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Environmental fate and effects of poly- and perfluoroalkyl substances (PFAS)

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Environmental fate and effects of poly- and perfluoroalkyl substances (PFAS)

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ABSTRACT

Aqueous Film Forming Foam (AFFF) and Fluoroprotein (FP)/ Film Forming Fluoroprotein Foam (FFFP) foam have been used since the 1960s and 1970s, respectively, for the suppression of class B (flammable liquid) fires at airports, refineries and other major petroleum facilities. In recent years, however, the use of these has been challenged due to concern that certain poly and perfluoroalkyl substances (PFAS) used in their formulation exhibit PBT characteristics (Persistent, Bioaccumulative and Toxic). While alternative PFAS-free foams are now commercially available, concerns have been raised that these may be less effective for fighting large-scale flammable liquid fires and that other issues such as shelf life, compatibility with conventional application equipment and suitability of different materials for storage have not been fully evaluated.

It is important that users of class B fire- fighting foams understand and manage both environmental and fire safety aspects of foam use. An assessment of site foam stocks is recommended to ensure that any legacy stocks containing >0.001wt% PFOS (banned for use in the EU since June 2011) are set aside for safe disposal by high temperature incineration. A similar assessment should be completed for foam stocks that may be brought to site from third parties in the event of an emergency. At locations where fluorochemical- based foams have been used for fire- fighting or fire-fighting training, users should consider how to manage the potential issues.

Fire- fighting foams designated “C6” by manufacturers are formulated using PFAS that cannot degrade to form PFOS or PFOA and so these seem of less concern from an environmental standpoint. It should be noted, however, that given the range of compounds present there is still uncertainty about their properties. In addition, low environmental concentration limits have been set for short chain PFAS (i.e. <C6 PFSA; <C7 PFCA) in many EU countries due to their persistence. Where possible, therefore, water containing PFAS- based fire- fighting foam residues should be captured for treatment and not discharged to the environment.

This report, which is a review of published literature on the environmental fate and effects of PFAS, has been produced to help Concawe members understand and manage environmental and human health risks associated with current and legacy formulations of PFAS- based class B fire- fighting foams. It describes the main types of PFAS, their use, fate and transport properties, toxicity data, regulation, and gives an overview of chemical analysis and remedial techniques.

The report has been reviewed by members of the Concawe Special Taskforce on Soil and Groundwater, and the Emerging Contaminant Working Group of the Network for Industrially Contaminated Land in Europe (NICOLE).

KEYWORDS

PFOS, PFOA, PFAS, perfluorooctane sulfonate, perfluorooctanoic acid, poly- and perfluoroalkyl substances, toxicity, bioaccumulation, environmental quality standard, environmental fate, regulation, chemical analyses, remediation

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SUMMARY

Background
Poly and perfluorinated substances (PFAS) are used in a wide range of industrial applications and commercial products due to their unique surface tension/levelling properties. These include textile stain guards, grease-proof paper, fluoropolymer manufacture, coatings, and aqueous film-forming foams. Relevant to the refining industry is the use of PFAS in class B (flammable liquid) fire-fighting foams, including Aqueous Film Forming Foam (AFFF), Fluoroprotein (FP) and Film Forming Fluoroprotein Foam (FFFP). PFAS are used in fire foam products because of their ability to wet the surface of liquid hydrocarbon, resulting in a much higher foam spreading rate than is possible using only hydrocarbon-based surfactants. At sites where fire-fighting foams have been used, PFAS source zones may include fire-fighting training areas, areas where large fires have occurred historically, foam storage and dispensing locations and locations where AFFF has been repeatedly used for flammable vapour suppression during 'hot work'.

Regulation
Concern around the environmental effects of PFAS use began in the late 1990s when it was realised that, due to their resistance to biodegradation, perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), two of the most abundant PFAS, were ubiquitous in various biological and environmental matrices, and could biomagnify. Simultaneously, it became clear that they could have effects on human health and the (aquatic) environment. The degree of biomagnification is proportional to perfluorocarbon chain length and so regulation to restrict the manufacture and use of PFAS substances has focussed on PFAS containing more than 6 fully fluorinated carbon atoms

In 2009, PFOS was added to Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs), meaning that measures must be taken to restrict its production and use. With global restrictions now in place for PFOS, further regulation is proposed in Europe and elsewhere to restrict the manufacture and use of any PFAS substance that contains a C7 or C8 perfluorocarbon moiety in its molecular structure. The use of legacy firefighting- foam products containing >0.001wt% PFOS has been banned in the EU since 27th June 2011.

In 2013, PFOS and its derivatives were included in the Directive on "Environmental Quality Standards" (EQSD). The EU annual average environmental quality standard (AA-EQS) for PFOS in surface freshwater is set at a very low criterion of 0,00065 µg/l, based on the potential for secondary poisoning in humans due to fish consumption. The AA-EQS of 0,00065 µg/l is derived from starting points that are considered by many as very conservative, and is lower than background levels typically recorded in surface waters. It is also lower than the limit of quantitation (LOQ) typically achieved by commercial laboratories. The date set for EU-wide compliance with the AA-EQS is 22nd December 2027, with member states required to submit to the Commission a supplementary monitoring programme and a preliminary programme of measures to achieve compliance by 22nd December 2018.

Provisional drinking water standards developed by EU member states are generally around 0.1 to 0.5 µg/l PFOS, which is 3 orders of magnitude higher than the AA-EQS. In those countries where target values for groundwater have been derived these are within a similar range. Environmental standards may also encompass a range of other both short and long chain poly- and perfluorinated compounds with limits set both for individual substances and also the total PFAS concentration.

Toxicity

Available data on PFAS toxicity is dominated by PFOS, PFOA and also perfluorohexane sulfonate (PFHxS) due to the widespread detection of these compounds in humans and the environment, and concern that these could biomagnify to a level whereby humans consuming fish may be adversely affected. Much less data is available on the toxicology of other PFAS, and this is often inconsistent and fragmentary. For the less investigated polyfluorinated chemicals, toxicology is often estimated based on structure- activity relationships, or structural homologues.

Human exposure to PFAS is mainly by ingestion of contaminated food or water. These compounds are not metabolised, bind to proteins (not to fats) and are mainly detected in blood, liver and kidneys. Elimination of PFOS, PFHxS and PFOA from the human body takes some years, whereas elimination of shorter chain PFAS is in the range of days. The half-life of PFOS and PFOA in rodents is in the range of months which differs significantly from humans and can cause extrapolation issues in tests. There is significant data available on the impact of (sub)chronic PFOS and PFOA exposure on reproductive and/or developmental and other types of effects in both humans and animals. However, the results from epidemiological studies are not always consistent.

Animal studies show mainly effects from PFOS and PFOA on the liver, the gastrointestinal tract and on thyroid hormone levels. In general, PFOS is more toxic compared to PFOA. Carcinogenic effects of PFOS and PFOA have also been studied (human and animal studies, no focus on other PFAS). Several authorities, including ATSDR, U.S. EPA and IARC do not classify PFOS and PFOA as “proven carcinogens”, but instead as “suggestive carcinogens” or “possibly carcinogenic to humans” because of existing uncertainties. PFOS has been categorised as moderately acute and slightly chronically toxic to aquatic organisms. The MAC EQS (Maximum Allowable Concentration Environmental Quality Standard) derived by the European Commission for European freshwater and saltwater are based on the lowest NOEC reported (No Observed Effect Concentration of < 2,3 µg/l for Chironomus tentans) to protect the most sensitive species.

