CHEMICALS

DO WITHOUT PER- AND POLYFLUORINATED CHEMICALS AND PREVENT THEIR DISCHARGE INTO THE ENVIRONMENT

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for our Environment

Imprint

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Do without perfluorinated chemicals and prevent their discharge into the environment

Background

Perfluorinated und polyfluorinated chemicals (PFC) are the subject of increasing public debate. Particular interest has been focussed on studies carried out by the Ruhr University in Bochum, which show that certain of these chemicals are absorbed into the human body through drinking water, where they accumulate [1].

The best-known PFCs are perfluorooctanoic acid (PFOA) and perfluorooctanoic sulfonate acid (PFOS), which have been manufactured by fluorine chemical companies for over 50 years. Some PFCs are frequently referred to as perfluorinated tensides (PFT). PFCs are used in many areas; for example, as non-stick coatings for frying pans, as rain protection for clothing, in fire-fighting foam and for paper finishing.

But why are these chemicals found in drinking water? Farmers in the Hochsauerland district of the State of North-Rhine Westphalia in Germany make use of sewage sludge as a fertilizer, which contains very high residue levels of perfluorinated chemicals. Among the water bodies affected was the Möhne reservoir, which supplies the population of the Arnsberg district with drinking water.

PFCs, however, are not only a problem in the Arnsberg district. Scientists throughout the world discover these chemicals in water bodies, even in the deep sea, as well as in dust, animals and, unfortunately, in human blood. On account of their stability, PFCs have also been detected in remote areas, such as the Arctic and Antarctic. According to recent reports, PFCs are also found in the atmosphere and even in foods [2,3].

Many PFCs – for example, PFOA and PFOS – are water-soluble and spread by way of water flow. The worldwide spread – for instance, in Arctic snow – raises the question of how the chemicals are able to reach even remote areas. Chemists have shown that there are a large number of volatile precursor substances that occur in the atmosphere. They are distributed globally by means of airstreams and converted into persistent perfluoro carbon acids and perfluoro sulfonate acids.

Once they have been taken up, PFOA and PFOS remain in the human body, particularly in the blood, for several years. Uptake takes place, above all, through food and air, and in isolated cases also through drinking water. Since in animal experiments PFOA and PFOS have proven to be a danger to reproduction, the public is rightly concerned.

With this background paper the German Federal Environment Agency (Umweltbundesamt UBA) would like to resolve unanswered questions concerning PFCs, clarify the risks for man and the environment, impart current underlying scientific issues and show how the PFC-contamination could be reduced.

A little chemistry to aid understanding

The term PFC brings together perfluorinated and polyfluorinated chemicals. PFCs do not occur naturally, but are created by man. From a chemical point of view, PFCs comprise carbon chains of varied length, in which hydrogen atoms have been wholly (perfluorinated) or partly (polyfluorinated) replaced by fluorine atoms (see Table 1). The bond between carbon and fluorine is so stable that it loosens only under great input of energy. For this reason, many PFCs are hardly, or not at all degradable in the environment. Some of these compounds can only be destroyed by high-temperature combustion and disposed of with subsequent waste-air purification.

Up to 2002, perfluorocarboxylic acids (for example, PFOA) and perfluorosulfonic acids (for example, PFOS) were largely produced electrochemically. With this so-called ECF (electro-chemical fluorination) process different products emerge, from the conglomerate of which the desired compound is enriched in several steps. It is still contaminated with residues of other fluorine chemicals. The American company 3M, which until 2002 was the worldwide leading manufacturer of PFCs, ceased production of PFOS in 2002. Since then, the Italian company Miteni claims to manufacture the worldwide largest share of perfluorinated chemicals on the basis of the ECF process.

Most PFCs can be manufactured on the basis of the so-called telomerization, a special chemical synthesis process. Beginning with tetrafluoroethylene (C_2F_4), the molecule is gradually lengthened at one end. The company primarily manufactures fluorinated monomers with this process, which can be further processed into fluorinated polymers. To distinguish them from compounds manufactured according to the ECF process, these monomers are also called fluorinated telomers. „Fluorinated telomer alcohols“ are an important intermediate product of this process (see Table 1).

PFCs also include so-called fluorinated polymers, whose most important and well-known representative is polytetra fluorine ethylene PTFE, better known under its trade name Teflon®. Fluorinated polymers are solid, and can be formed and processed. They are water-, dirt- and fat-repellent as well as resistant against aggressive chemicals, and they are additionally characterized by high thermal stability. In this connection, one distinguishes between fluorine polymers, whose units are all perfluorinated, and fluorinated polymers (see BOX 1).

The compounds and products mentioned above are only a sample of fluorine compounds. The OECD lists a total of 853 different PFCs, including 369 substances that can be traced back to perfluorosulfonic acid or perfluorocarboxylic acids. Further information on some of these substances can be found in the Annex.

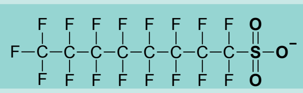
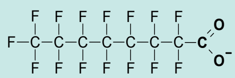
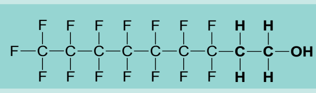
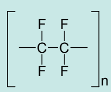
We encounter fluorine chemicals daily

Teflon®, Scotchgard®, Stainmaster® und SilverStone® are just four of many familiar trade names, behind which PFCs are to be found. They are very popular due to their unique properties, and they are therefore found in many everyday products.

Almost nothing sticks to polytetrafluoroethylene (PTFE), which is why it has been employed as

Table 1: Examples of some PFCs and their chemical structures

Blue-marked areas indicate the different lengths of fluorine carbon chains, while green-marked areas highlight the different head groups of molecules

	Exemplary compound	Chemical structure
Perfluorosulfonic acids	Perfluorooctanoic sulfonate acid (PFOS)	
Perfluorocarboxylic acids	Perfluorooctanoic acid (PFOA)	
Fluorinated telomer alcohols	8:2 Fluorinated telomer alcohol (FTOH)	
Fluorine polymer	Polytetrafluorethylen (PTFE)	

Box 1: Fluorinated polymers

Polymers are chains, or branched molecules, which are made up of identical or similar units. Fluorinated polymers are synthesized from a fluorine-free base with perfluorinated „branches“ (Table 1). They give products their water- und dirt-repellent properties.

