Perfluoroalkylcarboxylates and –sulfonates

Emerging Contaminants for Drinking Water Supplies?

Rhine Water Works
The Netherlands

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Association of River Waterworks – RIWA

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Contents

1

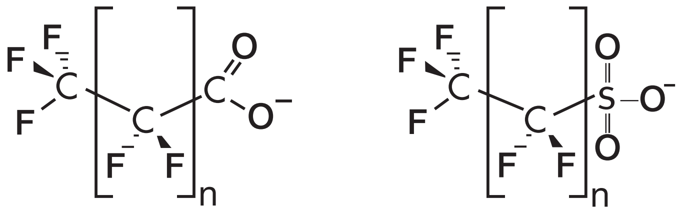
Introduction

1.1 Background

Hazard assessment is a key step in the establishment of Water Safety Plans (WSPs), an approach of the WHO Guidelines for drinking-water quality. WSPs should be developed for individual drinking-water systems. One important aspect of the WSP approach is the assessment of chemical hazards in drinking-water resources. For ubiquitously occurring anthropogenic compounds, like the fluorochemicals regarded in this survey, it is possible to perform a first hazard assessment by means of a desktop study. This study will provide a first insight of a potential threat to drinking water prepared from surface water.

In perfluorinated organic compounds or perfluorochemicals (PFCs1) all hydrogen atoms of the corresponding hydrocarbon compound are substituted for fluorine atoms. The polar carbon-fluorine bond is the most stable bond in organic chemistry. Therefore, PFCs are thermally and chemically more stable than the analogue hydrocarbons. One important group of PFCs is the group of perfluorinated surfactants, two of which, perfluorinated alkylsulfonates and –carboxylates, are considered in this survey. They consist of a hydrophilic end group, i.e. sulfonate or carboxylate end group, and a hydrophobic perfluorinated carbon chain (Figure 1).

Perfluorinated alkylsulfonates and -carboxylates occur in numerous consumer products as active ingredients, impurities or as degradation products of derivatives, e.g. in oil, water and stain repellents for paper, leather and textiles or in fire fighting foams. They may be emitted to the aquatic environment during production and application and also after waste disposal. The most important key compounds are perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA).



Perfluorinated alkylcarboxylates
n=4-10 (C_6-C_{12})

Perfluorinated alkylsulfonates
n=5-11 (C_6-C_{12})

Figure 1: Structural formula of perfluoroalkycarboxylates and sulfonates; in technical products also molecules with shorter and longer perfluoroalkyl chain may occur to some extent.

These chemicals are globally distributed, extremely persistent, bioaccumulative, and of toxicological concern. Particularly, they accumulate in human blood serum in the µg/L concentration range. They are considered with concern in some parts of the world since the end of the last century. As a consequence of the recent positive PFOA and PFOS findings in Japanese drinking waters and in the course of a claim of ten thousands of residents living close to a Teflon® production plant in the US and being exposed to PFOA via contaminated drinking water for years, it is only a question of time until the European public will be interested in the occurrence of these compounds in drinking waters. Thus, the knowledge of the pollution situation is of major importance for drinking-water utilities in order to identify the potential risks and to establish adequate measures.

The Dutch Association of Rhine Water Works RIWA is responsible for a wide variety of source water quality protection issues for its member utilities. RIWA initiated this literature study in order to obtain more insight in the potential relevance of perfluorinated compounds from the viewpoint of drinking water production.

1.2 Scope of the survey

This survey comprises a selection of polar perfluoroalkyl carboxylates (PFCAs) and sulfonates (PFASs) with variable chain-lengths usually between about 6 and 15 carbon atoms. The parent compounds of the target molecules are either the free acids or different salts, which can dissociate in water into the perfluorinated anions and protons, ammonium or metal cations. Furthermore, there is a large number of derivatives containing the basic molecular moiety of one of the target compounds. Regardless of the original parent compounds, only the free anions are the target compounds of this survey. These anions are active ingredients, impurities, intermediates or degradation products of other fluorinated derivatives in technical products. Higher molecular fluorinated compounds, i.e. fluoropolymers are considered to be of minor importance regarding a possible occurrence in drinking water. Nevertheless, they have to be taken into account as potential precursors of PFCAs and PFASs, respectively.

The manifold of compounds, which might give a certain perfluorinated compound, its homologues or isomers is exemplified in the case of perfluorooctanesulfonate (PFOS). PFOS is the perfluorooctanesulfonate anion. The term PFOS-related substance is used to refer to any or all of the substances which contain the PFOS moiety (defined as the $C_8F_{17}SO_2$ group) and may break down in the environment to give PFOS. In the Significant New Use Rule[1] the U.S. Environmental Agency (EPA) states: “EPA is issuing a significant new use rule (SNUR) ... for 75 substances including perfluorooctanesulfonic acid (PFOSH) and certain of its salts (PFOSS), perfluorooctanesulfonyl fluoride (POSF), certain higher and lower homologues of PFOSH and POSF, and certain other chemical substances, including polymers, that are derived from PFOSH and its homologues.”

Similarly, the PFOA acronym is used to indicate not only perfluorooctanoic acid itself, but also its principal salts.

Some individual precursors like the volatile perfluorosulfonamides and the fluorotelomer alcohols, which are important in understanding possible sources and transport of perfluorinated compounds in the environment, are also considered in this survey.

The number of scientific publications, reports, and other documents of relevance for this survey on perfluorinated compounds is rapidly increasing since about the year 2000. There are several recent reviews, exhaustive reports and special internet sites on this issue, which allow to obtain even more detailed information on individual topics[2-12]. The intention of this survey is to provide the interested reader a quick overview on the properties and environmental behavior of PFASs and PFCAs, with a special focus on the potential relevance for drinking water supplies.

2

Properties

2.1 Physical-chemical properties

Little reliable quantitative data is currently available on the physical-chemical properties, for example Henry's Law constant, vapor pressure, water solubility, and octanol-water partition coefficient that are required to predict the behavior of fluorinated alkyl substances under various environmental conditions [2;13]. Due to the surface active properties of PFCAs and PFASs, these data are difficult or impossible to measure. For example, the octanol-water partition coefficient cannot be determined8 when the test compound generates a third phase besides n-octanol and water.

Qualitatively, the properties of perfluorocarboxylates and –sulfonates, which determine their mode of action during application as well as their environmental behavior and fate, could be well understood in terms of:

- dissociation of the corresponding free acids,
- combined hydrophobic and oleophobic properties of the perfluorinated alkyl chain, and
- the stability of the carbon-fluorine bond.

Perfluoroalkylsulfonic and –carboxylic acids are stronger acids than the corresponding hydrocarbon compounds. Perfluoroalkylsulfonic acids are among the strongest acids known[14]. The pKa of the PFOA free acid [9;15] is reported to be 0.6 or 2.5. Therefore, at pH values of natural waters these acids are completely dissociated and anionic perfluoroalkylsulfonates and carboxylates like PFOS and PFOA occur.

The high ionization potential of fluorine (401.8 kcal/mol) and its low polarizability leads to weak inter- and intramolecular interactions. This is demonstrated by the low boiling points of fluorochemicals relative to molecular weight and their extremely low surface tension and low refractive index [13]. The perfluorinated alkyl moiety of PFCAs and PFASs is hydrophobic and lipophobic at the same time [3;16]. When functionalized with a charged moiety, such as sulfonic acid or carboxylic acid group, the resulting fluorochemicals can have surfactant properties [13]. Polymeric derivatives containing perfluoroalkyl chains have soil, stain and water repellent properties and are used for paper, carpet, textile, and leather protection. Furthermore, perfluorinated compounds rather accumulate in liver tissue and blood serum of humans and wildlife than in lipid tissues (see below).

Fluorine is the most electronegative element (electronegativity value of 4.0 on the Pauling scale). Thus, the polar carbon-fluorine bond is the strongest in nature (~110 kcal/mol13). This extraordinary stable bond makes perfluorinated compounds resistant to chemical or biochemical attack. Due to their stability PFCAs and PFASs can be applied under extreme conditions, e.g. as active ingredients in fire-fighting foams or as foaming agents for mist suppression in acidic baths used in chromium electroplating. Under ambient environmental conditions PFOA, PFOS and their homologues are considered end products of the degradation of a number of possible precursors.

2.2 Transformation and degradation

As mentioned above, PFCAs and PFASs are two very persistent classes of perfluorinated compounds. They are stable against hydrolysis, photolysis, acidic and basic attack, oxidizing and reducing agents and against biodegradation [2;16]. Therefore, these compounds behave in the environment like persistent organic pollutants (POPs), with the exception that they do not accumulate in fatty tissues.

Some recent papers report on the decomposition of PFACs and PFOS under more drastic conditions, potentially suited for wastewater treatment. These methods include decomposition of PFOA by different oxidative approaches (UV[17], UV/H_2O_2[17], UV/heteropolyacid catalyst[17], UV/persulfate[18]), and sonochemical decomposition of PFOS and PFOA[19]. Less bioaccumulative, shorter chain PFCAs, fluoride ions, and CO_2 were detected among the degradation products.