Environmental fate and effects

Emissions of PFAS to the environment include stable perfluoroalkyl sulphonic and carboxylic acids (PFSAs and PFCAs) and also less stable precursor compounds that may undergo abiotic or biotic transformation to PFSAs and PFCAs. While many studies have been published on environmental concentrations of PFSAs and PFCAs, much less data is available for precursor substances due to the difficulty inherent in their identification and analysis. Precursors are likely to have different physical and chemical properties to their breakdown products, leading to differences in their transport behaviour. For example, cationic or zwitterionic precursors may bind to clay minerals through ion exchange.

PFSAs (e.g. PFOS) and PFCAs (e.g. PFOA)) are widely distributed in the global environment due to their high solubility in water, low/moderate sorption to soils and sediments and resistance to biological and chemical degradation. Monitoring data from across the EU show the widespread occurrence of PFSAs and PFCAs in surface water, with the very low EQS for PFOS in freshwater (0,00065 ug/l) often exceeded.

Little or no breakdown of PFOS and PFOA by photolysis is anticipated under environmental conditions.

Analysis
While a range of standard methods are available for the analysis of PFSAs and PFCAs, the quantitative analysis of other PFAS substances is often difficult due to a lack of appropriate reference materials. To address this difficulty, analytical techniques have been developed whereby PFAS are quantitatively oxidized to fluoride (adsorbable organic fluorinated compounds (AOF) method), or a mixture of PFSAs and PFCAs (total oxidisable precursor (TOP) method). The TOP method is most sensitive, with a detection limit around 0,002 µg/l range, vs 1 µg/l for AOF. Whereas the regulatory limits applicable for PFOS in groundwater (typically 0.02 to 1 µg/L) can sufficiently and reliably be measured and are above background levels, the AA-EQS of 0,00065 µg/l is so low that background levels are higher in many cases, and the AA-EQS is beyond the operational range of most commercial laboratories.

Specific precautions have to be taken in the sampling of environmental media since PFAS adsorb strongly to glass. Teflon-containing materials can lead to increased blank values if AOF is analysed, and may also interfere with the analysis by adsorbing PFAS. Currently the most appropriate material for sampling seems to be polyethylene or polypropylene.

Remediation
The remedial options available to address PFAS contamination are limited by the unique physical and chemical properties of these compounds. Many remediation methods utilized to address hydrocarbon contamination, such as air stripping, sparging, soil vapour extraction and bioremediation, are ineffective due to the low volatility of these compounds and their resistance to microbial degradation. Technologies currently used for the remediation of PFAS in soil and groundwater include excavation to landfill for soil (where authorised), and abstraction combined with activated carbon or resin treatment for groundwater. Groundwater extraction volumes may be high if remediation is required to very low environmental quality standards (e.g. for PFOS). Current best practice disposal routes for spent PFAS adsorption media are high temperature incineration at >1000°C, or regeneration at a specialist facility. Possible alternative remedial techniques include soil washing, soil solidification and the use of in-situ permeable reactive barriers or funnel and gate systems.

Emerging water treatment technologies for PFAS, such as photolysis/ photocatalysis, reductive decomposition, advanced oxidation and sonolysis, require high energy input per unit water volume and long residence times. Careful monitoring of treatment performance is also required to ensure complete breakdown of the various PFAS substances that may be present. Consequently, these technologies are unlikely to be feasible for high flowrate, low concentration applications.

Implications for users of class B fire fighting foams
It is important that users of class B fire- fighting foams understand and manage both environmental and fire safety aspects of foam use. An assessment of site foam stocks is recommended to ensure that any legacy stocks containing >0.001wt% PFOS (banned for use in the EU since June 2011) are set aside for safe disposal by high temperature incineration. A similar assessment should be completed for foam stocks that may be brought to site from third parties in the event of an emergency. At locations where fluorochemical- based foams have been used for fire- fighting or fire-fighting training, users should consider how to manage the potential issues.

In response to global regulatory initiatives to limit the production and use of long-chain PFAS substances, class B fire- fighting foam suppliers have developed foams that are completely free of fluorochemicals, and also “C6” foams based on

fluorotelomers containing 6 or fewer fully- fluorinated carbon atoms. C6 foams cannot degrade to PFOS or PFOA and so they seem of less concern from an environmental standpoint. It should be noted, however, that given the range of compounds present there is still uncertainty about their properties. In addition, low environmental concentration limits have been set for short- chain PFAS (i.e. <C6 PFSA; <C7 PFCA) in many EU countries due to their persistence. Where possible, therefore, water containing PFAS- based fire- fighting foam residues should be captured for treatment and not discharged to the environment.

While many sites now use fluorine- free foams for fire- fighting training and other non-critical application, there is still an ongoing debate with regard to their performance on larger in-depth fires (e.g. storage tank fires). It is therefore important that sites give careful consideration to both safety and environmental risk factors, and consult with fire safety experts, when determining the optimal foam type for any given application.

1. INTRODUCTION

Poly- and perfluoroalkyl substances (PFAS) have been used globally since the 1960's for a wide range of industrial, commercial and domestic applications due to their unique surface-active properties. PFAS have the ability to repel both oil and water, which has led to their use in stain guard products for carpets and soft furnishings. They are also used as specialist surfactants for industrial processing and fluoropolymer production. The ability of PFAS to form an aqueous film that will wet and flow across the surface of liquid hydrocarbon has led to their application in high performance fire-fighting foams used at airports, refineries, bulk storage terminals and other facilities handling large volumes of flammable liquid hydrocarbons. Their unique properties make it difficult to find equally effective replacement compounds for some applications, including in fire-fighting foams.

The perfluoroalkyl moiety within a PFAS molecule is highly resistant to abiotic and biotic degradation, which has led to the accumulation of PFAS breakdown products (perfluoroalkyl sulphonic and carboxylic acids) in the environment. Some of these substances (principally perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA)) have been identified as PBT, being persistent in the environment and having bioaccumulative and toxic properties in humans and wildlife. Therefore PFAS have emerged as a group of Constituents of Potential Concern (COPC), with an increasing regulatory focus regarding use, clean-up and protection of human health and the environment.

This technical report has been produced to help Concawe members understand and manage potential environmental risks associated with the presence of PFAS in current and legacy fire-fighting foam formulations. The information contained may be useful in the design of site investigations, the development of conceptual site models and in the evaluation of potential risks and risk-management options. The report is structured as follows:

- **Section 2**: PFAS types, production methods and use;
- **Section 3**: Physical-chemical properties, and fate and transport behaviour;
- **Section 4**: Toxicity and potential risks to human health, ecology and the wider environment;
- **Section 5**: Regulatory values and environmental quality standards;
- **Section 6**: Current condition of European waters;
- **Section 7**: Chemical analysis methods;
- **Section 8**: Remediation options;
- **Section 9**: Conclusions.

