prior to restriction in accordance with the Stockholm Convention in 2011. The use of PFAS-containing foam extinguishing agents in firefighting foams has led to massive soil and groundwater contamination in many places. In particular, large quantities of such firefighting foam concentrates are stored at civil and military airports, and industrial plants such as refineries and fuel tank terminals. In the past, large quantities of PFAS-containing extinguishing agents have also been released as part of fire exercises. Every fire station also represents a potential entry point, as foam concentrates are refilled, and extinguishing equipment is maintained and tested, as well as cleaned after operations. In addition, a large number of stationary extinguishing systems are known to contain PFAS-containing extinguishing agents.

Another major area of application of PFOS is in the field of electroplating for chrome plating (Umweltbundesamt 2020b). Both in Germany and globally, a great deal of contamination has occurred in recent decades at sites referred to as "point sources" due to the relatively small-scale pollutant input (Schroers S. et al. 2020, Umweltbundesamt 2020c). The widespread replacement of PFOS with other fluorinated sulfonic acids such as 6:2 FTS poses comparable risks to soil and water.

PFAS can enter the groundwater via the soil and, depending on the nature of the aquifer, lead to contamination plumes several kilometers long due to their mobility. If these remain undetected, the PFAS can reach soil and crops via the groundwater through garden wells and the irrigation of agricultural land. Due to their persistence, PFAS then accumulate in the topsoil and subsequently enter the food chain via the soil –> plant pathway. The production of drinking water can be affected by these impurities.

There are numerous examples of PFAS-contaminated sites from point sources. Almost every civilian or military airport is affected. Three examples include:

- Bremen Airport: Massive soil and groundwater contamination with PFAS resulting from decades-long use of PFAS-containing firefighting foam in the functional testing of extinguishing equipment and firefighting exercises was detected at Bremen Airport. Through the drainage system of the airport grounds and the adjacent water systems, pollutants have also spread beyond the airport grounds. Studies of fish show elevated, sometimes very high loads, which is due to an accumulation in muscle meat and organs (Freie Hansestadt Bremen, Bethke H. & Budde J. 2020).

- The City of Düsseldorf: There are massive areas of groundwater pollution with PFAS in the city. The first investigations were carried out in 2007 in the vicinity of the airport. In addition, systematic research identified further groundwater contamination. The damage is due largely to the use of PFAS-containing fire extinguishing agents. As a preventive and health protection measure, the use of groundwater for irrigation purposes was generally banned by decree in several pollution areas (City of Düsseldorf).

- Manching Airport (Bavaria): Large areas of groundwater contamination with PFAS are located to the north and northeast of Manching Airport. These were caused by various incidents on the grounds of the military airfield there. In the affected areas, the unrestricted use of groundwater and surface water for irrigation purposes was prohibited by general decree. Information on the level of contamination and the status of rehabilitation measures is provided to the people affected through, among other things, "round tables" with the participation of the Ministry of Defense, the Federal Armed Forces, the Free State of Bavaria, the district and other specialist authorities (Pfaffenhofen/Ilm district).

Similar burdens are reported, for example, at Wiesbaden-Erbenheim and Spangdahlem airports. Spreading compost produced with contaminated paper sludge has led to large-scale contamination of agricultural soils in the Rastatt and Baden-Baden area (Regierungspräsidium Karlsruhe, Stolzenberg-Hepp K. & Striegel G. 2020). An area of more than 1,000 hectares is affected.

Starting from an industrial plant for the production of PFOA as a precursor to the production of PTFE and other fluoropolymers, large-scale contamination of soil has also occurred in the Gendorf area in the district of Altötting (Bayer. Landesamt für Umwelt). Here, in addition to wastewater and ingress into the groundwater, the air pathway was decisive for the extensive contamination. Such extensive pollution in the vicinity of production plants has also been observed in Dordrecht (Netherlands) (Wouter A. et al. 2020) and Venice (Italy) (arpa, Ronco P. et al. 2020). In these cases, soil contamination across a wide area has led to very extensive groundwater contamination going well beyond areas in which input via the soil initially took place. The use of drinking water is often affected. These "mega sites" are among the most massive known contaminated sites, for which remediation is no longer possible, but instead only limiting the extent and spread of damage.