In laboratory closed-loop degradation experiments Meesters and Schröder[20] observed elimination of PFOS and PFOA from a spiked wastewater effluent under anaerobic conditions, while both compounds were stable under aerobic conditions. However, no increased fluoride ion concentration was measured, which suggests that no degradation of the perfluoroalkyl chain occurred.

2.3 Bioaccumulation[2]

Extensive screening analyses of PFASs and PFCAs in biota samples from all over the world have identified PFOS, PFHxS, and FOSA and also PFCAs with C_8 to C_{15} chain lengths as global pollutants[21-41].

In contrast to chlorinated or brominated POPs PFASs and PFCAs are not accumulated in fatty tissues. They mainly accumulate in liver, kidney, and muscle tissues and bind to blood serum proteins. The source of these contaminants in biota and in humans is not well understood and therefore, is the subject of ongoing research.

There is some evidence for geographic trends of PFAS and PFCA distribution in wildlife. Highest levels of PFOS and PFOA were found in marine mammals and fish eating animals in industrialized areas, e.g. in the Baltic Sea, in the Mediterranean Sea, in the Great Lakes in North America and along Asian coasts. However, perfluoroalkyl compounds were also detected in remote areas like Alaska and the Arctic.

PFOS was detected most often in these analyses and usually at the highest level among the identified PFASs and PFCAs. Today, PFOS is detected in every investigated European wildlife sample. Typical PFOS concentrations in liver tissues of fish, bird, and mammals comprise a broad range from several ng/g to several thousand ng/g wet weight.

Mammals feeding at higher trophic levels had greater concentrations of PFOS and PFCAs than mammals feeding at lower trophic positions. In the liver of polar bears from the Arctic PFOS concentrations >4000 ng/g wet weight (mean: 3100 ng/g) were found [32]. The highest PFOS concentrations (470 ng/g-179 µg/g, mean: 28,2 µg/g) were measured in the liver of wood mice in Belgium close to a production plant of the 3M Company in Antwerp [35]. Accumulation of certain perfluoroalkyl compounds along the food chain also implies a possible route of exposure for humans.

A few studies report on temporal trends of PFOS and PFCA concentrations measured in biota. There is some evidence for an exponential increase of PFOS levels in biota within the last about 30 years. Such an increase has been demonstrated by the increase of PFOS levels in Lake Ontario lake trouts [33], white-tailed sea eagles from eastern Germany and Poland [23], guillemot eggs from the Baltic Sea[40], and in polar bears in the North American Arctic[42]. For PFOS this observation would be in line with the increase in POSF production from the 1980s until its phase-out by the 3M Company, beginning in 2001[42]. For PFOA and its long chain homologues a similar comparison is not possible due to the non-availability of corresponding production amounts.

2.4 Human exposure and toxicity

First evidence of human exposure with organofluorine compounds was gained in the late 1960s[43;44]. Subsequent research identified several perfluoroalkyl compounds in occupationally exposed workers from fluorochemical production sites. Typical serum PFOS and PFOA levels of occupationally exposed humans are in the low mg/L range [8;15].

For the purpose of this survey, i.e. dealing with contaminations originating from drinking water, only the PFC exposure of non-occupational exposed humans is of relevance. Most data is available for

PFOS and PFOA. Table 1 gives an overview on typical levels measured in the general population. Some more perfluoroalkyl compounds with six to fourteen carbon atoms have also been identified in human blood samples in the last years in the µg/L range [45-47]. Besides PFOS and PFOA the following perfluoroalkyl compounds were detected in human blood: PFHxS, PFDS, FOSA, N-MeFOSAA, and N-EtFOSAA as members of the class of PFAS compounds and PFHxA, PFNA, PFDA, PFUnA, PFDoA, and PFTA as PFCA members.

N-MeFOSAA (synonym: M570) and N-EtFOSAA are oxidation products of N-methyl perfluorooctanesulfonamidoethanol (N-MeFOSE) and N-ethyl perfluorooctanesulfonamidoethanol (N-EtFOSE), which are used primarily in consumer-related applications, e.g. paper and packaging protectants, carpets, and textiles. Occurrence of these markers in human blood samples suggests human exposure through consumer related applications.

There is lot of information on toxicity and toxicokinetics of perfluorinated chemicals in the literature, mainly for the persistent and bioaccumulative key compounds PFOS and PFOA [5;6;8;9;15;48]. In the following some important properties of these two compounds are summarized.

PFOS and PFOA are readily absorbed by mammals following oral and inhalation exposure [4;8;9]. Once absorbed in the body, they distribute mainly in the serum and the liver [4;8;9]. PFOS and PFOA can cross the blood-brain and placental barrier [4;9;49-51]. Therefore, after exposure these compounds were detected in brain and after maternal exposure also in fetal and neonatal organisms. There is no evidence for any metabolic degradation of PFOS and PFOA [4;8;48;52]. Both chemicals are poorly excreted in both urine and feces [4;8]. There is evidence that PFOS and PFOA undergo enterohepatic circulation resulting in reduced amounts of fecal excretion [4;8;48]. Enterohepatic circulation means that these compounds are eliminated in the bile with subsequent reuptak e in the intestine. The rate of urine excretion was found in rats to increase with decreasing chain length of perfluorocarboxylic acids [53]. Biological half-life of PFOA in plasma of a few days for mice and rats and approximately 4.4 years for humans are reported [4]. Half-life of PFOS varies from 7.5 days in rats through 200 days in Cynomolgus monkeys to 8.7 years in humans, estimated from retired 3M production workers [8;50].

There is no evidence of genotoxic properties, neither for PFOS nor for PFOA [8;15].

Table 1: Blood PFOS and PFOA levels in non-occupationally exposed humans

Place	Number of investigated persons	PFOS range [µg/L]	PFOA range [µg/L]	Reference
USA, children	599	6.7–515	1.9–56.1	8;9
USA	645	4.3–1656	1.9–52.3	8;9
USA, St Paul (Minnesota)	31	28–96		8
USA, Atlanta (Georgia)	20	3.6–164	0.2–10.4	46
USA	75	<1.3–124	3–14.7	54
USA	175	<1.3–164	<3–88	47
Colombia	56	4.6–14	3.7–12.2	47
Japan, Tokio	30	33–96.7		8
Japan pregnant women	15	4.9–17.6	<0.5–2.3	55
cord blood	15	1.6–5.3		
Japan	205	3.5–28.1$^{\#)}$	2.5–12.4$^{\#)}$	56
Japan	38	4.1–38	<6.8–12.3	47
Korea	50	3.0–92	<15–256	47
Malaysia	23	6.2–18.8		47
Germany	6	32–45.6		8
Germany	116	5.5–104	1.4–57.7	57
Belgium	20	4.5–27	<1–13	47
Italy	50	<1–10.3		47;54
Sweden	66	2–37	0.5–12.4	45
Poland	25	16–116	9.7–40	47
Brazil	27	4.3–35		47
India	45	<1–3.1	<3–3.5	54

#) Geometric mean

Acute toxicity of PFOS and PFOA is not of concern considering environmental relevant concentrations. LD_{50} values determined in rats typically are on the high mg/kg level. For PFOS a LD_{50} of 251 mg/kg [8]and for PFOA of >500 (male) and 250-500 mg/kg (female)[15] are reported.

Subchronic toxicity of PFOS and PFOA has been studied in rodents and primates. At high doses the mortality of the exposed animals increased. Lower concentrations resulted e.g. in hepatotoxic, immunotoxic and neurotoxic effects and in abnormal behavior. Some studies report on developmental effects and an enhanced carcinoma incidence. Tumors have been observed in liver, pancreas, testis, breast, and thyroid gland [4;8;9;49-51;58-60].

Developmental toxicity of PFOS and PFOA found in animal studies is of major concern considering their concentration in human serum of non-occupationally exposed humans [58]. In rats adverse effects have been observed at a serum PFOA level of 370 µg/L [9;10;61]. First evidence for adverse reproductive effects in mice can be derived for a PFOS dose corresponding to an estimated maternal serum PFOS level of approximately 1,000 µg/L [50].

Typical human serum PFOS and PFOA concentrations range from 7 to 82 µg/L and 3 to 35 µg/L, respectively [62]. These levels are close to those levels at which in animal experiments first adverse toxic effects were observed [10].

These differences are smaller than the safety factor of 100 usually applied in risk assessments, which accounts for the differences between humans and animals and within the human population.

Therefore, for precautionary reasons a significant reduction of human exposure should be aimed at 10. This is especially true, because the toxicity profiles of PFOS and PFOA overlap to some extent. The source of PFOS and PFOA in the serum of the general population is currently unclear. Among other routes of exposition also the drinking water pathway was identified [63;64]. Kinetic estimations demonstrated that uptake of these chemicals with drinking water can contribute to a non-negligible amount to the total serum PFC exposure [63;65]. The unfavorable toxicokinetics may lead to an increase in serum levels on the µg/L level, which is in the same order of magnitude as found in the general population (3-35 µg/L) [62]. For example, assuming a 50 ng/L PFOS contamination in drinking water, which is about the concentration found in the most contaminated tap water in a Japanese survey, would lead to an increase of serum PFOS concentration by 8-16 µg/L (25-50% of the mean serum PFOS levels of 28.4 µg/L reported [62]).