2. PFAS TYPES, PRODUCTION AND USE

Poly- and perfluorinated alkyl substances comprise a large group of compounds (> 6,000) consisting of a hydrophobic alkyl chain of varying length, typically 2 to 16 carbon atoms, which is completely fluorinated (perfluorinated alkyl substances) or partly fluorinated with at least two fully fluorinated carbons (polyfluorinated alkyl substances). In Buck et al. (2011) PFAS are defined as compounds containing the perfluoroalkyl moiety C_nF_{2n+1}-, or more specifically:

- Perfluoroalkyl substances: aliphatic substances for which all of the H atoms attached to C atoms in the non-fluorinated substance from which they are notionally derived have been replaced by F atoms, except those H atoms whose substitution would modify the nature of any functional groups present (e.g. hydroxyl -OH).
- Polyfluoroalkyl substances: aliphatic substances for which all H atoms attached to at least one (but not all) C atoms have been replaced by F atoms, in such a manner that they contain the perfluoroalkyl moiety C_nF_{2n+1}-.

The above definition encompasses the group of fluorinated compounds that are of concern to global regulators. In particular, the definition excludes compounds containing "scattered" multiple F atoms (such as in $CH_2FCHFCHFCH_2OH$). The widely used term "PFCs" (perfluorinated compounds) is not adopted since it is non-specific and encompasses perfluorinated chemicals in general, e.g. the greenhouse gas (CF_4).

PFAS addressed by this review include perfluorinated carboxylic acids (PFCAs), perfluorinated sulfonic acids (PFSAs) and perfluorinated phosphonic acids (PFPAs). Polyfluorinated compounds include fluorotelomer alcohols (FTOHs), fluorotelomer sulfonic acids (FTSs), polyfluorinated alkyl phosphates (PAPs), perfluorooctane sulfonamine (PFOSA) and their derivatives.

PFAS production prior to 2001 was dominated by the 3M electrochemical fluorination process, which yielded 30-45% perfluorooctane sulfonylfluoride (POSF) as the main product and a range of other PFCAs and PFSAs. Since 2001, when production of PFAS by electrochemical fluorination ceased due to environmental concerns around PFOS, the main route for PFAS synthesis has been fluoro-telomerisation, which produces no PFOS or PFOS precursors.

Because of their unique surface characteristics (surfactant properties) and resistance to degradation in the presence of heat or acids perfluorinated alkyl substances have been used extensively in a variety of products and industries since the 1960s. Relevant to the refining industry is the use of PFAS in class B fire-fighting foams, including Aqueous Film Forming Foam (AFFF), Fluoroprotein (FP) and Film Forming Fluoroprotein Foam (FFFP).

This section provides an overview of the different types of PFAS and the production and use of what are viewed as the most important PFAS.

2.1. TYPES OF PFAS

The family of PFAS comprises 42 families and subfamilies and several hundred compounds (Buck et al., 2011). The focus of this report is on the families of compounds described in the following sections.

2.1.1. Perfluoroalkyl sulfonic acids

Perfluorooctane sulfonate (PFOS) is a perfluoroalkyl sulfonic acid (PFSA), and is the most prominent PFSA (DEPA, 2013). It is the most commonly encountered perfluorinated compound in the environment and tissues of wildlife (Giesy, 2010). There are multiple other perfluorinated sulfonic acids with carbon chain lengths generally from C2 to C16.

PFOS consists of a chain of 8 fully fluorinated carbon atoms with a sulfonate group as the functional group on the terminal carbon. The structure of PFOS is given in **Figure 2.1**.

Figure 2.1 Chemical structure of PFOS

In reality, PFOS is a mixture of linear (70%) and branched (30%) isomers[1] of PFOS, depending on the production process. PFSAs bearing a shorter perfluoroalkyl chain than PFOS can also be by-products of the production of PFOS. Furthermore, they are being introduced as alternatives for PFOS (Hori, 2006). For example, PFBS (perfluorobutane sulfonate; $C_4F_9SO_3$-salt) is one important replacement substance for PFOS (Herzke, 2007).

PFOS is used as either the undissociated sulfonic acid or one of its sulfonate salts. The following salts are commonly known for PFOS:

- Ammonium salt,
- Potassium salt; and
- Lithium salt.

When dissolved in water, under most conditions, PFOS and its salts will dissociate to form the sulfonate anion.

2.1.2. Perfluoroalkyl carboxylic acids

Perfluoroalkyl carboxylic acids (PFCAs) are compounds that can contain a perfluorinated carbon chain of between 2 and 16 carbons in length with a terminal carboxylic acid functional group. Perfluorooctanoic acid (PFOA) is the most commonly encountered PFCA. PFCAs are widely used as products or raw materials for surfactants or surface treatment agents. PFOA is used as either the undissociated carboxylic acid or one of its carboxylate salts with ammonium perfluorooctanoate (APFO) as an example PFOA salt. PFOA has been widely used as an emulsion polymerization aid in the production of Teflon (Lindstrom, 2011).

PFOA consists of a chain of 7 perfluorinated carbon atoms, and a carboxyl head group. The structure of PFOA is given in **Figure 2.2**.

[1] Isomers: compounds with the same formula but different molecular structures.

Figure 2.2 Chemical structure of PFOA

2.1.3. Potential PFSA and PFCA precursor compounds

Emissions of PFAS to the environment include stable PFSAs and PFCAs and also less stable precursor compounds that may undergo abiotic or biotic transformation to PFSAs and PFCAs. From a regulatory standpoint, precursors of long- chain PFSAs and PFCAs are of greatest concern. OECD (2013) define long chain PFSAs and PFCAs as:

- PFCAs with 7 and more perfluoroalkyl carbons, e.g. PFOA and PFNA
- PFSAs with 6 and more perfluoroalkyl carbons, e.g. PFHxS and PFOS

In the OECD report the following classes of PFCA and PFSA precursors are identified:

- Substances that have the potential to degrade to long-chain PFCAs or PFSAs, i.e. precursors such as PASF- and fluorotelomer-based compounds.
- Side-chain fluorinated polymers: fluorinated polymers consisting of variable compositions of non-fluorinated carbon backbones with polyfluoroalkyl (and possibly perfluoroalkyl) side chains. The fluorinated side-chains, including PASF- and fluorotelomer-based derivatives, are potential precursors of PFCAs.

PFSA and PFCA precursor compounds are reported (Backe et al., 2013; Martin et al., 2006 and Toms et al., 2009) to include:

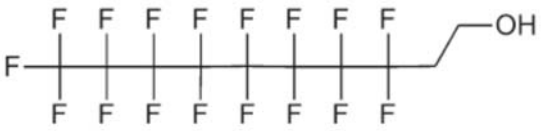
- fluorotelomers (polyfluorinated compounds);
- perfluoro sulfonamido carboxylates;
- perfluoro betaines;
- perfluoro sulphonamides;
- perfluoro sulfonamidoethanol;
- perfluoro thioamido amino carboxylates;
- perfluoro sulfonamido amines;
- perfluoro alkyl amido betaines;
- perfluoro sulfonamido amine oxides;
- perfluoro thioamido sulfonates;
- perfluoro thiohydroxyl ammonium;
- perfluoro sulfonamide ketones, aldehydes and ethers;
- perfluoro sulfonamide (acetic) acids.