In order to systematically investigate suspected areas, in particular the damage caused by firefighting foams, an extension of conventional methods is required. Relevant guidelines have been available since 2015 (Länderfinanzierungsprogramm). For the municipalities, however, there is so far no obligation to systematically explore suspected areas and to verify or negate any suspicion of contamination by means of appropriate investigations.

The remediation of PFAS-contaminated sites is extraordinarily expensive and time consuming: In the case of groundwater damage, a "pump and treat" approach is often followed. This involves collection of contaminated groundwater and treatment by, for example, adsorption of PFAS by activated carbon. However, what has proved its value with other organic pollutants, such as chlorinated solvents and polycyclic aromatic hydrocarbons, has reached its limits with PFAS. Because of the properties of PFAS, little is adsorbed by the activated carbon before breakthrough occurs. Long dwell times in the filters are also necessary, and this requires very large systems. A second problem also arises: Once the activated carbon is loaded, it must either be transported as waste to a high-temperature incinerator or regenerated in a rotary kiln and the resulting exhaust gas incinerated at suitably high temperatures. There is still no concrete specification of the required temperatures and treatment times for either regeneration or incineration after use. As an alternative to activated carbon, ion exchange resins are also used. In drinking water treatment, where similar challenges arise, membrane processes

such as nanofiltration and reverse osmosis with subsequent electrochemical oxidation of the concentrates are also being tested (Rohn A. 2021). A method for precipitation of dissolved PFAS via a special active ingredient is being tested (Cornelsen M. 2021).

The remediation of contaminated soil is also quickly reaching its limits: Landfill space for PFAS-contaminated soils is in short supply in Germany. In the case of contamination across wide surface areas as described above, decontamination by means of excavation and landfilling is not possible simply because of the sheer quantities involved. However, disposal of smaller quantities is also difficult due to the lack of uniform national standards for recycling and disposal. Without reliable trigger and/or limit values for soil, excavated material and sediments, further uncertainty in the enforcement of soil and groundwater protection is to be anticipated (Frauenstein J. 2021). In-situ remediation methods are not available and the possibility of immobilizing PFAS in the soils using clay minerals or other adsorbents, as well as large-scale soil cleansing, is still in a very early phase[21]. There is still a considerable need for research into the (further) development of rehabilitation technologies.

As a rule, the polluters are not held responsible or legal proceedings go on for years. But even where polluters could be held responsible, the very high remediation costs quickly reach the limits of what is possible. Due to the high speed of spread of PFAS in environmental media and the danger posed to humans and the environment by PFAS-contaminated sites, Germany's government and the federal states should set up a special funding program for recording, risk assessment and remediation. This funding program must have financial resources of at least € 150 million and be made available to the municipalities. In addition, the federal government must assume responsibility for land areas currently in active use by the Federal Armed Forces and allied armed forces, as well as for areas intended for return and properties previously used for military purposes that have actually been returned as part of the conversion program at the Federal State level and must give priority to the remediation of contaminated sites. This also applies to other properties of the federal government which are thought to have been affected by PFAS contamination. When taking a holistic view of all environmental media, it must also be borne in mind when drawing up integrated remediation plans that various remediation processes are not yet fully developed. In this respect, both the immobilization and also the relocation of PFAS-containing soils with corresponding duties of documentation (entry in land registry) are of particular importance.

Legal prerequisites must also be established that make PFAS manufacturers or substance producers in general liable for the costs of necessary remediation measures.

Current knowledge of potentially ubiqitous background contamination of the topsoil with PFAS is insufficient. Investigations in North Rhine-Westphalia and Baden-Württemberg, as well as a recent study from the state of Vorarlberg in Austria (Humer M. & Scheffknecht C. 2021) provide evidence of widespread soil pollution, whose origin has not yet been completely established. Inputs via air pathway could be playing a previously underestimated role. In addition to toxicological assessments, determining such background values is also important for establishing critical values in the context of contaminated site processing and recycling of soil materials. Appropriate investigation programs must therefore be implemented vigorously.