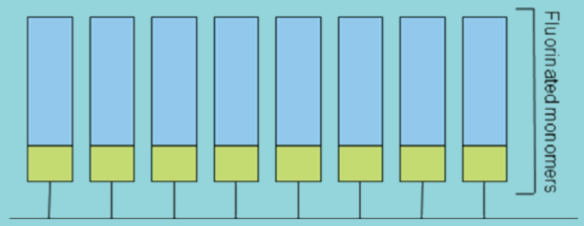


Figure 1: Schematic representation of a fluorinated polymer

non-stick coating in frying pans and saucepans since the 1950s. PTFE has other qualities besides chemical and heat resistance, which is why it is a popular material. PTFE slides on PTFE just as easily as wet ice on wet ice. For this reason, sealings and bearings are often made of or coated with PTFE. PTFE is very much in demand in electrical engineering for cable sheathing. Applications are also found in aviation, military and medical technology (implants), in optics (lenses) and in the coating of laboratory instruments. The use of PTFE and other fluorine polymers as breathable membranes in rainwear and functional clothing is also widespread and greatly increasing. Perfluorooctanoic acid (PFOA) is used as an auxiliary substance in the manufacture of PTFE, and is therefore found in traces as a contaminant in finished products.

Fluorinated telomer alcohols (FTOH) and other substances are converted on a large scale into different surface-active chemicals (surfactants), and are found as residues in polymers. Annual worldwide FTOH production is estimated at 11,000 to 14,000 tonnes. Synthetic fibre coatings are manufactured from these compounds for the finishing of textiles, paper and building materials, making them water- fat- and dirt-repellent. In the case of textiles this primarily concerns outdoor and sports clothing, health-protection textiles, seat covers and carpets. These substances can also be found in polishes, wax, all-purpose cleaners, window cleaners and impregnation sprays, and they are used in the manufacture of paint and adhesives. Manufacturers of food packaging use certain PFCs for water- and fat-repellent coatings. This growing market is of great importance for manufacturers and processors of fluorine chemicals.

How are perfluorinated chemicals taken up into the human body?

The uptake of per- and polyfluorinated chemicals into the human body has not yet been finally resolved. What is certain, however, is that water-soluble PFCs, such as PFOS and PFOA are absorbed by way of contaminated drinking water.

PFOS and PFOA can also be absorbed with contaminated food. Scientists have found evidence of PFCs in fish, meat, milk products and plants, including grain that grows on contaminated soil. In the case of certain food products, the transfer of PFCs from fat-repellent paper has been proven, for example, with popcorn. In the opinion of the Federal Environment Agency (UBA), the uptake of PFCs from non-stick coated frying pans and saucepans is negligible.

PFCs, such as fluorotelomer alcohols, which are found in indoor air and the atmosphere, are taken up into the body through the lungs. Textiles finished with PFCs (upholstery, seat covers and carpets) can contribute to an increased concentration of PFC elements in indoor air and also in dust. Scientists have proven that these PFCs are partially converted to stable perfluorinated compounds (for instance, PFOA) in the body and in the atmosphere.

It is questionable whether the wearing of coated or membrane-fitted clothing (Gore-tex® raincoats, shoes etc.) also results in the direct uptake of PFCs into the body. According to the German Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung, BfR) it has not been shown that consumers are realistically exposed to PFOA and FTOH from clothing fabrics. The BfR estimates that the maximum quantity amounts to 20 nanograms – a nanogram is a billionth part of a gram – per kilogram of body weight. A recently published report came to the conclusion that less than one per cent of the daily uptake of PFOS and PFOA is through the skin [4]. Similar reports on the uptake of other PFCs through the skin are presently not available.

Perfluorinated chemicals in human beings (blood and mother's milk)

It is of particular concern that scientists have found evidence of polyfluorinated chemicals in human blood. PFOS concentrations of 1 to 1,600 micrograms per litre (µg/l) – a microgram is one millionth of a gram – and PFOA concentrations of <0.5 to 60 µg/l in blood samples from Europe, the United States and Asia. Much higher concentrations have been found in the blood of individual employees of fluorine chemical manufacturers in the Netherlands and the USA [2]. Concentrations of PFOA and PFOS measured in the blood of the population at large (see Figure 2) are around 0.5 per cent of those in the blood of persons subject to exposure at their place of work.

A Bavarian study detected 2.1 to 55 µg/l PFOS and 0.5 to 19.1 µg/l PFOA in the blood plasma of participants [5]. Particularly noticeable was the fact that the blood samples were from young adults who were not specifically exposed to these substances. Different studies have proven that men have rather higher PFC concentrations in their blood than women [1,5].

Investigations in Arnsberg [1] established up to eight times higher concentrations of PFOA in the blood of persons who had demonstrably consumed contaminated drinking water (see Section: „Water bodies"). In an investigation carried out by the German Environmental Specimen Bank (UPB) with blood plasma samples from the years 1982 to 2007, concentrations amounted to 3.5 to 103 µg/l PFOS and 1.5 to 13 µg/l PFOA. The UPB, where human and environmental specimens have been stored since 1981, investigates and documents the environmental status and contamination exposure of persons in Germany. A study with anglers at Möhne reservoir showed that the consumption of fish can also have an influence on the level of PFOS in the blood [3].