The commercial analyses commonly used to quantify PFAS (e.g. US EPA method 537) only evaluate PFCAs and PFSAs and do not detect the range of PFCA and PFSA precursors mentioned above. Research into the presence of precursors in urban runoff water in the San Francisco Bay area has shown that PFSA and PFCA represent less than 25% of the total amount of PFAS present (Houtz, 2012). Therefore, more comprehensive analytical methodologies are required.

2.1.3.1. Fluorotelomers

Fluorotelomers have an ethyl (CH_2-CH_2) group between the fully fluorinated carbon chain and the functional group, and are therefore polyfluorinated molecules. In **Figure 2.3** an example is given of the fluorotelomer alcohol 8:2 FTOH, which has 8 fully fluorinated carbon atoms, an ethyl group, and an alcohol functional group. 8:2 FTOH is an example of a PFCA precursor: a number of studies have shown that it can transform to PFOA in the environment (Parsons et al., 2008).

Figure 2.3: Fluorotelomer alcohol 8:2 FTOH



Another widely- used fluorotelomer is the compound 1H-1H-2H-2H perfluorooctane sulfonate (also referred to as 6:2 FTS since it has 6 fully fluorinated carbon atoms, an ethyl group and a sulphonate functional group). Fluorotelomer sulfonates are used in place of PFOS for various applications, including class B fire- fighting foams and industrial surfactants.

Fluorotelomers are produced with a variety of different functional groups including alcohols, sulphonamides, sulfonamidoethylacrylates and methacrylates, and sulfonamidoacetic acids. The majority of the fluorotelomers are used for manufacturing various fluorotelomer-based products (e.g. building blocks for polymers, surfactants and side-chain fluorinated polymers). There is concern that many of these could eventually transform to PFSAs and PFCAs in the environment (Lindstrom et al., 2011).

2.1.3.2. Fluoropolymers

Fluorinated polymers may or may not be PFAS depending on whether they contain perfluoroalkyl moieties. The fluoropolymer polytetrafluoroethylene (Teflon, PTFE), is a PFAS and is used as a non-stick coating for cookware. It is virtually inert at normal temperatures, it starts to degrade above 260°C. Teflon resins contain part per million concentrations of hexafluoroacetone (HFA). PFOA is an essential processing aid in the formulation of these polymers. The manufacturing of non-stick cookware includes a sintering step at high temperature, which theoretically volatilizes residual PFOA (Herzke et al., 2007).

In PTFE-coated textiles (jackets, table-cloth etc.), primarily fluorotelomer alcohols and fluorotelomer carboxylic acids have been detected in relatively large quantities (up to 11 mg/m^2 fluorotelomers and 0,4 mg/m^2 PFCA, Berger and Herzke, 2006). During thermolysis of PTFE polymers trifluoroacetate and chlorodifluoroacetate can be produced (Herzke et al., 2007).

2.2. PRODUCTION PROCESSES

Historically, two processes have been used for the production of PFAS: electrochemical fluorination (ECF) and telomerization (TM). These synthesis routes result in different (isomeric) purities. In general the ECF process yields even- and odd-numbered, branched and linear chains of perfluoroalkyl compounds, whereas TM

produces only even-numbered, linear chains. Most production is nowadays undertaken via the telomerisation process (Buck et al., 2011).

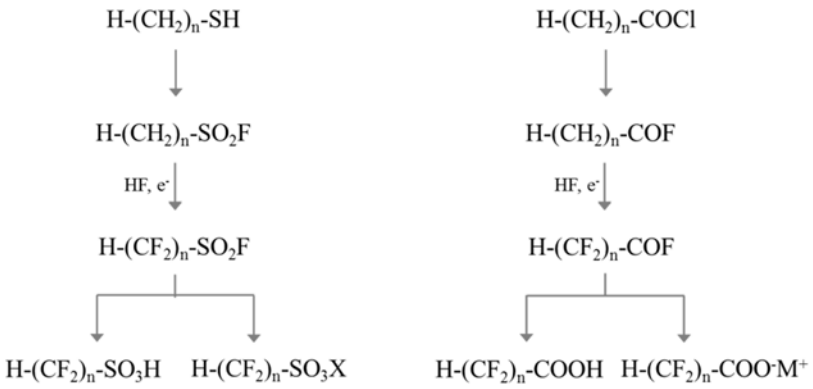
2.2.1. Electrochemical Fluorination

The source compound for manufacture of PFOS-related chemicals is perfluorooctane sulfonylfluoride (POSF). POSF is manufactured through a process known as electro-chemical fluorination (**Figure 2.4**), in which an electric current is passed through a solution of anhydrous hydrogen fluoride (HF) and an organic feedstock of octane sulfonyl fluoride. The ECF process replaces the hydrogen within the carbon-hydrogen bonds of the organic feedstock with fluorine. Although for production of PFOS-related substances the starting material is linear octane sulfonyl fluoride, the product will contain some branched C8 compounds since the fluorination process is expected to lead to partial fragmentation and rejoining of the chain (EFSA, 2008).

The ECF process yields between 30% – 45% linear-chained POSF. The output of the ECF process thus is a mixture of isomers and homologues including shorter and longer linear-chained homologues; branched perfluoroalkyl fluorides of various chain lengths; linear-chained, branched, and cyclic perfluoroalkanes and ethers; and other by-products (OECD, 2002).

PFOA can also be produced through ECF using octanoyl fluoride as the feedstock with HF.

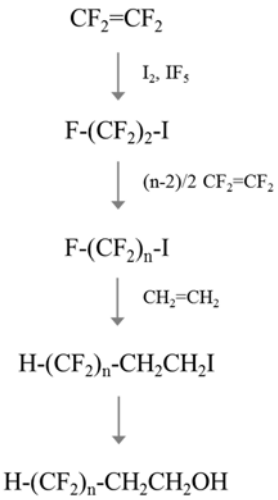
Figure 2.4: Production routes of PFOS and PFOA via electrochemical fluorination (Buck et al., 2011)



2.2.2. Fluoro Telomerization

The fluoro telomerization process (**Figure 2.5**) used by the industry leads to a successive addition of an ethyl group to the fluoroalkyl chain. It involves the reaction of perfluoroethylene (tetrafluorethene, CF_2=CF_2) and perfluoroethyl iodide (trifluoriodoethene, CF_3-CF_2I) to produce linear-chained perfluorinated iodides with chain lengths that are generally even numbered. These perfluorinated iodides are then used as a feedstock to produce linear-chained perfluorinated carboxylic acids, fluorotelomer alcohols, and fluorotelomer olefins (Lindstrom, 2011). Through this process no PFOS or PFOS precursors are produced.

Figure 2.5: Production route of fluorotelomers via telomerisation (Buck et al., 2011)



2.3. USE

2.3.1. General Use

PFAS are used in a variety of products and production processes. From 1966 to the 1990s, the production and use grew due to their unique chemical stability and their surface tension/levelling properties. The annual production rate of PFOS increased significantly from 500 tonnes/year in the 1970's to almost 5000 tonnes/year in 2000 (Carloni, 2009). The use of PFOS included inks, varnishes, waxes, fire-fighting foams, metal plating and cleaning, coating formulations, lubricants, water and oil repellents for leather, paper and textiles (Paul et al., 2009). An overview of the uses of a selection of the different PFAS is given in **Appendix 1**.