The difficulties associated with treating contaminated soil as waste also apply to all other PFAS-contaminated waste products: consumer products, waste from production processes, special textiles, and so on. Regulations governing landfill deposits do not exist; PFAS are only destroyed by very high temperatures, which waste incineration plants cannot always achieve (see "What happens to waste that contains PFAS?" in chapter 1). For PFOS, the Stockholm and Basel Conventions stipulate that low POP content, in which case the waste does not have to be disposed of separately, is only present if a content of 50 mg/kg is not exceeded (UNEP-Basel 2021). The value for waste containing

[21] *An overview of remediation procedures is provided by the publication "Remediation Management for Local and Widespread PFAS Contaminations" by UBA (Umweltbundesamt 2020c) (in English) https://www.umweltbundesamt.de/sites/default/files/medien/5750/publikationen/2020_11_11_texte_205_2020_handbook_pfas.pdf.*

PFOA is under discussion. When this standard is applied to all PFAS containing waste, the scale of the problem for waste management becomes clear.

5. Research gaps

PFAS are affecting all areas of life. Scientific findings have not kept pace with the pace of dissemination and marketing. While a decade ago it was still believed that control was gradually being exerted over the problem with regulation of PFOA and PFOS, it has now become quite clear that there is an urgent need for research in many areas, such as in:

- Accumulation of PFAS in crops
- Toxicology of short-chain PFAS and fluorinated oxo-carboxylic acids
- PFAS-free alternative processes and products
- Waste-disposal technologies
- Decontamination technologies

The investigation of these aspects cannot be achieved without further development and validation of the analysis of PFAS and their decomposition products (including sampling methods). The large number of PFAS and the low concentrations for which the analysis must be validated require the selection of representative indicator substances for the analysis of the exhaust air of thermal plants (e. g., waste incineration).

The full dimensions of the PFAS problem are made plain by the fact that the Fifth Soil Protection Report of the German Federal Government (BMU 2021b) highlights organic fluorine compounds as a key topic. The projects outlined here within the framework of the BMU's departmental research are suitable approaches, but are far from sufficient to solve impending problems. The Federal Ministry of Education and Research (BMBF) is thus called upon to initiate a joint research project with financial support of at least € 100 million, bundling research work in several thematic networks for a period of at least six years based on experiences with KORA[22].In view of the challenges of a far-reaching phase-out of fluorine chemistry, the EU Commission should also make this a research focus.

It is a priority task for all parties involved to come to grips with and solve the problems associated with these "forever chemicals".

[22] *KORA stands for "controlled natural retention and removal of pollutants during the remediation and contaminated groundwater and soil." See http://www.natural-attenuation.de/.*

Annex A: Analysis of per- and polyfluorinated alkyl substances (PFAS)

1. Analysis of individual PFAS substances

For more than 10 years, the sensitive quantitative detection of individual perfluorinated carboxylic and sulfonic acids with four or more carbon atoms in aqueous and solid samples from the environment, food and human samples has been well established. First, the substances from the sample are enriched with a methanol extraction. The analytical determination is carried out by coupling high-performance liquid chromatography with tandem mass spectrometry (LC-MS/MS). Since most perfluorinated carboxylic and sulfonic acids are available as isotope-labeled reference substances, adding these standard substances before extraction makes the determination of even low concentrations reliable and accurate.

For aqueous samples, an analytical limit of detection (= quantification limit) of < 1 ng/L to 10 ng/L is routinely achieved with each individual substance. The German standard DIN 38407-42:2011-03 describes the analysis of 7 perfluoroalkylcarboxylic acids and 3 perfluoroalkylsulfonic acids with a quantification limit of 10 ng/L in each case. Various laboratories have successfully extended the analysis method to include long-chain perfluorocarboxylic acids with 11 to 14 carbon atoms, fluorinated oxocarboxylic acids (PFOA substitute substances DONA[23] and HFPO-DA[24]), polyfluorinated sulfonic acids (e.g., H4PFOS) and to some extent further PFAS. Although the ISO standard 21675 published in 2019 covers 30 individual substances and low quantification limits (>= 0.2 ng/L), it does not yet cover all 20 perfluorinated carboxylic and sulfonic acids (each with 4 to 13 carbon atoms), for which a total limit of 100 ng/L is specified in the new EU Drinking Water Directive. In addition, a more stringent limit imposed at the member-state level is possible. A comparison with EFSA's TWI value (4.4 ng/kg body weight for the sum of PFHxS, PFOS, PFOA and PFNA) is required. Consequently, for the analysis of the 20 PFAS in the EU Drinking Water Directive, a quantification limit of 1 ng/L per single substance[25] must be routinely achieved. Standardization at the European level which was adopted in November 2020 must be swiftly implemented. The analysis of 7 perfluoroalkyl carboxylic acids and 3 perfluoroalkyl sulfonic acids in soil, compost and sludge is described in DIN 38414-14:2011-08 with limits of quantification of 10 µg dry matter each. In practice, similarly to water analysis, the method has already been extended to include the determination of further PFAS (see above), but has not yet been standardized. In addition, a quantification limit of 10 µg is clearly too high to be able to detect PFAS background soil contamination. (Pre-)contamination must already be assumed starting from a concentration of 2 to 4 µg dry matter for the total of PFOA and PFOS (Humer M. & Scheffknecht C. 2021). Individual laboratories are already achieving a quantification limit of 0.5 to 1 µg dry matter for each substance individually. **There is an urgent need for development and standardization here.**