The UPB study showed that PFOS concentrations have declined strongly since the beginning of the present decade, while blood contamination

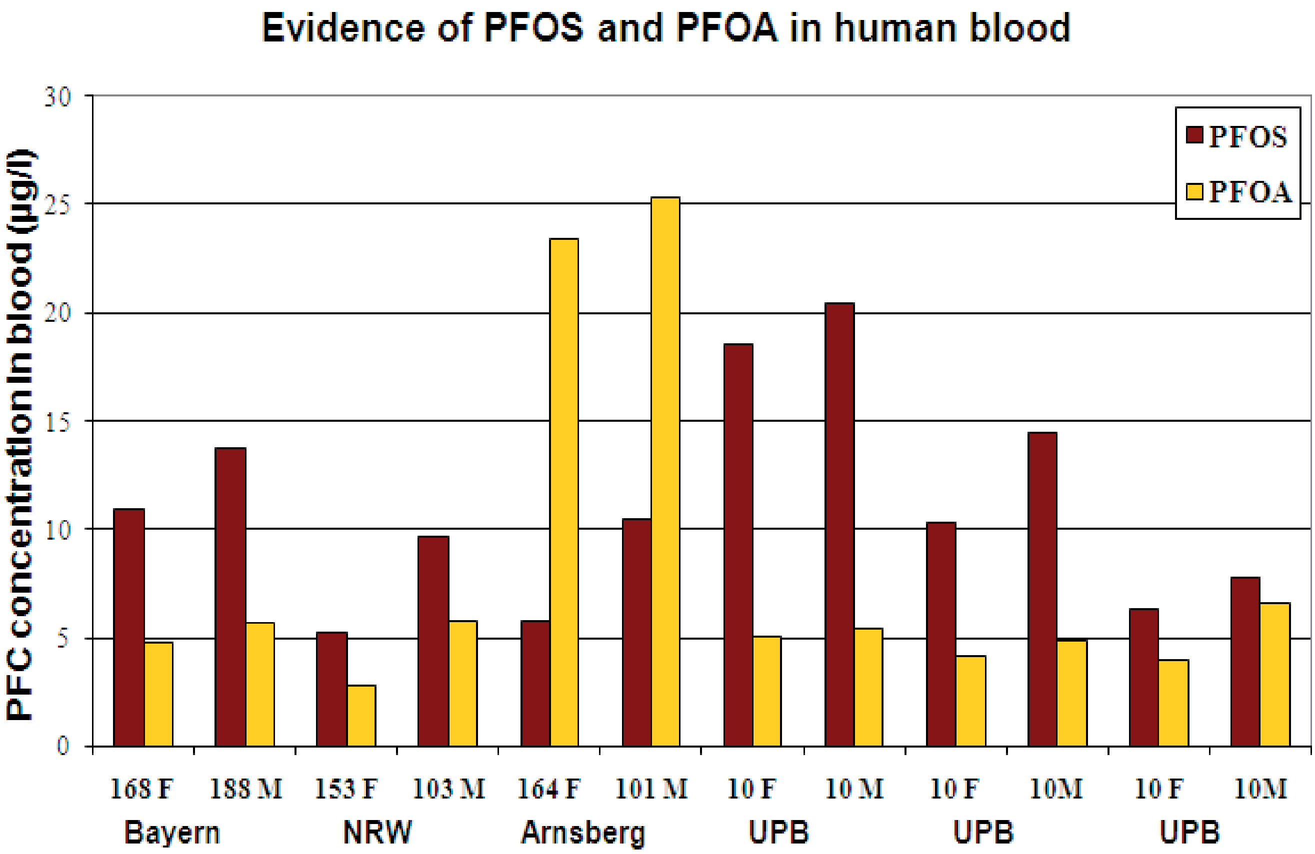


Figure 2: Concentration of PFOS and PFOA in the blood of adult women (F) and men (M) in Germany who are not exposed to occupational risk [geometric average; median for Bavaria 2005]; UPB = Umweltprobenbank des Bundes (German Environmental Specimen Bank).

with PFOA has not diminished. Stored specimens also show that concentrations of perfluorohexane sulfonic acid are growing. Reports from the USA indicate a doubling of the blood-content of other PFCs (for example, perfluornonyl acid) within five years. This indicates that known critical PFCs, such as PFOA and PFOS are being increasingly replaced by other, less familiar and less analysed PFCs.

PFOS and PFOA are likewise detectable in mother‘s milk. Their concentrations are, however, about one per cent of those in the blood. PFOA concentrations lie mostly below the detection limit [1,2]. For babies, however, this represents a PFC source that cannot be ignored.

In the light of currently available data, PFC taken up by babies through mother‘s milk is below the provisionally stipulated TDI value for babies of 0.1 µg/kg of body weight for PFOA and PFOS, as proposed in 2006 by the Drinking Water Commission of the Federal Ministry of Health at the federal Environment Agency and laid down by the Federal Institute for Risk Assessment (BfR) (See Section: What is the Federal Environment Agency doing?) The TDI value defines the tolerable daily intake, that is, the quantity that a baby may take up into the body daily without risk. Despite these findings, the UBA advises young mothers to follow the recommendations of the National Breastfeeding Commission, which expressly recommends breastfeeding during a baby‘s first 4 to 6 months. Breastfeeding provides children with the best start to a healthy life and gives optimum protection against varied health disorders and illnesses.

Are PFCs dangerous for humans?

In animal experiments, PFOS and PFOA have proven to be moderately toxic after brief contamination by way of food, air and the skin. In long-term studies with rats and mice, however, both compounds enhance the development of liver, pancreatic and Leydig cell tumours. The applicability of these findings to humans is, however, in discussion.

PFOA and PFOS are not mutagen; this means, they do not alter the human genom. Neither of these compounds itself reacts with genetic material. At most, in high-dosage experiments with rats, they are able to damage genetic makeup indirectly through the release of so-called „oxidative stress“. Although „oxidative stress“ can be effectively neutralized in the metabolism, it is not certain that this always occurs at the right time. It has been proven that human beings react less sensitively to the release of oxidative stress through PFCs than a rat.