In 2000, the key global producer 3M started to phase out the production of PFOS. Between 2000 and 2003, the global production dropped sharply as a concequence of 3M's initiative. In this period the production of PFOS in China increased, but not to the same global production level as before the year 2000 (Paul et al., 2009; Carloni, 2009).

In May 2009, PFOS was added to Annex B of the Stockholm Convention. Since that date, the use of PFOS and related compounds has been restricted in signatory countries to the Convention, although it is still being used for certain applications in which PFOS cannot be replaced by other chemicals (more information is included in Section 5).

PFAS have been found at a wide range of sites including manufacturing sites and within landfills, but is also encountered at airports, military sites and other large industrial (e.g., petrochemical) facilities where fires have occurred and/or fire-fighting trainings have been carried out.

2.3.2. Fire-fighting foam use

PFAS-based class B fire- fighting foams have been used since the 1970s for vapour suppression, firefighting and fire-fighting training at airports, refineries, bulk storage terminals and other facilities handling large volumes of flammable liquid hydrocarbon. PFAS are used in fire foam products because of their ability to produce a foam that will wet the surface of liquid hydrocarbon, resulting in a much faster foam spreading rate than is possible using only hydrocarbon-based surfactants.

Class B fire-fighting foam types likely to include PFAS include Aqueous Film Forming Foam (AFFF), Fluoroprotein (FP) and Film Forming Fluoroprotein Foam (FFFP). Supplier safety data sheets *may* list PFAS as "fluoroalkyl surfactant", but the identity of the PFAS substances present is not usually provided (regarded as proprietary information).

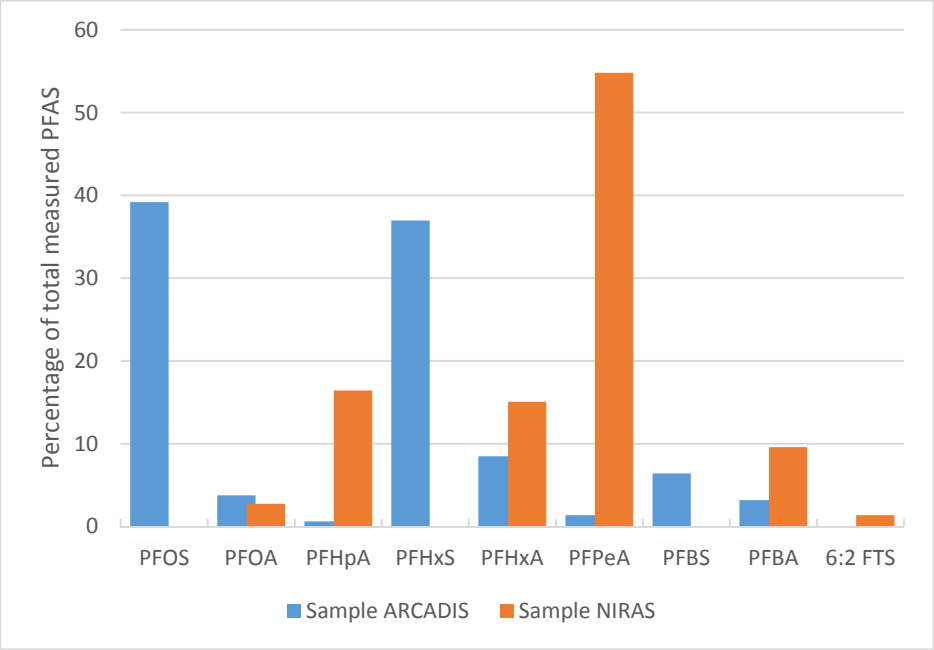
PFOS and its derivatives were used extensively in fire-fighting foam manufacture prior to 2001, when the production of PFOS was phased out in the USA due to environmental concerns. Since 2001 fire foams have been manufactured using fluorotelomer-based fluorosurfactants (Seow, 2013). However due to the long shelf-life of foam concentrates, it is likely that the use of PFOS-based foam products manufactured prior to 2001 continued after cessation of production: an EU ban on the use of foams containing PFOS as a primary component (>0,001 wt%) only came into force in June 2011. In countries not complying with the Stockholm convention, PFOS might still be used, and stockpiles of AFFF containing PFOS might still be present.

At sites where fire-fighting foams have been used residual PFAS may be present in soil and groundwater below fire-fighting training areas, areas where large fires have occurred, foam storage and dispensing locations and locations where PFAS-based foam has been repeatedly used for flammable vapour suppression during 'hot work'. The Danish Environmental Protection Agency (DEPA) investigated the relationship between groundwater contamination and point sources of PFAS (DEPA, 2014) at both civil and military airports. The authors concluded that fire training is a high potential source for PFAS contamination of groundwater. During a further study conducted by NIRAS for the Danish Defence (military airfields), contaminated groundwater at a fire-fighting training area was analysed (Falkenberg et al., 2015). In this sample, PFPeA, PFHxA and PFHpA were the dominant PFAS in the groundwater, caused by contamination from the AFFF. PFOS was not observed in the groundwater.

ARCADIS analysed groundwater samples known to be contaminated with AFFF in a confidential study (the Netherlands, 2011). Based on this study, PFOS, PFHxS and PFHxA represented 82% of the total PFAS concentration detected in groundwater associated with contamination by this type of AFFF.

Results from both studies are illustrated in **Figure 2.6** and clearly show very different PFAS profiles in the groundwater, possibly reflecting the use of different fire- foam types.

Figure 2.6: PFAS concentrations in groundwater at two AFFF contaminated sites



These are just two examples of fire-fighting foam related PFAS impacts in groundwater. They are not to be assumed representative of typical impacts. A great deal of variability in PFAS mixtures used in fire-fighting foams and encountered in groundwater has been reported.

Backe et al. (2013) developed a new method to quantify an extensive range of PFAS in groundwater and fire-fighting foam. The authors concluded that "the profiles of PFAS in groundwater differ from those found in AFFF formulations, which potentially indicates environmental transformation of PFAS".

In another study, Barzen-Hanson et al. (2015) analysed 5 different 3M AFFFs manufactured in the period 1989 – 2001, with focus on ultra-short PFSAs (C2 PFSA: PFEtS, perfluoroethane sulfonate, and C3 PFSA: PFPrS, perfluoropropane sulfonate). The five types of AFFF were dominated by the following PFSAs: PFOS, PFHxS and PFBS. However, relatively high concentrations of PFPrS (120 – 270 mg/l) and PFEtS (7 – 13 mg/l) were detected, representing 3,5% and 0,2% of the total PFSA concentration in AFFF. The relative ratio of these compounds in groundwater varies between sites and is different from the ratio detected in AFFF.