Routine analysis of perfluorinated carboxylic acids (PFCAs, also called perfluorocarboxylic acids) and perfluoroalkylsulfonic acids in food is currently possible with a quantification limit of 1 µg for each substance individually. Following the drastic reduction in tolerable weekly intake (TWI) by EFSA for four common PFAS in September 2020, there is now a **need to achieve significantly lower analytical limits**.

The determination of PFAS in air is currently limited to research projects; monitoring programs for PFAS in the air are practically non-existent. As a result, there are large gaps in knowledge of the volatilization of PFAS and their spread in the atmosphere. **The decisive need for development and standardization lies in sampling and enrichment** for the instrumental analytical determination of PFAS levels. For the semi- and low-volatile perfluorinated carboxylic and sulfonic acids with >= 4 carbon atoms as well as DONA, taking air samples – as standardized for chlorinated dioxins, PCBs and other persistent organic pollutants – seems to be generally suitable (Ulman M. et al. 2013).

There are virtually no studies of the occurrence of PFAS in exhaust gas and exhaust air from incineration and industrial plants and thus of its release into the atmosphere. Suitable sampling methods – even for the long-established PFAS such as perfluorinated carboxylic and sulfonic acids with 4 to 10 carbon atoms

[23] DONA: perfluoro-4,8-dioxa-3H-nonanoic acid

[24] HFPO-DA (GenX): perfluoro-2-propoxypropanoic acid

[25] The limit value of 100 ng/L for the sum of 20 PFAS corresponds to a limit of 5 ng/L per individual substance. As a rule of thumb, the quantification limit of an analytical method for limit value monitoring must be lower than the limit value by a factor of 5.

– have not yet been established. Individual, unpublished emission measurements carried out in Germany suggest that the complete detection of PFAS from exhaust gas and exhaust air is probably the greatest challenge faced in sampling. The achievement of correspondingly low quantification limits is also essential, as is the case with air measurement. In thermal plants, fragments of PFAS can also occur, for which the selection of indicator substances could be useful. **There is a comprehensive and urgent need for development and standardization here,** especially as many industrial plants are potential PFAS emitters.

Basic development and standardization work for the analysis of individual PFAS substances in products and waste is also necessary for sample preparation, in particular the extraction step.

1.1 Non-targeted analysis

For about 10 years, mass spectrometers with very high mass resolution and mass accuracy (HRMS, high resolution mass spectrometry) have been available. This makes it possible to determine the exact mass of the molecular and fragment ions of a substance contained in the sample and ultimately the molecular formula of the (unknown) compound. On this basis, the identification of unknown substances contained in the sample is basically possible using user-specific or external mass spectrometric databases.

By coupling high-performance liquid chromatography with a high-resolution mass spectrometer (LC-HRMS), this non-targeted analysis can be applied particularly well to aqueous samples, as they can be injected directly without a previous extraction step. This makes it possible to assess a large number of compounds of different groups of substances, provided the substances can be detected by analysis under the chromatographic and mass spectrometric conditions applied. Unknown fluorine-containing compounds can also be detected with non-targeted analysis.

However, since a previous enrichment step would not capture numerous groups of substances or would only detect them incompletely, the necessary direct measurement of the water samples results in higher quantification limits than is the case with specific PFAS single-substance analysis. Non-targeted analysis is thus currently still too insensitive for PFAS monitoring of surface water. However, an important potential application could lie in the study of wastewater samples, because quantification limits would be sufficient for this.