The adverse effects of PFOS and PFOA on reproduction in animal experiments are undisputed. The dosages for such effects are, however, very high. The values measured in human blood are only a fraction of those of concentrations in animal experiments.

The applicability to humans of observations of the behaviour of PFOA in animals is questionable. The time observed for excretion of 50 per cent of chemicals from the body (half-life period) of employees in fluorine chemical production is more than four years. Follow-up examinations of affected persons from the Hochsauerland district (see Box 2) appear to confirm that this half-life period applies also to persons in general. Rats, dogs and monkeys, on the other hand, excrete PFOA within a few days [6]. It can therefore presently be assumed that the human body is exposed to these substances for a considerable longer period. An investigation, which is currently being conducted, indicates a possible effect of PFOS and PFOA on the fertility of women [7].

Evidence in the environment

Atmosphere

A team of German scientists discovered that volatile PFCs occur in considerably higher concentrations in the atmosphere in Europe than off the coast of South Africa. The further the research ship was from Europe the fewer the PFCs detected in the atmosphere.

Chemists throughout the world detect volatile precursor substances of persistent perfluorocarbxylic and perfluorosulfonic acids in the atmosphere. The concentrations of certain fluorinated telomer alcohols and other PFCs in the atmosphere exceed even the values for so-called persistent organic pollutants (POPs). POPs are particularly alarming, since their degradation rate in the environment is extremely low. They belong to those organic compounds that occur in their highest concentrations in the atmosphere, and are spread throughout the world [8].

Canadian researchers detected volatile PFCs – for instance, fluorinated telomer alcohols (FTOH) – in the Arctic atmosphere in concentrations of 2.8 to 29 pg/m3 air (1 picogram = one trillionth of

Table 2: Evidence of PFOS and PFOA in water bodies

Sample	PFOS [ng/l]	PFOA [ng/l]	Source
Surface waters			
Pacific (1,000 – 4,400 m depth)	0.003 – 0.02	0.05 – 0.12	[12]
North Atlantic, Arctic	0.01 – 0.05	0.04 – 0.1	[9]
Japan, Tokyo Bay	13 – 25	154 - 192	[12]
Great Lakes, USA	11 – 121	15 - 70	[13]
Resolute Lake, Arctic	49 – 90	12 - 16	[14]
North Sea, mouth of the Elbe river	0.03 - 7.3	0.2 - 6.8	[9]
Po, Italy	2 – 12	2 - 337	[15]
Möhne*	135 – 405	11 – 7,070	[16
Steinbecke*	3,160 – 5,900	16,800 – 33,900	[16]
Möhne Reservoir*	17	654	[15]
Alz*	1	7,500	[17]
Groundwater			
Wutsmith Air Force Base (Michigan, USA)	8,000 – 105,000	4,000 – 110,000	[18]
San Jose, CA, USA	31 – 192	0 - 22	[19]
Drinking water			
Washington County, Ohio, USA		6,500	DuPont 2002
NRW, varied waterworks	< 2 – 22	< 2 - 56	[16]
Japan	0.16 - 22	2.3 – 84	[20]

*For background information see BOX 2

a gram), and showed that under the prevailing conditions, without the help of man, they are converted into perfluorcarbon acid and washed out of the atmosphere by precipitation.

A current study confirms high pollution of indoor air. Concentrations of PFCs in houses, flats and offices were 30 to 570 times higher than in outdoor air. The assumed sources are effluviums – for example, from dirt-repellent carpets or other products containing PFCs.

Water bodies (including groundwater and drinking water)

Water-soluble PFCs, such as PFOS and PFOA, are mainly emitted into water, irrespective of how they get into the environment. These PFCs, which have been used for over 50 years, spread relatively slowly by way of water bodies into the deep sea and the Arctic. They have been detected in oceans, in most rivers and in lakes. In places where chemicals are manufactured, processed or used, water bodies are more heavily polluted (Table 2). This applies, in particular, to industrialized countries. Tokyo Bay, for instance, is polluted with concentrations of certain PFCs that are up to 400 times higher than in the water of the open Pacific.

A UBA report on residues of perfluorinated chemicals in the North Sea and Baltic Sea shows the highest concentrations in the mouth of the Elbe river near Stade [9]. The report shows strikingly that municipal sewage, which comes mainly from private households, discharges water-soluble PFCs into the Elbe. The PFCs are then discharged into the North Sea by way of the German Bight, where they are diluted by seawater. Here, it is obvious that PFCs in sewage also stem from consumer products, such as textiles.

The occurrence of PFCs in drinking water is of particular concern. In the Hochsauerland district in North-Rhine Westphalia (NRW), drinking water in the Möhne reservoir was contaminated with PFCs (for background information see BOX 2). In an extensive study on behalf of the State of NRW, scientists from Ruhr University in Bochum, Germany, examined blood samples of the population in the District of Arnsberg as well as from the Brilon and Siegen region. The findings clearly showed that the blood of the inhabitants of Arnsberg contained five to eight times higher concentrations of PFOA than that of the neighbouring communities of Brilon and Siegen. In contrast to the District of Arnsberg, the people of Brilon and Siegen do not obtain their drinking water from the Möhne reservoir. This study proved that drinking water is a source for the uptake of perfluorinated chemicals, and that they enrich in the human body [1].

Raw water intended for the production of drinking water is endangered not only by leached polluted soil, as occurred in Hochsauerland; PFCs can also infiltrate into the soil or enter groundwater from polluted waters through bank filtration (that is, infiltration in the peripheral area of waters). Analyses in the USA in the area surrounding important fluorine chemical companies have confirmed this hypothesis.