2.4 Ecotoxicity

Numerous tests have been carried out on PFASs and PFCAs, mainly with PFOS and PFOA[6;8;15]. Data quality sometimes is questionable, because of the poor purity of the test compounds or because different salts of the same anion were tested.

Nevertheless, lowest observed effect concentrations in aquatic toxicity tests with PFOS, PFOA and a few more perfluoroalkyl compounds are in the mg/L range. This is true both for tests on acute toxicity and for subchronic/chronic toxicity tests. As outlined in more detail in section 5.2 typical concentrations in surface waters and even in wastewater are in the ng/L or ng/L to low µg/L range, respectively. Therefore, there is a factor of about 105 or more between typical concentrations in surface waters and lowest effect concentrations found in tests with aquatic organisms. Based on these data adverse ecotoxic effects cannot be expected, except in the case of accidental spills, e.g. due to hazards.

3

Industrial synthesis

In order to understand, which homologues and isomers may occur in the environment, it is helpful to describe in short the principal synthesis routes for the production of perfluoroalkylcarboxylates and -sulfonates.

3.1 Electrochemical fluorination

This so-called ECF process was applied by the 3M Company. In this process perfluoroalkyl sulfonates and their derivatives are produced from the intermediate perfluoroalkylsulfonyl fluoride, which is made by electrochemical fluorination of alkylsulfonyl starting materials, typically the chlorides or fluorides (Formula 1)[2;3;5;16]. Perfluorinated compounds with even and odd numbers of carbon atoms in the carbon chain are obtained by this non-selective process. The resulting homologues contain between about 4 and 13 carbon atoms. PFOS with 8 carbon atoms is the main product. Besides the linear perfluorinated products also approximately 30% branched isomers are obtained.

$$C_nH_{2n+1}SO_2F + (2n + 1)\ HF \rightarrow C_nF_{2n+1}SO_2F + (2n + 1)\ H_2$$

Formula 1: Industrial synthesis of perfluoroalkylsulfonyl fluorides by electrochemical fluorination (Simons process, ECF process,); PFOS and its homologues are transferred from the fluorinated key intermediates to their salts and derivatives by further reactions. For more details refer to 2;3;5;13;16;66.

Using POSF as a basic building block, unique chemistries can be created by derivatizing POSF through the sulfonyl moiety of the molecule using conventional hydrocarbon reactions [66]. POSF is reacted with methyl or ethyl amine to produce either N-methyl or N-ethylperfluorooctanesulfonamide (FOSA: NMeFOSA, NEtFOSA). FOSA is subsequently reacted with ethylene carbonate to form either N-methyl or N-ethylperfluorooctanesulfonamidoethanol (FOSE: NMeFOSE, NEtFOSE). The FOSA and FOSE intermediates are the principal building blocks of 3M's product lines.

In 2000, the 3M Company produced an estimated three million kilograms of these chemicals for global industrial and commercial applications. The 3M Company phased out this chemistry until the end of the year 2002.

It is important to notice that PFOS will result from the chemical or metabolic hydrolysis of POSF-derived fluorochemicals. Furthermore, PFOS and its precursors NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE can be found at a concentration of roughly 1-2% in final products [66].

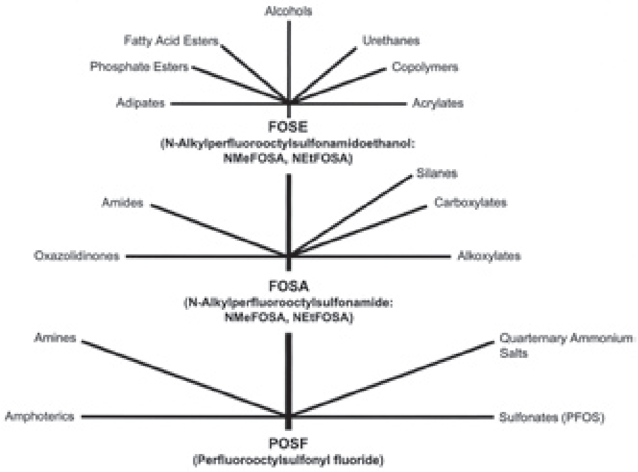


Figure 2: POSF fluorochemical reaction tree (adopted with modifications66). Starting from POSF, conventional reactions yield a number of versatile fluorochemicals. Breakdown of the derivatives may give PFOS as a persistent dead end product.

Perfluoroalkyl carboxylates and their derivatives are manufactured from the intermediate perfluoroalkylcarbonyl fluorides, which are synthesized likewise by fluorination of alkylcarbonyl chlorides or fluorides. These intermediates and therefore, also the derivatives, again comprise compounds with even and odd numbers between about 4 to 13 carbon atoms in the alkyl chain. Approximately 70% linear and 30% branched isomers occur in these products.

$$C_nH_{2n+1}COF + (2n + 1)\ HF \rightarrow C_nF_{2n+1}COF + (2n + 1)\ H_2$$

Formula 2: Industrial synthesis of perfluoroalkylcarbonyl fluorides by electrochemical fluorination (ECF process); PFOA and other homologues are transferred from the fluorinated key intermediates to their salts and derivatives by further reactions. For more details refer to [2;3;5;16;66].

Instead of subjecting perfluoroalkyl fluorides to hydrolysis, they can be reacted with other reagents to create the alcohols used to synthesize acrylate and metacrylate polymer intermediates [2]. Due to the environmental concerns the 3M Company also discontinued manufacturing of PFOA using electrochemical fluorination until the end of the year 2002.

3.2 Telomerization

The so-called telomerization is a process mainly developed by DuPont. Fluorinated alkyl substances based on telomerization are produced by a number of companies, including DuPont, Asahi Glass, Atofina, Clariant, and Daikin, but no production numbers are available for the telomere-based fluorinated alkyl substances 2.

The perfluorinated alkylchains are generated from the monomer perfluoroethylene with perfluoroalkyl iodides as intermediates (Formula 3). The resulting key compounds for the manufacturing of PFOA and its homologues and their salts and derivatives are the perfluoroalkylethyl iodides (Telomer A). Telomerization chemistry exclusively provides linear products with even numbers of carbon atoms in the perfluoroalkyl chains.

$$5\ CF_2{=}CF_2 + 2\ I_2 + IF_5 \rightarrow 5\ F(CF_2CF_2)I$$
$$F(CF_2CF_2)I + n\ CF_2{=}CF_2 \rightarrow F(CF_2CF_2)_{n+1}I$$

Formula 3: Industrial synthesis of perfluoroalkyethyl iodides (Telomer A) by telomerization

These iodides are converted into olefins (FTOs), fluorinated carboxylic acids, fluorotelomer alcohols (FTOHs), and other intermediates (Figure 3).

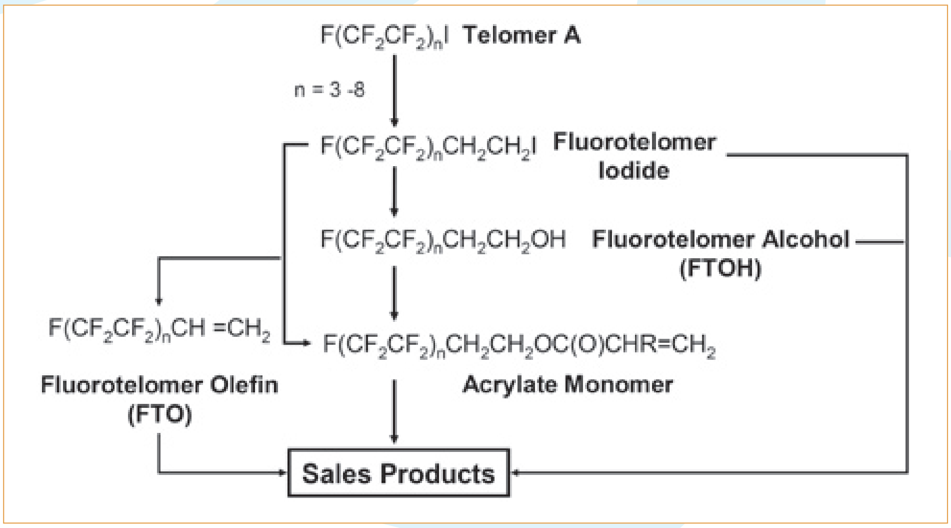


Figure 3: Fluorotelomer-based product manufacture schematic [12]

4

Uses and possible sources

Fluorochemical products can include PFASs or PFCAs either as active ingredients or impurities. In addition, they contain precursors, which may break down to PFASs or PFCAs of different chain lengths. The final breakdown products are the sulfonates and carboxylates like PFOS and PFOA.