The relationship between fire- fighting foam type and potential impacts to groundwater quality can be summarized as follows:

- PFAS-based fire-fighting foam formulations have changed over time. Before 2001, the main PFAS compound was PFOS. After 2001, this changed to 8:2 FTS, 6:2 FTS and other fluorotelomer based PFAS. Recent investigations show also a portion of ultra-short PFSA (C2 and C3).
- Studies to date do not indicate a strong link between the ratio of PFAS in fire-fighting foam products and the ratio of PFAS in groundwater where they were used. Reasons for this could include: (1) Groundwater PFAS ratios being

dominated by a foam type other than the one tested, in the event that foam composition changed over time or different foams were used (2) Groundwater PFAS ratios changing due to differential transport during groundwater migration (3) Groundwater PFAS ratios being dominated by the degradation of precursors, rather than the PFAS present in the foam products (4) Interactions of PFAS with co-contaminants (e.g. differential partitioning into NAPL).

Further information on PFAS transport in groundwater is provided in Section 3.2.2.

2.4. ENVIRONMENTAL CONCERNS

Although the use of PFOS is now restricted in many markets including the EU, PFOS can still be present in fire-fighting foam at levels up to 0,001 wt% (see Section 5.2.1).

PFOS is being replaced by alternatives, for example fluorotelomer derivatives based on mainly 6:2 FTS for fire-fighting (Seow, 2013) and smaller PFAS such as PFHxS and PFBS for their stain repelling properties (Stockholm Convention, 2014). Although these compounds are likely to be less toxic and have reduced bioaccumulative properties, concerns have raised about their transformation products becoming ubiquitously present in the global environment and about the lack of alternatives for PFAS (Scheringer, 2014). The unique PFAS properties make it difficult to find equally effective replacement compounds for some applications. Regarding fire-fighting foams specifically, there are concerns about finding the right balance between safe and effective fire-fighting and environmental protection.

Furthermore, although currently regulatory efforts are mainly focussed PFOS and PFOA, it is important to realize that several thousands of different PFAS are known to exist (Lindstrom, 2011). A few countries already regulate several additional PFAS (see Section 5.2). In addition proposed regulation specifically targeting fluorinated fire-fighting foam management may affect fire-fighting foam selection.

3. PROPERTIES, FATE AND BEHAVIOR

From the standpoint of environmental fate and effects, PFAS substances can be broadly divided into:

- Perfluoroalkyl sulphonic and carboxylic acids (PFSAs and PFCAs), for which environmental analysis is commercially available according to standardised test protocols. For these compounds a significant quantity of high-quality environmental fate data is available
- Other PFAS substances, including PFSA and PFCA precursors, for which very little environmental fate data is available due to the difficulties inherent in their analysis.

Perfluoroalkyl sulphonic and carboxylic acids (PFSAs and PFCAs) are widely distributed in the global environment due to their high solubility in water, low/moderate sorption to soils and sediments and resistance to biological and chemical degradation. While many studies have been published on environmental concentrations of PFSAs and PFCAs, little data is available for precursor substances due to the difficulty inherent in their identification and analysis.

Over the pH range normally found in soil, groundwater and surface waters (pH 5-9) PFSAs and PFCAs are normally present as anions, and this reduces sorption by soils and sediments, which usually carry a net negative charge. Their retardation during transport in groundwater increases with perfluorocarbon chain length and the fraction of organic carbon in the soil, with PFSAs binding more strongly than PFCAs of the same carbon number. The presence of co-contaminants has a variable impact on the mobility of PFAS, depending on PFAS chain length, PFAS concentrations and the characteristics of the co-contaminant. The environmental mobility of other PFAS substances is not well understood due to the lack of analytical data. Precursors are likely to have different physical and chemical properties to their breakdown products, leading to differences in their transport behaviour. For example, cationic or zwitterionic precursors may bind to clay minerals through ion exchange.

PFOS and PFOA have not been demonstrated to undergo significant biotransformation under normal environmental conditions. Little or no breakdown of PFOS and PFOA by photolysis is anticipated under environmental conditions.

More information is presented in the sections below.

3.1. PHYSICOCHEMICAL PROPERTIES

Physicochemical properties for a number of PFAS, derived from scientific literature (Wang Z. et al., 2011), are summarized in **Appendix 2**, including:

- PFAS name and acronym;
- CAS registry number;
- Molecular formula;
- Molecular weight;
- Density;
- Solubility in water;
- Melting point;
- Boiling point;
- Vapour pressure;

- Henry's coefficient (i.e., air-water partition coefficient);
- Octanol-water partition coefficient (Kow);
- Organic carbon-water partition coefficient (Koc);
- Soil distribution coefficient (Kd) ;
- Dissociation constant (pKa).

As shown in **Appendix 2**, over 50 individual PFAS were identified for this review and fall into the following categories:

- Perfluorinated carboxylic acids; e.g. PFBA, PFPeA, PFHxA, PFHpA, and PFOA;
- Perfluorinated sulfonic acids; e.g. PFBS, PFPeS, PFHxS, PFHpS, and PFOS;
- Perfluorinated phosphonic acids (PFPAs);
- Polyfluorinated compounds and/or precursors to PFSAs and PFCAs, fluorotelomer alcohols (FTOHs), fluorotelomer sulfonic acids (FTSs), polyfluorinated alkyl phosphates (PAPs), perfluorooctane sulfonamine (PFOSA) and derivatives.

While PFOS and PFOA are comparatively well studied compared to other PFAS, many of which have not been studied at all, the available data is still relatively scarce. It should be noted that reported physicochemical properties vary in the literature. For example, 6:2 FTS exhibits a significant correlation between pH and solubility: the further the pH falls below pH 7 the greater the solubility decreases. This correlation is not likely to be due to the different form of a salt (carboxylate) or free acid, since this compound is already completely dissociated with a pKa of less than 1,31.

Some of the parameters in **Appendix 2** are calculated parameters from literature. These parameters are based on the neutral form of the substances and not the conjugate base, which predominates for some PFAS at neutral pH (Wang Z. et al., 2011).

In addition, it is often observed that the physicochemical properties within a homologous PFAS series (i.e., the same terminal functional group with different CF_2 chain length) change non-linearly. The reason may be that with increasing chain length, the geometry of the molecules changes (Wang Z. et al., 2011). When a PFAS molecule contains up to eight fluorinated carbon atoms, the molecule remains in a linear conformation. When a PFAS molecule contains more than eight fluorinated carbon atoms, a helix can be formed. The resulting increase in electron density leads to changes in physicochemical properties.

Structure of PFAS

Fluorine has the highest electronegativity of all atoms, a high ionization potential, and very low polarizability due to the low deformability of the outer electron shell. The covalent carbon-fluorine bond is one of the strongest bonds in organic chemistry (450 kJ / mol) due to the effective overlap of the molecular orbitals involved in the bond. Fluorine-carbon bonds are very infrequently found in naturally occurring organic compounds, although some plants and microorganisms synthesize organofluorine compounds (Murphy et al., 2003). The dense packing of fluorine electrons can also act as "shield", protecting PFAS from external attacks and thus causing the high thermal, chemical, photolytic (UV-radiation) and biological stability of these materials. The energy required for reduction of fluorine ($F^- \rightarrow F + e^-$) is exceptionally high (E^0 =3,6 V).