PFC contamination of the raw water of German drinking water reservoirs lies mostly in the single- or two-digit ng/l range. Concentrations in excess of the precautionary value of the Drinking Water Commission of the Federal Ministry of Health at the UBA are the exception and the result of the discharge of PFCs from temporary point sources [10]. According to a report of the Bavarian State Office for Health and Food Safety (Bayrisches Landesamt für Gesundheit und Lebensmittelsicherheit - LGL), most of the drinking water sources investigated in Bavaria lie below the precautionary value laid down by the Drinking Water Commission. In no water sample since November 2006 has the health-related indication value (HRIV) of 0.3 µg/l PFCs for adults been exceeded [11]. In reservoirs in the neighbourhood of Gendorf, the important fluorine-chemical location in Bavaria, however, PFOA concentrations exceeded the precautionary value of the Drinking Water Commission of 0.1 µg/l. Contamination of drinking water with PFCs is therefore not only an issue where drinking water is produced from surface waters, but can also be attributed to point sources.

In the Hochsauerland district, drinking water has to be purified of PFCs with activated carbon filters in order to meet the target value. To remain effective, these expensive filters have to be frequently replaced and disposed of at the cost of the taxpayer.

Sewage sludge and soil

Most PFCs are not degraded in sewage treatment plants. The Environment Ministry of the State of Baden-Württemberg ordered the investigation of 157 sewage treatment plants situated in catchment areas of indirect industrial dischargers. In 47 treatment plants (30 per cent), PFC contamination >100 µg/kg of sewage sludge was measured. In all, findings were between 5,136 und 102 µg/kg of sewage sludge.

How do PFCs get into sewage sludge? The metal, paper and textiles industries use a wide range of products containing PFCs. These are discharged into sewage treatment plants with wastewater. Private households are also a possibility, since PFCs are found in many consumer products. In sewage treatment plants, part of the chemicals remain in sewage sludge, the rest is discharged with purified water into rivers and lakes.

Due to its high nutrient content – and in compliance with specific limit values – sewage sludge is in great demand as an agricultural fertilizer. This way, PFCs are discharged into soil and groundwater, can be leached into adjoining surface waters, and can also be taken up by plants. It is certain that other chemicals enter soils by way of sewage sludge that – as is the case up to now with PFCs – no-one has searched for. Sewage sludge is therefore a potential source of further groundwater contamination.

It is difficult to rehabilitate soils once they have been contaminated with PFCs. The technical and financial costs quickly exceed the limit of reasonableness. It is better to take precautionary measures; that is, to limit contamination of soils, so that such harmful changes in soil structure can be prevented. In some federal Länder, for instance in North-Rhine Westphalia and Baden Württemberg, limit values for PFCs in sewage sludge used as an agricultural fertilizer are already in force (less than 100 µg PFC/kg in dry-matter sewage sludge). In the study described above, this limit was exceeded in 30 per cent of the sewage treatment plants investigated [11].

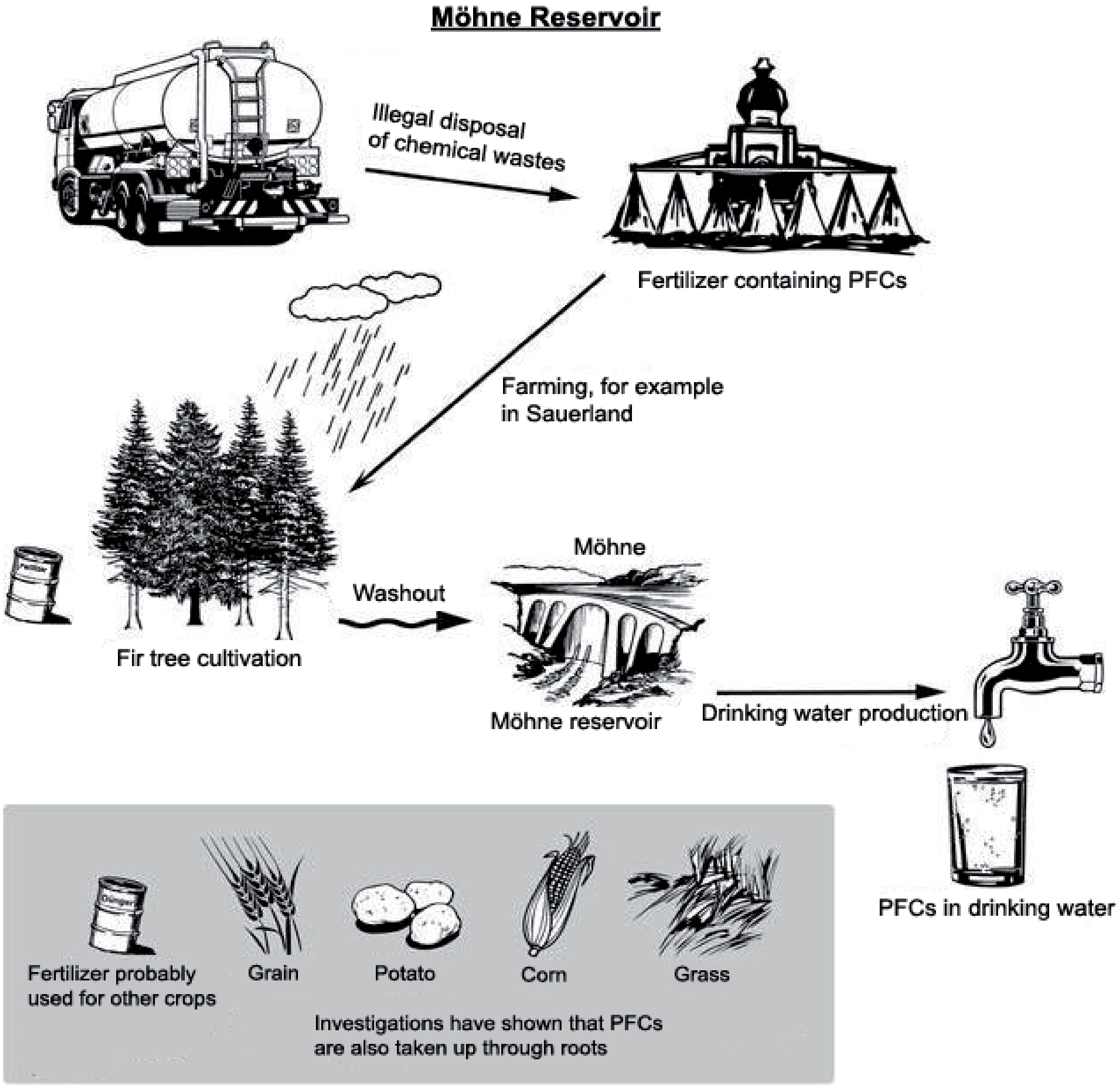
It is planned to adopt a nationwide limit value for sewage sludge in the amended Sewage Sludge Ordinance, taking particular account of the