4.1 PFOS-related substances

Global production of the key intermediate POSF, which was used to make PFOS and other fluorochemical products, provides a representative quantity for the production volume of sulfonyl-based fluorochemicals. According to information provided by the 3M Company the global POSF production increased from an average annual rate of 1,900 t in 1985-1989 to about 4,500 t in 2000[42]. It has been suggested that, at the end of the last decade, there were a total of six companies manufacturing PFASs by the ECF process with a total global capacity of 4,650 t per year [7].

According to their uses PFOS-related fluorochemicals can roughly be divided into three categories [8;66]:

- **Surface treatments:** high molecular weight polymers or formulated products with low percentages of non-polymeric fluorochemical solids
- **Paper and packaging protectors:** phosphate esters or high molecular weight polymers
- **Performance chemicals:** low molecular chemical substances

Table 2 lists the typical uses of PFOS-related substances and Table 3 the estimated uses in the EU.

Applications of PFASs used in these fields are based on the water, soil and grease repellent properties of the perfluoroalkyl chains, and on the surfactant properties and/or on the outstanding stability of these products. Some examples might illustrate the mode of action of these chemicals. For a more detailed discussion of the mode of action of fluorochemicals the reader is referred to the literature [7;16;66].

A typical surface treatment application is the use of polymeric fluorochemicals as soil repellent coatings on carpets. Emissions of the polymeric materials and the inherent low molecular impurities may occur within the whole lifecycle of the coated products. PFASs can be emitted during fiber and carpet production, during cleaning and after disposal, e.g. landfilling.

The use of fire-fighting foams is a typical example for the application of low molecular fluorochemicals. After application, the foam is disposed of, typically through wastewater treatment, but uncontrolled releases to surface water and groundwater are known to occur.

Due to the combination of surfactant properties and their chemical stability, PFOS-related substances are used as mist suppressing agents in metal plating, especially under the extremely oxidizing conditions in Cr(VI) metal plating baths. These agents form stable foam on the metal plating bath, which protects workers from the harmful mist. Disposal of the spent baths is either to wastewater treatment facilities or to hazardous waste landfills or incinerators when the baths qualify as hazardous waste.

Table 2: Overview of uses for PFOS-related substances [7]

Group	Uses/Applications	End Product	Substances Used (if known)
Surface Treatment Applications	Treatment	Apparel/Textile Fabric/upholstery Carpets Automotive interiors	FOSE alcohols FOSE silanes FOSE alkoxylates FOSE fatty acid esters FOSE adipates FOSE urethanes FOSE acrylates FOSE polyesters FOSE copolymers
	Treatment of metal and glass	Metal/glass	
	Leather treatment (water/oil/solvent repellence)	Leather	As above including PFOSA amphoterics
	Mist suppressant Corrosion inhibitors	Metal plating baths	PFOSA K+, Li+, DEA andNH4+ salts
Paper Protection Applications	Water/oil grease/solvent repellence	Plates and food containers Bags and wraps Folding cartons Containers Carbonless forms Masking papers	FOSE acrylates FOSE copolymers FOSE phosphate esters
Performance Chemical Applications	Surfactants	Surfactant in fire fighting foams Surfactant in alkaline cleaners Mine and oil well surfactants	PFOSA K+, Li+, DEA and NH_4+ salts
	Cleaning agents	Denture cleaners Shampoos Carpet spot cleaners Mould release agents	
	Waxes and polishes	Emulsifier in wax and floor polishes	PFOSA K+, Li+, DEA and NH_4+ salts
	Coatings	Coating additives	
	Photography	Antistatic agents; Surfactants for paper, films, photographic plates	FOSA carboxylates
	Photolithography	Coatings for semi-conductors (anti-reflective coatings)	
	Pesticides/insecticides	Pesticides active ingredient	FOSA amides
		Active ingredient for ant bait traps	PFOSA amines
	Chemical synthesis	Chemical intermediates	PFOSF, PFOSA, FOSA, FOSE
	Medical applications	Waterproofing casts/ wound dressings	FOSA oxazolidones
	Hydraulic fluids	Hydraulic agents	

Table 3: Estimated uses of PFOS-related substances in the EU [7]

Industry sector/Application	Estimated Current Demand [t/a]
Metal Plating	10
Photolithography and Semiconductors	0.47
Photographic Industry	1
Aviation Industry	0.73
Fire Fighting Foams	0.57*
Protective Treatment of Fabrics (Carpets, Textiles and Leather)	240
Paper and Packaging	160
Coatings	90

*Amount released into the environment

4.2 Perfluoroalkylcarboxylates

Perfluoroalkylcarboxylates (PFCAs) like PFOA and its homologues were produced in lower quantities compared to PFOS and related compounds. The estimated total global production is 4,400-8,000 t between 1951 and 2004 [12]. According to Prevedouros et al. [12] emissions of PFCAs with chain lengths between 4 and 15 carbon atoms occur either from direct or indirect sources.

Direct sources are the production of APFO and APFN (ammonium salts of PFOA and PFNA) and the use of these PFCAs in fluoropolymer manufacture, fluoropolymer dispersions, fire-fighting foam products and in numerous consumer and industrial products. Documented uses of PFCAs are based on their chemical stability, surface tension lowering properties, and ability to create stable foams. Besides the above mentioned applications these uses include metal plating and cleaning, coating formulations, polyurethane production, inks, varnishes, vinyl polymerization, lubricants, gasoline, and oil, and water repellents for leather, paper, and textiles. APFO and APFN are used primarily as processing aids in fluoropolymer manufacture such as polytetrafluoroethylene and polyvinylidene fluoride. These PFCAs act to solubilize fluoromonomers to facilitate their aqueous polymerization. In 2000, it is estimated that 230-375 t of PFCAs were produced and used globally for this purpose: 85% APFO and 15% APFN [12].

Indirect sources for PFCAs comprise impurities and degradation products of POSF-based and fluorotelomer-based products.

POSF-based products contained between 200 and 1600 mg/kg of PFOA [67]. In a series of consumer spray application products PFCAs from six to nine carbons ranging in concentration from 5 to 100 mg/kg were found 12. POSF-based products used as surfactants in fire-fighting foams contained between 0.1 and 1.0 wt % of PFCAs with PFOA as the largest component [27;68;69]. Although no longer manufactured, such products are still in use from existing inventories 7. In a biodegradation study it was found that 0.6% of N-EtFOSE alcohol was transformed to PFOA when exposed to municipal wastewater treatment sludge70. In addition, it was reported that atmospheric degradation of perfluoroalkylsulfonamido raw materials gives PFCAs [71;72].

Degradation of fluorotelomer alcohols (FTOHs) and olefins (FTOs) is another possible indirect source of PFAC in the environment. It is estimated that about 2 wt % of FTOHs and FTOs are present as unreacted residuals and by-products in fluorotelomer-based products. This accounts for approximately 100 t per year, each of FTOHs and FTOs, calculated from the global Telomer A production of 5000-6000 t per year (data for 2000-2002).

Fluorotelomer-based products may contain trace levels of PFCAs, including PFOA, as unintended reaction by-products in concentrations of 1-100 mg/kg. Estimated historical global emission of

PFCAs to air and/or water, e g. during industrial application of fluorotelomer-based products are between 0.3 and 30 t [12]. However, FTOHs and FTOs have sufficient vapour pressure to be present in air and might be responsible for the global distribution of PFCAs through atmospheric transport and degradation. Atmospheric degradation can occur, initiated by reaction with OH radicals [73]. In addition, PFOA was reported to be formed in studies to determine the biodegradation of fluorotelomer alcohols in sludge [74-76].

Up to date, there is no evidence of fluoropolymer degradation to PFCAs.

In summary, PFCA emissions from indirect sources are estimated to be of minor importance compared to emission from direct sources such as fluoropolymer production. However, such emission might explain, at least in part, the global distribution of PFCAs.

5

Occurrence

Occurrence in the aquatic

Different PFCAs and PFASs as well as some of their possible precursors were detected in wastewater[77] and sewage sludge[78], surface water, groundwater, seawater, marine sediments, and in drinking water.

5.1 Wastewater and sludge

The investigation of possible sources, fate, and transport of PFCAs and PFASs is a matter of ongoing research. The input by wastewater effluents is considered an important source of perfluorosurfactants in the aquatic environment [79]. They can occur in wastewater and sludge either as transformation products of fluorinated precursors or through direct use and disposal of products containing residual amounts of these compounds. Figure 4 shows the proposed degradation pathway of N-EtFOSE, a key compound in 3M's former product lines. The findings of Boulanger et al. [77] suggest transformation of precursors within wastewater treatment is not an important source of fluorosurfactants compared to direct input of residual amounts.