In its guidelines, the Society for Water Chemistry of the German Chemical Society laid down basic quality criteria for the application of non-targeted analysis using LC-HRMS in water analysis (Schulz W. et al. 2019), which should also be adhered to when identifying unknown PFAS. Reliable and unambiguous identification of unknown substances with non-targeted analysis is ultimately only possible if the compound thought to be present is available as a reference substance for confirmatory measurements (Hollender J. et al. 2019).

2. Determination of sum parameters

2.1 Adsorbable organically bound fluorine (AOF)

In this sum parameter for aqueous samples, the PFAS contained in the sample are first adsorbed by activated carbon. This is then burned and the inorganic fluoride formed is quantitatively analyzed by using ion chromatography (combustion ion chromatography, CIC). Based on this, indirectly, the sum of the fluorinated organic compounds contained in the sample can then be determined. The analytical quantification limit is currently 2 µg (see von Abercron E. et al. 2019), which is sufficiently low for the monitoring of (industrial) wastewater. However, the AOF method is too insensitive for monitoring the limit of 0.5 µg for the PFAS sum specified in the new EU Drinking Water Directive.

Since short-chain PFAS in particular do not adsorb well onto activated carbon, the AOF can underestimate the true total PFAS content in a sample to a greater or lesser degree, depending on the type and composition of the fluorinated substances. On the other hand, the AOF also encompasses fluorine-containing compounds which are not PFAS, such as a number of fluorine-containing medications and pesticides and their

metabolites, so that in individual cases, primarily in low concentrations up to approximately 10 µg, PFAS content can also be overestimated. According to an initial pilot study, this seems to occur to some extent in surface water (see von Abercron E. et al. 2019). A draft standard for AOF determination in aqueous samples is available (DIN 38409-59). The necessary validation ring test was carried out in 2021, so the standard may be officially published in 2022.

If PFAS can be extracted from food packaging and converted into an aqueous solution, AOF could also be used for the investigation of such materials.

2.2 Extractable organically bound fluorine (EOF)
In this sum parameter for solid samples, PFAS contained in the sample are first extracted (see note in Section 3) and then burned, similarly to the AOF method, and the fluoride formed is quantitatively determined by ion chromatography. DIN 38414-17 for EOX determination (sum of organohalogen compounds containing chlorine, bromine or iodine) does not include fluoroorganic compounds. There is still no standardization activity for determining EOF.

2.3 TOP (total oxidizable precursor) assay
The TOP assay is suitable for aqueous samples, solid samples, and soil eluates. In this case, polyfluorinated precursor compounds are oxidized by adding a strong oxidizing agent (e. g., peroxodisulfate) to the extract (see note in Section 3 of this Annex) or, in the original sample, to the perfluoroalkylcarboxylic acids and perfluoroalkylsulfonic acids, and then their levels are determined using the established single-substance analysis (see above). As a result, the quantification limits are significantly lower than for AOF and EOF.

The TOP assay is initially limited by the spectrum of perfluorinated oxidation products captured by the analytical method used. In addition, some precursor substances are oxidized only incompletely or not at all. For example, perfluorinated oxocarboxylic acids such as HFPO-DA and fluoropolymers are not detected. A more detailed discussion of this problem is found in Zhang et al. (2019) and Held (2020). In addition, the transformation products trifluoroacetic acid (TFA) and/or perfluoropropionic acid can be formed during the oxidation of various polyfluorinated substances, which, however, are not recorded in the standard analysis of perfluorocarboxylic acids. This requires a modification of the TOP assay and an additional analysis of these two short-chain acids with ion chromatography (Janda J. et al. 2019; Held T. 2020).

The TOP assay needs to be standardized for aqueous soil eluates. Appropriate action for this purpose is currently being taken at the national level and in individual federal states. A draft standard is planned for 2022.

2.4 TOF (total organic fluorine) assay
With this sum parameter for solid samples, the entire sample is burned in accordance with DIN 51723:2002-06. Hydrogen fluoride is formed from the fluorinated organic compounds it contains, including fluoropolymers and polymers with fluorinated side chains. The hydrogen fluoride is collected in an aqueous buffer solution and quantitatively assessed as inorganic fluoride by means of ion chromatography, according to DIN EN ISO 10304-1:2009-07. The resulting sum of the PFAS contained in the sample includes not only the small molecules but also fluorinated polymers (unlike AOF for water samples). However, the proportion of fluoropolymers in the TOF value cannot be determined.