The PFAS considered in this review generally consist of a hydrophobic, polyfluorinated or perfluorinated carbon chain and a hydrophilic functional consisting

of, for example, sulfonate or carboxylate or their salts. This amphiphilic (both hydrophobic and hydrophilic) characteristic of PFAS makes them ideal for use as surfactants. However, in contrast to conventional surfactants, the perfluorinated carbon chain also has a lipophobic characteristic which renders many PFAS coatings resistant not only to water, but also to oil, grease, other non-polar compounds and dirt particles. The surface activity of PFAS surfactants is higher than analogous hydrocarbon surfactants. This property is one of the reasons for the wide use of PFAS in industry. Both the length of the carbon chain and the configuration of the polar functional group can vary widely in different PFAS and results in a variety of different materials with different physicochemical properties. However, not all PFAS exhibit surfactant properties. For example, the hydrophilic influence of the hydroxyl group found on telomeric alcohols is too small to act as a surfactant.

PFAS surfactants have the ability, on the one hand, to group together at phase boundaries and on the other, to form micelles. Thus, in the environment, there can be accumulation of PFAS at the phase boundary between groundwater (hydrophilic) and soil air (hydrophobic).

3.2. FATE AND TRANSPORT

3.2.1. Fate

The following PFAS fate and transport characteristics are important:

Water Solubility
Solubility values for the PFAS listed in **Appendix 2** were derived from literature sources where available, either measured values or estimated based on molecular weight using standard environmental chemistry calculations (e.g. COSMOtherm).

As shown, solubility values for **PFCAs** (PFBA, PFPeA, PFHxA, PFHpA, and PFOA) vary between 4,2 g/l and fully miscible, and solubility values for **PFSAs** (PFBS, PFPeS, PFHxS, PFHpS, and PFOS) vary between 0,5 and 56,6 g/l. These relatively high solubility values in the gram per litre (g/l) range for the PFCAs and PFSAs are due to the carboxylate and sulfonate groups on these molecules, because these groups are hydrophilic. The solubility of PFCAs and PFSAs tends to decrease with molecular weight, which is due to the concomitant increase in the length of the perfluorinated alkyl chains which are hydrophobic.

In natural waters, the predominant species of PFCAs and PFSAs will be their anionic forms, which is due to the very low dissociation constants of these compounds (**Appendix 2**). At very low pH, PFCAs and PFSAs can exist in water in their fully protonated forms. However, most natural waters exhibit approximately neutral pH values and therefore it can be reasonably assumed that PFCAs and PFSAs exist as anions when dissolved in water.

The **fluorotelomer alcohols** (FTOHs) are very hydrophobic and are of relatively low solubility in water. For example, PFOA has a solubility of 3,4 to 9,5 g/l and perfluorethylethanol (FTOH 4:2) has a solubility of 0,98 g/l (**Appendix 2**). Also, the water solubility decreases with increasing length of the alkyl chain. As with hydrocarbon-based surfactants, it can be assumed that the solubility of PFAS is affected by the chemical composition of the groundwater, particularly if the groundwater contains divalent ions.

The solubility of the **precursors** is estimated to vary over many orders of magnitude, as shown in **Appendix 2**, due largely to the significant variance in molecular type, structure, and weight of the various precursors. One important finding from this review is that very little research has been published on the water solubility for most PFAS.

Dissociation

When an acid dissolves in water, dissociation is the process by which the electronegative atom and a hydrogen atom, which are ionically bonded, separate into a proton (H^+) and a negative ion. The extent of this dissociation in water is described by a chemical-specific dissociation constant (pKa). The pKa value is a pH value at which half of the acid molecules dissociate into ions. The smaller the pKa value is, the greater the extent of dissociation will occur at any pH.

Both PFOS and PFOA have negative pKa values, which means both of these PFAS function as strong acids and exist as dissociated anions in aqueous solutions under almost all natural conditions. The tendency to release a hydrogen atom (proton) is a typical characteristic of an acid. The two compounds, PFOS and PFOA, are thus to be regarded as strong acids. In the salts of PFCAs and PFSAs, the counter-ion (e.g. lithium) is also ionically associated with the carboxylate or sulfonate anion. In aquatic systems, these salts will dissociate into the positively charged cation and the negatively charged carboxylate or sulfonate ions.

Investigations at AFFF-impacted sites and other sites with PFAS concentrations in the range of µg/l up to mg/l did not show a decrease in the pH due to the presence of PFAS. As described above, the pKa for PFOS and PFOA is negative, but pH is a function of the H^+ concentration. PFOS and PFOA are normally not present at a very high concentration when tested in the environment (mg/l maximum) or are present as salts, which means the concentration of H^+ (protons) in water is not sufficient to effectively influence the pH.

FTOHs are not acids and do not dissociate when dissolved in water.

Physical State

At typical environmental temperatures and pressures, PFAS and their salts exist predominantly as solids. Only the short-chain FTOH 6:2 exists as a liquid. The melting and boiling points of all PFAS in this review are comparatively high. PFOA has a relatively low melting point (59-60°C) and boiling point (192°C). For PFOS, the values are significantly higher. It is likely that shorter PFCAs melt and boil at lower temperatures than PFOS. FTOH 8:2 exists at room temperature as a solid, but sublimates from the solid form from open vessels and can volatilize from the liquid phase.

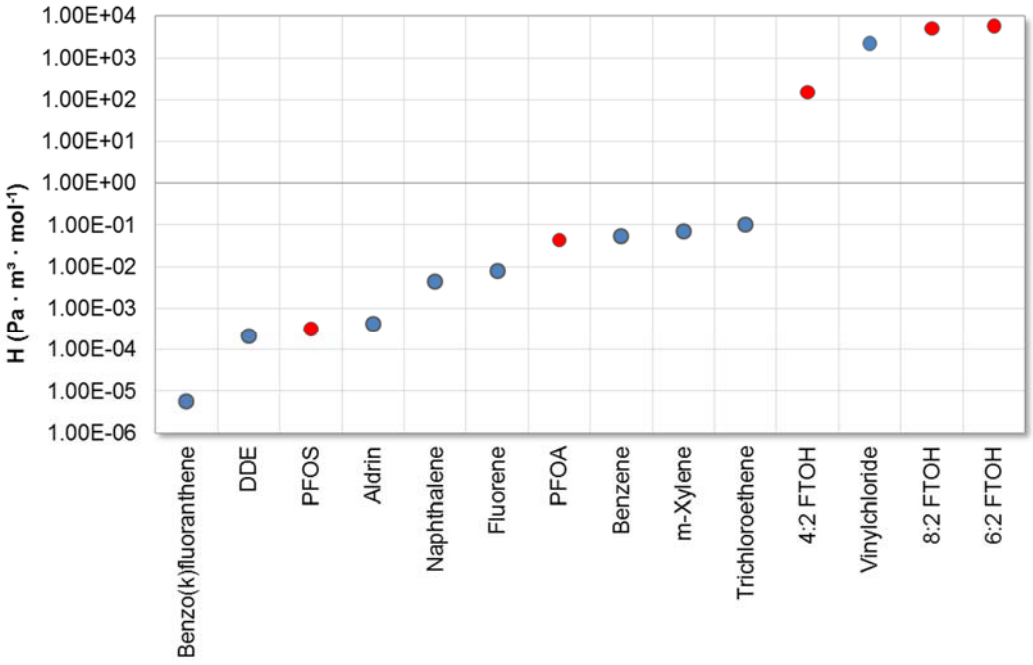
Vapour Pressure

Vapour migration plays only a minor role in assessing the mobility of most PFAS in the environment due to the low to very low vapour pressure of the PFAS.