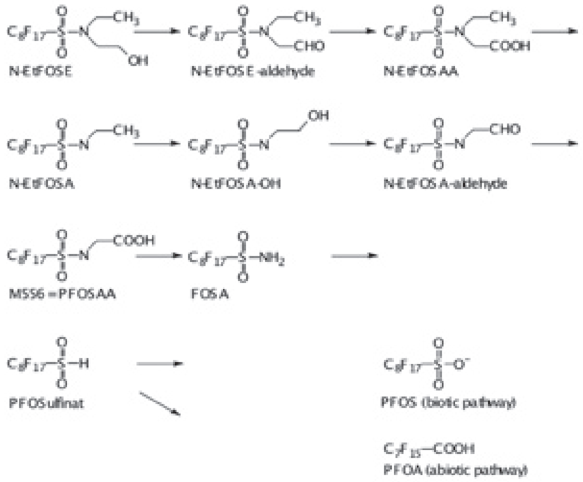


Figure 4: Proposed degradation pathway of N-EtFOSE in wastewater sludge to PFOS and PFOA[67] (adopted with modifications from Hekster and de Voogt [6])

Releases through an aqueous industrial wastestream was documented indirectly by a significant increase of PFOS and PFOA concentrations in the Tennessee River downstream of 3M's fluorochemical manufacturing plant at Decatur, AL[80].

In the so-called multi-city study of the 3M Company [81] PFOS, PFOA, and FOSA were found in publicly-owned treatment works (POTW) effluent and sludge samples. When detected and quantified, the following ranges were evaluated for the average concentrations of duplicate samples in POTW effluents: 48-4,980 ng/L for PFOS, 42-2,280 ng/L for PFOA and 56-85 ng/L for FOSA. The corresponding concentration ranges in sludge samples (dry weight) were: 58.9-2,980 µg/kg for PFOS, 0.297-173 µg/kg and 1.28-102.4 µg/kg. The concentrations were highly variable and differed much between the POTW of the so-called supply-chain cities and the control cities. Except for the FOSA concentration in POTW effluents, the highest concentrations in effluents and sludge were observed for the Decatur

POTW. However, PFASs were also detected in the two control cities Cleveland and Port St. Lucie. In the influent of the Iowa City wastewater treatment plant (WWTP) Boulanger et al.[77] detected PFOS, PFOA, and N-EtFOSAA. However, due to signal suppression in electrospray-mass spectrometric detection of PFOS and PFOA, only N-EtFOSAA could be quantified in the influent. The effluent concentration of PFOS and PFOA were 26±2.0 ng/L and 22±2.1 ng/L, respectively. These values were lower than the lowest concentrations reported in the 3M study for the control cities. The N-EtFOSAA concentrations decreased during treatment, starting from 5.1±0.8 ng/L in influent to 3.6 ng/L in effluent. This is an overall WWTP removal of 29%.

A limited survey of domestic sludge and marine sediments demonstrated adsorption of long chain PFCAs, PFASs and related PFCs to these solid matrices[78]. The following PFCs were detected in sewage sludge samples: PFHxS, PFOS, PFDS, FOSAA, N-MeFOSAA, N-EtFOSAA, PFOA, PFNA, PFDA, PFUnA, PFDoA, and PFTA. Substances that may be transformed to PFOS, such as N-MeFOSAA and N-EtFOSAA were present in sludge at levels often exceeding the PFOS concentration. The concentrations in sludge ranged from 5 to 152 µg/kg for total perfluorocarboxylates and 55 to 3370 µg/kg for total perfluoroalkyl sulfonyl-based chemicals. Due to the order of magnitude of these concentrations it can be well understood that in a former study [82] no PFOS was observed above the limit of detection of 6 mg/kg.

In a recently published report PFC concentrations in the influent and effluent of a public wastewater treatment plant were compared [83]. The influent contained five of the 12 analyzed PFCs. PFOS and PFOA were found in the highest concentrations in comparable quantities like in the 3M multi-city study. Also a shorter chain PFAS and shorter chain PFCAs, namely PFPA, PFHxA, and PFHxS, were detected in the influent. The concentrations of all these PFCs in the effluent were significantly higher than the levels found in the influent. A similar observation was made in a study of another research group, which is cited in this report. Although the samplings do not correspond with the retention time of the wastewater in the treatment plant this might be a first evidence for a possible breakdown of PFC precursors, which may break down during biological wastewater treatment to the recalcitrant PFASs and PFCAs like PFOS, PFOA, and their homologues.

5.2 Surface waters

Several studies report on the occurrence of PFCAs and PFASs in surface waters in the USA, Canada, Japan, Hong Kong, South China, and Korea, both in freshwater[64;80;81;84-86] and in seawater [28;64;85;87;88]. PFOS and PFOA typically occur in freshwater on a low ng/L level ranging up to several tens of ng/L. Elevated concentrations of PFOS and PFOA were detected in the Tennessee River, where concentrations of 114±19 ng/L and 394±128 ng/L were measured, downstream of the inflow of Baker's Creek, respectively. Baker's Creek is the receiving water of the 3M fluorochemical manufacturing facility at Decatur. Upstream, the concentration of PFOS was 32±11 ng/L and there were no measurable PFOA levels (<25 ng/L).

A comprehensive study on the occurrence of PFOS and PFOA at 78 sampling sites in Japanese rivers and creeks demonstrated the widespread occurrence of these compounds[64]. In different districts geometric means between 0.97 and 21.2 ng/L were evaluated for PFOA and between 0.89 and 5.7 ng/L for PFOS, respectively. Individual concentrations comprised a range from 0.10 to 456 ng/L for PFOA and from 0.24 to 37.3 ng/L for PFOS. Systematic searches revealed two highly contaminated sites, a public-water-disposal site for PFOA and an airport for PFOS.

On the Canadian coast of Lake Erie and Lake Ontario PFOS and PFOA were measured in concentrations ranging from 21 ng/L to 70 ng/L and 27 ng/L to 50 ng/L[86]. Also the PFOS precursors FOSA and N-EtFOSAA as well as PFOSulfinat were detected for the first time.

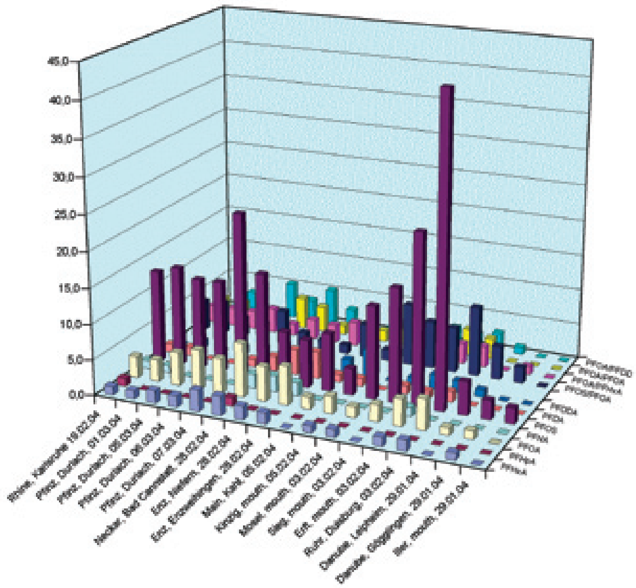


Figure 5: Concentrations of PFOS and homologue PFACs in German rivers

No publications were found in the open peer-reviewed literature on concentrations in European rivers or creeks. First measurements of TZW in German rivers, predominantly located in the Rhine River catchment area, demonstrated that PFCAs and PFOS also occur in comparable levels to those found in USA, Canada and Japan89. Concentrations in the low ng/L range were found (Figure 5). In most cases PFOS concentrations exceeded individual PFCA concentrations. Further unpublished measurements of TZW in the Rhine basin area in 2005 and 2006 confirmed these findings. Therefore, the question arises, whether these traces can be removed from the river water by natural attenuation processes such as bankside filtration. In the case of direct surface water intake additional water treatment would be necessary in order to remove these traces.

5.3 Drinking water

Some data is available on drinking water contamination with PFCAs and PFASs from the USA and Japan. No data on PFCA and PFAS pollution in European drinking waters have been found in the literature. In the USA studies were conducted to obtain data about the presence of fluorochemicals in drinking waters in the vicinity of fluoropolymer production plants and where secondary manufacturers use these chemicals[81;90].

In its fluoropolymer manufacturing process, DuPont has discharged large quantities of PFOA as waste material into the air and water surrounding its Washington Works plant near Parkersburg, West Virginia. In internal studies of tap water already in 1984 in the vicinity of this works, DuPont detected PFOA at concentrations of 1.5 µg/L in a store tap in Lubeck, at concentrations of 1.0 and 1.2 µg/L in a store tap in Washington, and at concentrations of 0.8 and 0.6 ppb in Little Hocking[90].

In the meantime detectible quantities of PFOA have been found in two water districts located in West Virginia and four water districts located in Ohio, and numerous private wells in these vicinities has been found to be contaminated with PFOA as well. The affected water districts are (1) Little Hocking, Ohio; (2) Lubeck Public Service District, West Virginia; (3) City of Belpre, Ohio; (4) Tuppers Plains, Ohio; (5) Mason County Public Service District, West Virginia; (6) Village of Pomeroy, Ohio[91].