The TOF assay is appropriate for assessing materials and products such as food packaging, but because of its very high quantification limit of 1 mg/kg (Straková J. et al. 2021) is not as a rule appropriate for environmental samples. Standardization is still necessary. In principle, the TOF assay is also appropriate for the investigation of solid waste.

2.5 Biological test
Since 2009, it has been known that many PFAS such

as PFOA bind strongly to transthyretin (TTR), the transport protein that carries the thyroid hormone thyroxine (T4) (Weiss J.M. et al). This can lead to a reduction in thyroid hormone levels in humans and animals. The binding of chemicals to transthyretin and the resulting displacement of T4 can be measured with the TTR-TRß-CALUX(R) bioassay, which combines two bioassays and can also be applied to extracts of samples (from the environment) (Behnisch P. A. et al. 2021). Here, the pre-purified extract is first mixed with TTR and T4 and incubated. After that, the TTR-bound T4 is separated and added to a culture of the human U2OS cancer cell line. In these genetically modified cells, the firefly luciferase gene is coupled to thyroid-responsive elements (TREs). In this way, a reporter gene is obtained for the presence of T4 and other substances that activate the TREs. When the cells are incubated with T4, they form not only proteins whose gene expression is associated with TREs under normal circumstances, but also the enzyme luciferase. After the addition of luminol, the substrate for luciferase, and incubation of the cells, the light emission of the luminescent product is measured. The higher the T4 concentration in the cell-culture medium, the stronger the light intensity. If, during incubation with TTR, the sample extract contains substances that also bind to TTR and compete with the binding of T4, the amount of TTR-bound T4 is reduced, in accordance with the concentrations and strength of the effects of the TTR-binding substances. The light intensity is correspondingly weaker.

Such biotests have the advantage vis-à-vis single-substance chemical analysis in that a defined biological effect is measured, which is triggered by the totality of all substances present in a sample that are, regardless of their structure and chemical analyzability, capable of binding to the specified protein. In the case of additional instrumental analysis of the sample for compounds known to induce this effect, a concentration with an equivalent effect may be calculated, taking into account the specific action potential of each substance. If the equivalent effect in the biotest is significantly higher than the value determined from the result of the chemical analysis, this indicates the presence of unknown substances that have not been detected with the single-substance method analysis used.

Since the effect of PFAS on thyroid function is a sensitive endpoint for humans, as relevant sum parameters this and possibly other biotests can offer a useful supplement to the instrumental analysis of individual PFAS substances.

3. Completeness of PFAS extraction

In PFAS analysis of soil and other solid samples (from the environment), extraction is always carried out with methanol, regardless of whether a single substance analysis or a determination of the sum parameter EOF or TOP follows. Methanol extraction provides good recovery levels for anionic PFAS (carboxylic and sulfonic acids) and as far as is known also for neutral PFAS (e. g., fluortelomer alcohols). However, cationic and zwitterionic PFAS are incompletely extracted from the solid sample in this way (Held T. 2020). Fluoropolymers are not detected. The determination of a PFAS sum parameter carried out with a conventional methanol extract can thus provide systematic lower quantifications. Nickerson A. et al. (2020) suggested optimized sequential extraction with alkaline methanol followed by acidic extraction for complete detection of all PFAS compounds in soil.

The optimized extraction of PFAS from solid samples must be included in the standardization of the TOP assay and the EOF determination.

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Imprint

Published by:
*Bund für Umwelt
und Naturschutz
Deutschland e. V. (BUND),
Friends of the Earth Germany
Kaiserin-Augusta-Allee 5
10553 Berlin*

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With special thanks to Claudia von Eisenhart Rothe, Hans-Joachim Grommelt, Jan Koschorreck, Martha Mertens, Axel Meßling, Tina Neef, Beatrice Pippia, Ninja Reineke and Roland Weber for their support and valuable input.

Responsibility under press law:
Petra Kirberger

Production:
Natur & Umwelt GmbH

Oktober 2021