Box 2: The example of the Hochsauerland district

Farmers in the Hochsauerland district treated their crops and forestry products with sewage sludge and mixed biowaste. These „fertilizers“ contained large PFC residues. Fertilizer samples confirmed that wastes from the chemical industry have also been illegally disposed of with these waste mixtures. Such mixtures give rise to considerable soil contamination with PFCs. In North-Rhine Westphalia, for instance, PFC concentrations in excess of 9,000 µg/kg of soil have been detected.

Surface waters, such as the Möhne reservoir have been contaminated with PFC on a large scale through soil washouts (see Table 2). Since the Möhne reservoir supplies drinking water, drinking water in the region of Arnsberg was also contaminated with PFC. Higher levels of PFC were measured in the blood of the Arnsberg population than in that of the population as a whole.

Irrespective of illegal disposal, occasionally high PFC contamination in sewage sludge is justification for the introduction of limit values also for PFCs. Since sewage sludge can also contain other persistent pollutants, some German Länder (states) have prohibited the use of sewage sludge as fertilizer in the farming industry.



BOX 3: Direct and indirect sources of PFCs in the environment

Direct sources
PFC can enter the atmosphere or waste water during their manufacture and processing; for example:
- in the production of perfluorinated chemicals,
- in the production of fluorine polymers or fluorinated polymers, and
- in the processing industry (for example, textile finishing, electroplating and the paper industry)

Indirect sources
PFCs can enter the atmosphere or waste water from the use or disposal of consumer products; for example through:
- residues in consumer products,
- washing textiles treated with PFCs,
- volatile perfluorinated chemicals in household textiles and carpets,
- PFCs in household chemicals (for example, impregnation sprays),
- degradation products of chemicals,
- processes for converting precursor substances into persistent compounds,
- sewage sludge (on disposal as a fertilizer)

currently best-known PFC compounds PFOS and PFOA. Further PFCs should be controlled through a monitoring programme.

Organisms

Most of the analyses of residues in plants and animals are carried out on aquatic organisms. PFOA, PFOS and other PFCs are found throughout the world in fish, in the liver of polar bears in Greenland, in seals, mink, foxes and kingfishers in the Canadian Arctic (Table 3).

While a very high concentration in organisms has been proven with regard to PFOS, PFOA does not greatly enrich after uptake from water into aquatic organisms such as fish. Recent Canadian studies with dolphins and Arctic mammals, however, indicate concentration within the food chain. Confirmation of this theory is still awaited. Since the decrease in PFOS production in 2002, Canadian researchers have recorded a decline ofthe concentration of perfluorinated compounds in the liver of Arctic ringed seals. This does not apply, however, to polar bears (Table 3).

The State Office for Nature Conservation and Environmental and Consumer Protection (North Rhine Westfalia) detected PFC concentrations of up to 459 µg/kg in fish from the highly contaminated Möhne, and up to 1,195 µg/kg in fish ponds in Brilon/Scharfenberg. The Federal Institute for Risk Assessment (BfR) sees no risk to health in consumption of these fish. It has been deduced from animal experiments that a person can absorb up to 0.1 µg of PFOS per kg body weight without health risks. Anglers have nevertheless been advised for the time being not to eat fish from this region.

The Bavarian State Office of Health and Food Safety (LGL) investigated the PFC concentration in fish in the neighbourhood of Gendorf industrial park. Measured concentrations were >0.2 to 15.4 µg/kg for PFOA and >0.2 to 18.9 µg/kg for PFOS. The highest values were measured in eel. No regulations on maximum limits for PFCs in food presently exist.

Investigations in the highly contaminated Hochsauerland region indicate that plants take up PFOA and PFOS – and probably other PFCs – through their roots. A particularly high transfer from soil into plants was recorded in the case of grass. As a result, an additional concentration could take place in the food chain by way of livestock. Human beings can absorb PFCs through the consumption of meat or milk.

The LGL has also reported accumulation of PFCs in eggs and milk in the Gendorf region. No PFCs

Table 3: Evidence of PFOS and PFOA in the liver of different organisms

Animal	PFOS [µg/kg]	PFOA [µg/kg]	Source
Polar bears (1990)	454 – 1474	0.6 – 14	[21]
Polar bears (2006)	2108 – 3868	11.8 - 17.6	[21]
Seals, Arctic (2005)	8.0 - 44.1	0.96 – 1.01	[22]
Seals, Lake Baikal	<0.55 – 18	<1.1	[23]
Eel, European rivers	up to 498	up to 23	[24]

were detected, however, in most of the vegetables that were investigated.

Are PFCs dangerous for the environment?

Harmful effects of perfluorinated chemicals on biocenoses in water bodies first occur in concentrations that are much higher than those measured up to now.

All perfluorinated compounds have in common that they are highly persistent; that is, they remain in the environment for a very long period. Substances, which are persistent, accumulate in organisms and are highly toxic (so-called PBT substances), can lead, on account of the combination of these properties, to long-term environmental damage. For this reason, EU Member States have agreed on common regulative criteria for PBT substances.

PFOS meets the PBT criteria of the EU, since besides persistence (P) and toxicity (T) a very high bioaccumulation (B) in aquatic organisms has been proven. PFOA, too, is persistent (P) and toxic (T). According to EU criteria, however, the bioconcentration factor for PFOA is clearly below the critical value, and PFOA is therefore not regarded in the EU as a PBT substance.