High measured tap water values were found in samples of Little Hocking Water Association (LHWA, Washington County, Ohio)[92]. The water wells of this water supply are located along the Ohio River directly across from DuPont's Washington Works plant. In measurements between 2001 and 2005 PFOA was detected in µg/L quantities in test wells, production wells, and in the distribution system of the LHWA. PFOA concentrations ranged from 0.4 to 17.9 µg/L in the production wells and from 1.6 to 6.9 µg/L in the distribution system. In 2005 DuPont has agreed to finance a so-called bottled water program until a new carbon filtration system for purification of the contaminated water is operational and effective, as agreed to by both DuPont and LHWA.

Recently, PFOA and PFOS contamination was reported in private groundwater wells in Lake Elmo, Minnesota and in some of the Oakdale, Minnesota municipal wells93-95. These contaminations originate from several landfills, where PFCs were disposed by the 3M Company decades ago. PFCs have been detected in 78 out of 239 sampled private wells. Twelve wells have levels of PFOS above the Health-Based Value (HBV), set by the Minnesota Department of Health and seven wells have PFOS and PFOA levels above the HBV. HBV is the concentration of a groundwater contaminant that is considered to pose little to no risk to health, even if consumed daily over a lifetime. The HBV for PFOA is 7 µg/L and for PFOS 1 µg/L. It should be noted that HBVs were developed to protect only the adult and are not necessarily protective of sensitive populations, i.e. children and pregnant women.

In September 2005, the 3M Company provided the City of Lake Elmo a community grant of 3.3 million dollars. This grant will cover all water related project costs to install and connect municipal water service for existing 214 homes in Tablyn Park and Lake Elmo neighborhoods. Currently, in Oakdale a granular activated carbon treatment (GAC) treatment for the removal of PFCs is planned[94].

PFOA and PFOS were also detected in treated drinking water and tap water in Columbus, Georgia, where several secondary manufacturers are located, which produce non-wovens, household additives, apparel, carpet, and home textiles[81]. The PFOS concentrations ranged from 53 to 63 ng/L, the PFOA concentrations from 25 to 29 ng/L.

In a Japanese study PFOA and PFOS have also been found in tap water samples64. Geometric means (GM) for a set of five samples each from six different local areas were given in this study. The mean levels ranged from 0.12 ng/L to 40.0 ng/L for PFOA and from <0.1 to 12.0 ng/L for PFOS. It has to be pointed out that at low levels near the limit of quantification (LOQ) the geometric standard deviation (GSD) exceeded the GM remarkably by a factor of 10.

6

Implications

The examples of drinking water pollution given in 5.3 demonstrate that ionic perfluoroalkyl chemicals like the PFOS and the PFOA anions are persistent and mobile enough to pollute drinking water at a trace level. As the Japanese study shows, the concentrations in tap water, when detected, typically are in the low ng/L range, if no direct point sources are situated in the near vicinity of the water supply. In the case of local point sources, e.g. landfills contaminating a groundwater aquifer, much higher concentrations up to µg/L levels can occur.

Current measures to prevent human exposure with PFCs are a bottled water program (short term measure), water treatment by GAC filtration, and connection to alternate water supplies delivering non-polluted drinking water (medium to long-term measures).

Information concerning effectiveness and life-time of GAC filters tentatively will be available, when the currently installed facilities will be in operation for a few months or years. From the scarce data on the behavior of PFASs and PFCAs in wastewater treatment it can be expected that PFOS might be removed better by adsorption than PFOA. In addition longer chain PFCs might be removed more effective by activated carbon filtration than short chain homologues. However, at present no reliable data have been found by the current authors on the effectiveness of this and other water treatment steps usually used in the treatment of surface water, e.g. bankside filtration, slow sand filtration, flocculation, and ozone treatment. Furthermore, it cannot be excluded that PFOS, PFOA, and their homologues will be generated through breakdown of PFC precursors during biological or oxidative steps in water treatment, such as biological processes during bankside filtration or on biologically active activated carbon and during ozone treatment of the water.

Summary and Conclusions

Members of the compound classes of PFASs and PFCAs are globally distributed in wildlife, humans and in the aquatic environment, including wastewater, drinking water resources, and drinking water. The wastewater pathway seems to be a major entrance pathway of PFASs and PFACs into the aquatic environment. The most intensively studied compounds are PFOS and PFOA. They are considered degradation end products of different kinds of fluorochemical precursors. If not related to local point sources, typical drinking water values of PFOS and PFOA, such as measured in a Japanese study, are in the low ng/L range. Comparable levels could be expected for European countries due to a similar degree of industrialization.

Based on their persistence, bioaccumulation potential, toxicological concerns, and global distribution, voluntary actions of the fluorochemical industry and regulatory measures have taken place or are currently underway. The main manufacturer of PFOS-related compounds, the 3M Company, phased out its perfluorooctanyl chemistry between 2000 and 2002. In the EU PFOS and related substances have been proposed on December 5, 2005 to be regulated by a change of the Directive of the European Parliament and of the council relating to restrictions on the marketing and use of perfluorooctane sulfonates (amendment of Council Directive 76/769/EEC) [96]. Health effects of long-term exposure of PFOA are the subject of a current U.S. Environmental Protection Agency risk assessment.

The occurrence of PFAS and PFAC trace pollutants in European drinking water resources, i.e. in surface waters, bank filtrates, and groundwaters is not well studied, yet. In Germany, DVGW-Technologiezentrum Wasser (TZW) is currently (July/2005-December/2007) dealing with a research project of the German Technical and Scientific Association for Gas and Water (DVGW), on this objective. Results are expected to be published in early 2007. First surface water data collected already in 2004 showed that even though the main manufacturer phased out PFOS production at the end of 2002, PFOS is still the predominant perfluoroalkyl compound measured in surface waters [89].

The detection of contaminated drinking waters in several water supplies in the US forced short-term to medium term measurements like bottled-water programs, connecting of private groundwater-well owners to alternate water supplies, and installation of granular activated carbon filters. No reliable quantitative data was found in the open literature on the effectiveness of activated carbon filtration or other treatment steps usually applied by waterworks for the removal of organic trace-pollutants. In addition, the potential formation of PFOS, PFOA, and their homologues from PFC precursors during biological and oxidative water treatment needs to be studied. This lack of information on the behavior of PFAS, PFAC, and related compounds in drinking water preparation urges for further research in this field.

8 References

(1) U.S. Environmental Protection Agency (EPA). Perfluoroalkyl Sulfonates; Significant New Use Rule: Federal Register / Vol. 67, No. 236 /Monday, December 9, 2002 / Rules and Regulations [FR Doc. 02-31010 Filed 12-6-02; 8:45 am].

(2) Schultz, M. M.; Barofsky, D. F.; Field, J. A. Env. Eng. Sci. 2003, 20, 487-501.

(3) Lehmler, H. J. Chemosphere 2005, 58, 1471-1496.

(4) Kudo, N.; Kawashima, Y. J Toxicol. Sci. 2003, 28, 49-57.

(5) Fricke, M.; Lahl, U. UWSF - Z. Umweltchem. Ökotox. 2005, 17, 36-49.

(6) Hekster, F. M., Voogt, P. de, Pijnenburg, A. M. C. M, and Laane, R. W. P. M. Perfluoroalkylated substances - aquatic environmental assessment. 1-7-2002.

(7) Risk & Policy Analysts Ltd. and BRE Environment. Risk reduction strategy and analysis of advantages and drawbacks for perfluorooctane sulphonate (PFOS), prepared for Department for Environment, Food and Rural Affairs and the Environment Agency for England and Wales. 3-8-2004.

(8) Organisation for Economic Co-operation and Development (OECD), Environment Directorate, and Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology. Co-operation on existing chemicals, Hazard assessment of perfluorooctane sulfonate (PFOS) and its salts. 21-11-2002.

(9) U.S.Environmental Protection Agency (EPA). Preliminary risk assessment of the developmental toxicity associated with exposure to perfluorooctanoic acid and its salts. 10-4-2003.

(10) Environmental Working Group. PFCs - A family of chemicals that contaminate the planet. http://ewg.org:16080/reports/pfcworld/ . 15-2-2006.

(11) Fluoride Action Network (F.A.N.) Pesticide Project. PFOS: Perfluorooctane sulfonate and PFOA: Perfluorooctanoic acid, Perfluorinated chemicals. http://www.fluoridealert.org/pesticides/pfos.pfoas-page.htm . 22-8-2005.

(12) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Environ. Sci. Technol. 2006, 40, 32-44.

(13) 3M. Sulfonated Perfluorochemicals in the environment: sources, dispersion, fate and effects. U.S. EPA public docket AR226-0620. 1-3-2000.

(14) Siegemund, G.; Schwertferger, W.; Feiring, A.; Smart, B.; Behr, F.; Vogel, H.; McKusik, B. Fluorine Compounds, Organic; in Gerhartz, W., ed.: Ullmann's encyclopedia of industrial chemistry, VCH: Weinheim, 1988; pp 349-392.

(15) U.S. Environmental Protection Agency (EPA). Revised draft hazard assessment of perfluorooctanoic acid and its salts. U.S. EPA public docket AR226-1136. 4-11-2002.

(16) Kissa, E. Fluorinated surfactants and repellents; Marcel Dekker: New York, 2001.

(17) Hori, H.; Hayakawa, E.; Einaga, H.; Kutsuna, S.; Koike, K.; Ibusuki, T.; Kiatagawa, H.; Arakawa, R. Environ. Sci. Technol. 2004, 38, 6118-6124.

(18) Hori, H.; Yamamoto, A.; Hayakawa, E.; Taniyasu, S.; Yamashita, N.; Kutsuna, S.; Kiatagawa, H.; Arakawa, R. Environ. Sci. Technol. 2005, 39, 2383-2388.

(19) Moriwaki, H.; Takagi, Y.; Tanaka, M.; Tsuruho, K.; Okitsu, K.; Maeda, Y. Environ. Sci. Technol. 2005, 39, 3388-3392.

(20) Meesters, R. J.; Schröder, H. F. Water Sci. Technol. 2004, 50, 235-242.

(21) Giesy, J. P.; Kannan, K. Environ. Sci. Technol. 2001, 35, 1339-1342.

(22) Giesy, J. P.; Kannan, K. Environ. Sci. Technol. 2002, 36, 146A-152A.

(23) Kannan, K.; Corsolini, S.; Falandysz, J.; Oehme, G.; Focardi, S.; Giesy, J. P. Environ. Sci. Technol. 2002, 36, 3210-3216.

(24) Kannan, K.; Newsted, J.; Halbrook, R. S.; Giesy, J. P. Environ. Sci. Technol. 2002, 36, 2566-2571.

(25) Kannan, K.; Hansen, K. J.; Wade, T. L.; Giesy, J. P. Arch. Environ. Contam. Toxicol. 2002, 42, 313-318.

(26) Kannan, K.; Choi, J. W.; Iseki, N.; Senthilkumar, K.; Kim, D. H.; Giesy, J. P. Chemosphere 2002, 49, 225-231.

(27) Moody, C. A.; Martin, J. W.; Kwan, W. C.; Muir, D. C.; Mabury, S. A. Environ. Sci. Technol. 2002, 36, 545-551.

(28) Taniyasu, S.; Kannan, K.; Horii, Y.; Hanari, N.; Yamashita, N. Environ. Sci. Technol. 2003, 37, 2634-2639.

(29) Van de Vijver, K. I.; Hoff, P. T.; Das, K.; Van Dongen, W.; Esmans, E. L.; Jauniaux, T.; Bouquegneau, J. M.; Blust, R.; De Coen, W. Environ. Sci. Technol. 2003, 37, 5545-5550.

(30) Van de Vijver, K. I.; Hoff, P. T.; Van Dongen, W.; Esmans, E. L.; Blust, R.; De Coen, W. M. Environ. Toxicol. Chem. 2003, 22, 2037-2041.

(31) Van de Vijver, K. I.; Hoff, P. T.; Das, K.; Van Dongen, W.; Esmans, E. L.; Siebert, U.; Bouquegneau, J. M.; Blust, R.; De Coen, W. M. Mar. Pollut. Bull. 2004, 48, 992-997.

(32) Martin, J. W.; Smithwick, M. M.; Braune, B. M.; Hoekstra, P. F.; Muir, D. C.; Mabury, S. A. Environ. Sci. Technol. 2004, 38, 373-380.

(33) Martin, J. W.; Whittle, D. M.; Muir, D. C.; Mabury, S. A. Environ. Sci. Technol. 2004, 38, 5379-5385.

(34) Corsolini, S.; Kannan, K. Organohalogen Compounds 2004, 66, 4079-4085.

(35) Hoff, P. T.; Scheirs, J.; Van, d., V; Van Dongen, W.; Esmans, E. L.; Blust, R.; De Coen, W. Environ. Health Perspect. 2004, 112, 681-686.

(36) Tomy, G. T.; Budakowski, W.; Halldorson, T.; Helm, P. A.; Stern, G. A.; Friesen, K.; Pepper, K.; Tittlemier, S. A.; Fisk, A. T. Environ. Sci. Technol. 2004, 38, 6475-6481.

(37) De Silva, A. O.; Mabury, S. A. Environ. Sci. Technol. 2004, 38, 6538-6545.

(38) Bossi, R.; Riget, F. F.; Dietz, R.; Sonne, C.; Fauser, P.; Dam, M.; Vorkamp, K. Environ. Pollut. 2005, 136, 323-329.

(39) Hoff, P. T.; Van Campenhout, K.; Van, d., V; Covaci, A.; Bervoets, L.; Moens, L.; Huyskens, G.; Goemans, G.; Belpaire, C.; Blust, R.; De Coen, W. Environ. Pollut. 2005, 137, 324-333.

(40) Holmstrom, K. E.; Jarnberg, U.; Bignert, A. Environ. Sci. Technol. 2005, 39, 80-84.

(41) Smithwick, M.; Mabury, S. A.; Solomon, K. R.; Sonne, C.; Martin, J. W.; Born, E. W.; Dietz, R.; Derocher, A. E.; Letcher, R. J.; Evans, T. J.; Gabrielsen, G. W.; Nagy, J.; Stirling, I.; Taylor, M. K.; Muir, D. C. Environ. Sci. Technol. 2005, 39, 5517-5523.

(42) Smithwick, M.; Norstrom, R. J.; Mabury, S. A.; Solomon, K.; Evans, T. J.; Stirling, I.; Taylor, M. K.; Muir, D. C. G. Environ. Sci. Technol. 2006, 40, 1139-1143.

(43) Taves, D. R. Nature 1968, 220, 582-583.

(44) Taves, D. R. Nature 1968, 217, 1050-1051.

(45) Kärrman, A.; van Bavel, B.; Järnberg, U.; Hardell, L.; Lindström, G. Organohalogen Compounds 2004, 66, 4058-4062.

(46) Kuklenyik, Z.; Reich, J. A.; Tully, J. S.; Needham, L. L.; Calafat, A. M. Environ. Sci. Technol. 2004, 38, 3698-3704.

(47) Kannan, K.; Corsolini, S.; Falandysz, J.; Fillmann, G.; Kumar, K. S.; Loganathan, B. G.; Mohd, M. A.; Olivero, J.; Van Wouwe, N.; Yang, J. H.; Aldoust, K. M. Environ. Sci. Technol. 2004, 38, 4489-4495.

(48) DePierre, J. W. Effects on rodents of perfluorofatty acids, in: Neilson, A. H. (ed) Handbook of

Environmental Chemistry, Vol. 3, 203-248. 2002. Berlin, Springer.

(49) Lau, C.; Thibodeaux, J. R.; Hanson, R. G.; Rogers, J. M.; Grey, B. E.; Stanton, M. E.; Butenhoff, J. L.; Stevenson, L. A. Toxicol. Sci. 2003, 74, 382-392.

(50) Thibodeaux, J. R.; Hanson, R. G.; Rogers, J. M.; Grey, B. E.; Barbee, B. D.; Richards, J. H.; Butenhoff, J. L.; Stevenson, L. A.; Lau, C. Toxicol. Sci. 2003, 74, 369-381.

(51) Austin, M. E.; Kasturi, B. S.; Barber, M.; Kannan, K.; MohanKumar, P. S.; MohanKumar, S. M. Environ.Health Perspect. 2003, 111, 1485-1489.

(52) Olsen, G. W.; Hansen, K. J.; Stevenson, L. A.; Burris, J. M.; Mandel, J. H. Environ. Sci. Technol. 2003, 37, 888-891.

(53) Kudo, N.; Suzuki, E.; Katakura, M.; Ohmori, K.; Noshiro, R.; Kawashima, Y. Chem. Biol. Interact. 2001, 134, 203-216.

(54) Kannan, K.; Kumar, K. S.; Corsoline, A.; Aldous, K. M. Organohalogen Compounds 2003, 64, 29-32.

(55) Inoue, K.; Okada, F.; Ito, R.; Kato, S.; Sasaki, S.; Nakajima, S.; Uno, A.; Saijo, Y.; Sata, F.; Yoshimura, Y.; Kishi, R.; Nakazawa, H. Environ. Health Perspect. 2004, 112, 1204-1207.

(56) Harada, K.; Saito, N.; Inoue, K.; Yoshinaga, T.; Watanabe, T.; Sasaki, S.; Kamiyama, S.; Koizumi, A. J Occup. Health 2004, 46, 141-147.

(57) Umweltbundesamt. Untersuchung archivierter Proben der Umweltprobenbank des Bundes auf perfluorierte organische Verbindungen. 2004.

(58) Lau, C.; Butenhoff, J. L.; Rogers, J. M. Toxicol. Appl. Pharmacol. 2004, 198, 231-241.

(59) Seacat, A. M.; Thomford, P. J.; Hansen, K. J.; Olsen, G. W.; Case, M. T.; Butenhoff, J. L. Toxicol. Sci. 2002, 68, 249-264.