The chemical industry has recently begun to make increased use of short-chain PFCs. Though the enrichment potential of these substances in the body is lower, they are also not degradable. Short-chain PFCs adsorb fewer particles and distinguish themselves through high soil mobility. Such substances have been increasingly detected in ground- and surface water. The risk for the environment that these substances represent cannot at present be estimated.

Statutory action and recommendations

Because PFOS is a PBT substance, the EU has prohibited its marketing and use since 27 June 2008 [25]. The respective Directive has been implemented in German law with the „11th Ordinance for the Amendment of Chemical Regulations". So long as alternative substances or technologies are not available, the following applications are permitted for the time being in the EU:

- Anti-reflection coatings for photolithographic processes and photographic coatings in the manufacture of processors.
- Under certain circumstances, application as an antifoggant.
- Application as a surface-active agent (surfactant) in general electrometallurgical systems as well as hydraulic liquid (aviation).

A period of permitted use applies for stocks of fire-extinguishing agents containing PFOS.

Furthermore, Sweden has proposed that due to its widespread circulation PFOS be classified as a persistent organic pollutant (POP). Negotiations are in full swing, and inclusion in the POP list is regarded as probable. That is the first step towards a worldwide prohibition of use.

In 2006, the Federal Environment Agency (UBA), together with the US Environmental Protection Agency (EPA) and the Organization for Economic Co-operation and Development (OECD), assessed the danger to human health and the environment from PFOA. The result: The main sources of environmental pollution in the chemicals industry are known. Further applications of PFOA and its precursor compounds, which lead to the endangering of man and the environment as well as to the worldwide spread of PFOA, need to be identified and quantified. Precise information is required on residues in different products as well as on contamination of drinking water and foods for the identification of decisive intake paths. Despite these uncertainties, the report urges OECD states to introduce risk-reducing measures, such as a voluntary reduction in emissions.

In a voluntary project, European manufacturers and users of PFOA assess the risks of PFOA for human beings and the environment in accordance with REACH, the new European chemicals regulation. The competent German authorities, the Federal Institute for Occupational Safety and Health (BAuA), the UBA and the BfR provide the companies with support. The final report has been submitted to the European Commission by April 2009.

Since PFOS and PFOA are classed as „reproduction-toxic Category 2“, both compounds are regarded under REACH as „substances of high concern“ and thus fulfil the condition for inclusion in the list of substances subject to authorization. PFOS is already sufficiently regulated. The Federal Ministry of the Environment (BMU) and the competent German authorities will propose that PFOA be subject to more far-reaching regulation (authorization or restrictions on use) under REACH.

In 2005, the American Environmental Protection Agency (EPA) and eight important fluorine chemical companies launched a „Product Stewardship Programme“. The objective of this voluntary agreement is the reduction of emissions of PFOA and possible precursor substances by 2010 to five per cent of the level of the year 2000. The agreement applies also for long-chain perfluorocarboxylic acids and to emissions from products, but unfortunately not to all companies. The programme for the complete reduction of emissions should be concluded by 2015. In Europe, too, some companies – such as DuPont and 3M – have already introduced measures to reduce the discharge of PFOA into the environment as well as residues in products.

What is the German Federal Environment Agency doing?

The problems of PFC cannot be resolved solely with the measures previously taken. The UBA has therefore initiated a series of more far-reaching measures.

The UBA and the Drinking Water Commission (TWK) of the Federal Ministry of Health at the UBA recommend for the protection of human health a permanent tolerable, health-related indication value (HRIV) of 0.3 µg/l PFC. They regard a maximum yearly average value of 0.1 µg/l – as a precautionary value – for totals of highly accumulating PFCs as adequate.

The Human Biomonitoring Commission of the UBA has deduced reference values for Germany as shown in Table 4 [25]. Such reference values enable the assessment of the internal contamination of individual persons or population groups compared to the reference contamination of the population as a whole. They can be applied as criteria for the classification of measured values as „increased“ or „not increased“. Assessment of contamination is not possible from the point of view of environmental and medical toxicology on the basis of reference values.

Initial measurements show that volatile PFCs occur in higher concentrations in interior areas than in the open air. A connection with household textiles and carpets has still not been proven. Detailed investigations of PFC release from treated products have also not been carried out. The UBA recommends as a precautionary measure that before purchasing household textiles and carpets consumers should ask themselves whether water- and dirt-resistant coatings on a PFC basis are really necessary.

The UBA proposes legally-binding quality standards and reduction targets for water bodies, waste water, soils and sewage sludge.
The UBA is examining together with the Länder Working Group on Water whether quality

Table 4: Reference values for PFOS and PFOA laid down by the Human Biomonitoring Commission of the Federal Environment Agency (UBA)

PFOA	
10 µg/l	blood plasma women, men and children < 10 years
PFOS	
20 µg/l	blood plasma women
25 µg/l	blood plasma men
10 µg/l	blood plasma children < 10 years

standards for a number of PFCs are required for surface waters in accordance with the EU Water Framework Directive.
In revising the Waste Water Ordinance, the UBA proposes measures – exemplarily for the metal and paper industries – for minimizing the emission of PFCs. In the medium term, closed water cycles should be utilized if PFC are used, or PFCs that are of relevance to waste water should be replaced by alternative compounds.

The UBA recommends that competent state authorities routinely check water bodies and organisms for PFCs. The objective of monitoring is proof that all uses – including drinking water production – remain possible and that plants and animals in the water bodies are not harmed.
The UBA is developing, together with a working group of the German Institute for Standardization (DIN), a standard for the analysis of PFCs in water, sludge and soil samples. With it, a quality standard for the measurement of PFCs in samples will be established. A draft standard for the analysis of selected PFCs exists, and it will very probably be adopted during the course of 2009 as DIN 38407.