(60) Kennedy, G. L., Jr.; Butenhoff, J. L.; Olsen, G. W.; O'Connor, J. C.; Seacat, A. M.; Perkins, R. G.; Biegel, L. B.; Murphy, S. R.; Farrar, D. G. Crit. Rev. Toxicol. 2004, 34, 351-384.

(61) Butenhoff, J. L.; Kennedy, G. L., Jr.; Frame, S. R.; O'Connor, J. C.; York, R. G. Toxicology 2004, 196, 95-116.

(62) Hansen, K. J.; Clemen, L. A.; Ellefson, M. E.; Johnson, H. O. Environ. Sci. Technol. 2001, 35, 766-770.

(63) Harada, K.; Saito, N.; Sasaki, K.; Inoue, K.; Koizumi, A. Bull. Environ. Contam. Toxicol. 2003, 71, 31-36.

(64) Saito, N.; Harada, K.; Inoue, K.; Sasaki, K.; Yoshinaga, T.; Koizumi, A. J Occup. Health 2004, 46, 49-59.

(65) Hawthorne M. Chemical concerns persist. Residents could have more C8 in blood than workers, a DuPont Model Indicates. The Columbus Dispatch . 2-3-2003.

(66) 3M. Fluorochemical use, distribution and release overview. U.S. EPA public docket AR226-0550. 26-5-1999.

(67) 3M. Environmental, health and safety measures relating to perfluorooctanoic acid and its salts (PFOA). U.S. EPA EDocket OPPTS2003-0012-0007. 2003. Washington, DC.

(68) Moody, C. A.; Field, J. A. Environ. Sci. Technol. 2000, 34, 3864-3870.

(69) Moody, C. A.; Hebert, G. N.; Strauss, S. H.; Field, J. A. J Environ. Monit. 2003, 5, 341-345.

(70) Lange, C. C. The aerobic biodegradation of N-EtFOSE alcohol by the microbial activity present in municipal wastewater treatment sludge; 3M project ID: LIMS E00-2252. 2000. St. Paul, MN, 3M Environmental Laboratory.

(71) Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. Environ. Sci. Technol 2006, 40, 864-872.

(72) D'eon, J. C.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A. Environ. Sci. Technol 2006, 40, 1862-1868.

(73) Wallington, T. J.; Hurley, M. D.; Xia, J.; Wuebbles, D. J.; Sillman, S.; Ito, A.; Penner, J. E.; Ellis, D. A.; Martin, J.; Mabury, S. A.; Nielsen, O. J.; Sulbaek Andersen, M. P. Environ. Sci. Technol 2006, 40, 924-930.

(74) Dinglasan, M. J.; Ye, Y.; Edwards, E. A.; Mabury, S. A. Environ. Sci. Technol. 2004, 38, 2857-2864.

(75) Wang, N.; Szostek, B.; Buck, R. C.; Folsom, P. W.; Sulecki, L. M.; Capka, V.; Berti, W. R.; Gannon, J. T. Environ. Sci. Technol. 2005, 39, 7516-7528.

(76) Wang, N.; Szostek, B.; Folsom, P. W.; Sulecki, L. M.; Capka, V.; Buck, R. C.; Berti, W. R.; Gannon, J. T. Environ. Sci. Technol. 2005, 39, 531-538.

(77) Boulanger, B.; Vargo, J. D.; Schnoor, J. L.; Hornbuckle, K. C. Environ. Sci. Technol. 2005, 39, 5524-5530.

(78) Higgins, C. P.; Field, J. A.; Criddle, C. S.; Luthy, R. G. Environ. Sci. Technol. 2005, 39, 3946-3956.

(79) Boulanger, B.; Peck, A. M.; Schnoor, J. L.; Hornbuckle, K. C. Environ. Sci. Technol. 2005, 39, 74-79.

(80) Hansen, K. J.; Johnson, H. O.; Eldridge, J. S.; Butenhoff, J. L.; Dick, L. A. Environ. Sci. Technol. 2002, 36, 1681-1685.

(81) 3M. Environmental monitoring – multi-city study; water, sludge, sediment, POTW effluent and landfill leachate samples - executive summary. 25-6-2001.

(82) Schröder, H. F. J Chromatogr. A 2003, 1020, 131-151.

(83) Oliaei, F., Kriens, D., and Kessler, K. Investigation of perfluorochemical (PFC) contamination in Minnesota – phase one, Report to Senate Environment Committee. 2006.

(84) Moody, C. A.; Kwan, W. C.; Martin, J. W.; Muir, D. C.; Mabury, S. A. Anal. Chem 2001, 73, 2200-2206.

(85) Saito, N.; Sasaki, K.; Nakatome, K.; Harada, K.; Yoshinaga, T.; Koizumi, A. Arch. Environ. Contam. Toxicol. 2003, 45, 149-158.

(86) Boulanger, B.; Vargo, J.; Schnoor, J. L.; Hornbuckle, K. C. Environ. Sci. Technol. 2004, 38, 4064-4070.

(87) Yamashita, N.; Kannan, K.; Taniyasu, S.; Horii, Y.; Okazawa, T.; Petrick, G.; Gamo, T. Environ. Sci. Technol. 2004, 38, 5522-5528.

(88) So, M. K.; Taniyasu, S.; Yamashita, N.; Giesy, J. P.; Zheng, J.; Fang, Z.; Im, S. H.; Lam, P. K. Environ. Sci. Technol. 2004, 38, 4056-4063.

(89) Lange, F. T., Schmidt, C. K., Metzinger, M., Wenz, M., and Brauch, H.-J. Determination of perfluorinated carboxylates and sulfonates from aqueous samples by HPLC-ESI-MS-MS and their occurrence in surface waters in Germany (SEATAC Europe, 14th Annual Meeting, Abstract Book). 2004. Prague, Czech Republic, SEATAC Europe. 18-4-2004.

(90) Environmental Working Group. DuPont Hid Teflon Pollution For Decades. http://www.ewg.org/issues/pfcs/20021113/20021213.php . 13-12-2002.

(91) Hill, Peterson, Carper, Bee, and & Deitzler, Pllc. C-8 Class Action Litigation Against DuPont. http://www.hpcbd.com/dupont.htm . 17-2-0006.

(92) The Little Hocking Water Association, Inc. C-8 Sample Summaries as of July 2005. http://www.littlehockingwater.org/index.html . 17-2-2006.

(93) City of Lake Elmo. Lake Elmo newsletter - special water issue. http://www.lakeelmo.org/d/2213/Water_Special_Issue.pdf . 17-2-0006.

(94) City of Oakdale. City of Oakdale, drinking water information. http://www.ci.oakdale.mn.us/Water.htm . 17-2-0006.

(95) 3M. Report on Drinking Water Near 3M Plants. http://solutions.3m.com/wps/portal/3M/en_US/PFOS/PFOA/Information/Drinking-Water/ . 17-2-0006.

(96) Commission of the European Communities. Proposal for a directive of the European Parliament and the Council relating to restrictions on the marketing and use of perfluorooctane sulfonates (amendment of Council Directive 76/769/EEC). 5-12-2005.

Appendix

Perfluoroalkylcarboxylates and related compounds

APFO	Ammonium perfluorooctanoate
APFN	Ammonium perfluorononanoate
PFCA	Perfluoroalkylcarboxylate (anion of perfluoroalkylcarboxilic acid; including different homologues and salts as well as the free acids)
PFPA	Perfluoropentanoate
PFHxA	Perfluorohexanoate
PFOA	Perfluorooctanoate
PFNA	Perfluorononanoate
PFDA	Perfluorodecanoate
PFUnA	Perfluoroundecanoate
PFDoA	Perfluorododecanoate
PFTA	Perfluorotetradecanoate

Perfluoralklysulfonates and related compounds

PFAS	Perfluoroalkylsulfonate (summarizing all derivatives, which may be degraded to PFOS or its homologues)
PFOSH	Perfluorooctanesulfonic acid
PFOSS	Perfluorooctanesulfonic acid salts
POSF	Perfluorooctanesulfonyl fluoride
PFHxS	Perfluorohexanesulfonate
PFOS	Perfluorooctanesulfonate
PFDS	Perfluorodecanesulfonate
FOSA	N-Alkylperfluorooctanesulfonamide
FOSE	N-Alkylperfluorooctanesulfonamidoethanol
N-MeFOSA	N-Methylperfluorooctanesulfonamide
N-EtFOSA	N-Ethylperfluorooctanesulfonamide
N-MeFOSE	N-Methylperfluorooctanesulfonamidoethanol
N-EtFOSE	N-Ethylperfluorooctanesulfonamidoethanol
N-MeFOSAA	2-(N-Methylperfluorooctanesulfonamido)acetic acid
N-EtFOSAA	2-(N-Ethylperfluorooctanesulfonamido)acetic acid

Miscellaneous

FTO	Fluorotelomer olefin
FTOH	Fluorotelomer alcohol
PFC	Perfluorochemical

Colofon

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