The rehabilitation of soils contaminated with PFCs is technically complex and costly, so that the limit of reasonableness is promptly overstepped. PFC limit values, which are already applicable in the states of North-Rhine Westphalia and Baden-Württemberg, have been infringed in one-third of investigated sewage treatment plants. The UBA therefore supports the adoption of PFC limit values in all regulations governing the spreading of materials on the soil for the purpose of fertilization. Legislators have already adopted a limit value of 100 µg/kg of dry matter in the amended Fertilizer Ordinance. A similar limit value, together with a monitoring programme, is being discussed for biowaste and, in particular, for sewage sludge. The UBA is conducting a research project with the aim of proposing a limit value that will guarantee the protection of the environmental media soil and water as well as their living organisms, and which will also counteract the accumulation of PFCs in the food chain.

PFCs are used in certain fire-extinguishing agents and can be emitted into local water bodies in the course of fire fighting. For certain fire classes (fuels and chemicals) no extinguishing agent of comparable efficacy is available on the market. The UBA is currently conducting discussions with the Association of Private Fire Brigades on the risks and benefits of poly- und perfluorinated chemicals in fire-extinguishing agents. An important item on the agenda of these meetings is restrictions on the use of PFCs and the promotion of research into fire fighting.

The UBA appeals to companies that manufacture or process products containing PFCs to further optimize their processes in order to reduce or – better still – prevent their emission into the environment. Only this way can the risk to human health and the environment through perfluorocarbon acid, perfluoro sulfonate acid and intermediate products as well as production residues be more or less ruled out.

Alternatives

The discussion about alternatives to PFCs is difficult, since the qualities of PFCs are up to now unique. With many applications the benefit is obvious. Possible alternatives frequently involve a loss in convenience. In some areas – for instance, in the fighting of fuel-spill fires – PFC-based products are superior to all other extinguishants.

The call for a general ban on the production and use of all PFCs, or „PFTs“, as can occasionally be heard in public debate, cannot presently be scientifically supported. Already now, however, the economic and social benefits of usage have to be weighed against the dangers, and this is a difficult process.

PFOS and PFOA consist, in each case, of 8 carbon atoms. The general rule is that the longer the carbon chain the greater the probability that chemicals reappear in organisms. Fluorine chemical companies therefore increasingly turn to short-chain fluorinated compounds with 4 to 6 carbon atoms. Human and animals apparently absorb these to a negligible extent. Short-chain compounds are also less toxic, but nevertheless persistent, which means that such compounds cannot be degraded. Furthermore, short-chain PFCs are better water-soluble, bind less well with surfaces – for example, with sediment and soil particles – and thus have an increased infiltration potential. Current data allow only a provisional estimate of the effects of „substitutes“ on man and the environment. On account of their great stability and possible contamination of ground- and drinking water, the UBA does not consider these chemicals to be an environment-compatible substitute.

Summary

Once released into the environment, perfluorinated chemicals (PFCs) remain there for a long period: they are persistent. The perfluorocarboxylic acid PFOA and the perfluorosulfonic acid PFOS have been thoroughly studied; they reappear worldwide in the blood of the population and are excreted from the body only very slowly. In animal experiments, both chemicals prove to be reproduction-toxic and they enhance tumour growing.

PFCs are emitted into the environment through production processes and as residues in a number of products in their use and disposal. Certain precursor substances, such as fluorinated telomer alcohols, play an important role in their spread. They are also released during their production, and can be spread as residues in coatings. These precursor compounds can be converted in the environment and the human body into perfluorocarboxylic acids and perfluorosulfonic acids. Frequent detection in the environment, particularly in drinking water and food, has led to justified concern on the part of the population. Concentrations, which could arouse concern about long-term health risks, have been achieved only in isolated cases, such as in Sauerland. The all clear can only be given when concentrations in the environment and in human blood have demonstrably and permanently declined.

PFCs need to be carefully monitored and „trakked" in the future. This naturally also includes examination, on a case-to-case basis, of the type of use of perfluorinated compounds and their benefits. The call for a general ban is not justifiable from a scientific point of view.

Manufacturers, in particular, are called upon to make the production and processing of PFCs environmentally more compatible, in order to better protect man and the environment. Consumers, for their part, should only accept the undoubted advantages of frying pans and raincoats manufactured with fluorine chemicals, when they are properly produced and free of residues.

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Annex: Survey of the use and occurrence in the environment of a number of relevant PFCs			
PFC	**Use**	**Occurrence in the environment**	**Comments**
Perfluorosulfonic acids (e.g. PFOS)	Electroplating AFFF fire-fighting foam Aviation	Worldwide in water bodies and organisms	Use of PFOS restricted to a few applications since June 2008 pursuant to Directive 2006/122/ EC Degradation product of other compounds Development-toxic
Perfluorocarboxylic acid, e.g.: Perfluorohexanoic acid - PFHxA, Perfluorooctanoic acid - PFOA, Perfluorononanoic acid - PFNA)	• Intermediate product in the manufacture of perfluorinated compounds • Potential degradation product of fluorinated polymers	Worldwide in water bodies and organisms	FTOH degradation product Persistent, non-volatile, development-toxic
Neutral volatile perfluorinated alkyl substances (PFAS) • Fluorinated telomer alcohols (FTOH) • Perfluorooctane-sulfone amide (FOSA) • Perfluorooctanoic sulfonamidoethanols (FOSE)	• Manufacture of paints, fluorinated coatings, surface-active modifications of consumer products, adhesives • Precursor for the manufacture of perfluorinated alkylsulfonates	Atmosphere, indoor air	Increased production FTOH is metabolised into, among others, persistent PFOA and PFNA FOSE is metabolised into PFOS
Fluorine polymers, PTFE	Non-stick coating of frying pans, coating of textiles to make them rainproof and breathable		PFOA can be contained as a residue in PTFE
Fluorinated polymers	Fibre and paper finishing		PFOA and volatile precursor substances can occur as residues or arise in their production or use