FTOHs are reported in the literature as having varying vapour pressures but, compared with other PFAS they have much higher vapour pressures and are therefore classified as volatile. It is therefore believed that FTOHs may migrate away from production/manufacturing processes in the atmosphere as a gas phase. FTOHs can, through various transformation processes discussed below, be transformed into PFOA and result in diffuse pollution of surface water and groundwater resources through precipitation.

Henry's Coefficient (H)
Henry's coefficient is an equilibrium partitioning coefficient that describes the extent to which a chemical partitions between the aqueous and gaseous phases. Henry's coefficients for PFAS, where known, are summarized in **Appendix 2**. Henry's coefficients for PFAS are also shown graphically on **Figure 3.1** along with values for some well-characterized hydrocarbons and solvents for comparison purposes.

Figure 3.1: Comparison of Henry coefficients for selected PFAS vs well-characterized hydrocarbons and solvents



As shown in **Appendix 2** and **Figure 3.1**, Henry coefficients for PFAS are quite variable, and range over nine orders of magnitude. For example, the Henry's coefficients for FTOH 8:2 and FTOH 6:2 are high and comparable to vinyl chloride. The Henry's coefficient for PFOA is comparable to those of benzene and xylenes. The Henry's coefficient for PFOS, on the other hand, is practically negligible and indicates that little PFOS will partition from the aqueous phase to the vapour phase from a fate and transport perspective. Because of this, volatilization of PFOS and PFOA from water is not considered to be a significant transport mechanism.

Since Henry's coefficients for most PFAS are not known, it is clear that more research is needed to understand the fate and transport of PFAS in the environment.

3.2.2. Transport

Mobility of PFAS in water will in part be influenced by the degree to which the PFAS sorb to sediments or soils during transport. The effect of PFAS sorption to sediments or soils during transport is to remove a portion of the PFAS from the aqueous phase, either permanently or temporarily, which can slow down or retard the velocity of the PFAS relative to the water velocity and attenuate PFAS concentrations over time and

distance. There are two sorption mechanisms which control the degree of PFAS sorption to sediments and soils during transport in water:

1. Hydrophobic sorption to naturally-occurring solid organic particles; and
2. Surface sorption to charged mineral surfaces.

Each of the sorption mechanisms is described below.

1. Hydrophobic Sorption of PFAS to Naturally-Occurring Solid Organic Carbon

PFAS can sorb to naturally-occurring solid organic carbon particles present in sediment or soil during transport in water, in a manner analogous to sorption to granular activated carbon in water treatment systems. However, this mechanism also occurs naturally during transport because all soils and sediments typically contain some level of naturally-occurring solid organic carbon. The degree to which a PFAS sorbs to naturally-occurring solid organic carbon particles in sediment or soil during transport in water can be estimated by the PFAS-specific organic-carbon partition coefficient (Koc), the PFAS-specific octanol-water partition coefficient (Kow), or the PFAS- and soil-specific distribution coefficient (Kd). Published values for these indicators are summarized in **Appendix 2**. It shall be noted however, that Kow values for most PFAS are difficult to measure as they do not follow the typical lipid partition dynamics, due to their anionic or cationic charge. Therefore, Kow is not an adequate parameter to predict sorption of PFAS.

The reason that three different indicators of PFAS sorption to sediments or soils were included in this review is that not all researchers measure or report each indicator, yet each indicator can provide some insight regarding the extent of PFAS sorption.

One implication regarding the degree of PFAS hydrophobic sorption and mobility in water from the information in **Appendix 2** is that there is a very wide range of reported values for all PFAS. Sorption of PFCAs and PFSAs will increase with increasing chain length and with increasing solid phase fraction of organic carbon (f_{oc}). In addition, sorption increases with decreasing pH and increasing concentration of Ca^{2+}. This finding suggests that the degree of PFAS hydrophobic sorption to soils and sediments is a site-specific phenomenon, and depends on the specific PFAS present at a site as well as the specific soil type.

Another implication regarding the degree of PFAS hydrophobic sorption and mobility in water from the information in **Appendix 2** is that no data were reported for hydrophobic sorption properties for more than half of the PFAS. This finding also indicates that more basic research is needed to determine the hydrophobic sorption properties of individual PFAS in soil and sediment. However, this issue may only be relevant for PFAS that are persistent in the environment. If a precursor exhibits rapid transformation in the environment, information on sorption properties is not that relevant.

2. Surface Sorption of PFAS to Charged Mineral Surfaces

Because all of the PFCAs, PFSAs, PFPAs, and some of the precursors are strong or weak acids that exist as anions in natural waters at almost all pH, surface sorption to charged mineral surfaces naturally present in soils or sediments may be a significant mechanism controlling the mobility of these PFAS in water during transport. While there are no numerical indicators of the extent to which anionic PFAS sorb to charged mineral surfaces that could be included in **Appendix 2**, several publications were

reviewed that provide some insight to this mechanism and implications for fate and transport.

Johnson et al. (2007) equilibrated several materials with solutions of PFOS to characterize surface sorption, including goethite, kaolinite, high iron sand and Ottawa sand (a silica sand produced by processing material obtained by hydraulic mining of massive orthoquartzite situated in deposits near Ottawa, Illinois). They found that PFOS sorption was significant, but lower than for many organic contaminants of similar molecular weight. The surface area normalized sorption of PFOS decreased for the materials in the following order: Ottawa sand > high iron sand > kaolinite > goethite.

Tang et al. (2010) investigated PFOS adsorption onto goethite and silica by batch adsorption experiments under various solution compositions. They found that PFOS adsorption onto silica surfaces was marginally affected by solution pH, ionic strength, and calcium concentration. However, in contrast, they found that PFOS uptake by goethite increased significantly at lower pH and higher calcium concentrations, which was likely due to enhanced electrostatic attraction between the negatively charged PFOS molecules and positively charged goethite surface.

Ferrey et al. (2012) investigated PFOS and PFOA sorption onto mineral surfaces by constructing laboratory microcosms with sediment from beneath a landfill and amending the microcosms with PFOS and PFOA. They found that sorption of PFOA and PFOS at near neutral pH was controlled by electrostatic sorption on ferric oxide minerals, and not by sorption to organic carbon, and that there was no evidence for degradation of the PFOA or PFOS. It should be noted that the batch microcosm experimental setup differs significantly from that typically used in batch sorption experiments, which may yield different results than batch sorption conditions designed to promote equilibrium conditions. Based on their results, the authors (Ferrey et al., 2012) recommended “that accurate predictions of PFOA and PFOS mobility in groundwater should be based on empirical estimates of sorption using affected soils or sediments.”

Lipson et al. (2013) investigated PFOS transport in bedrock groundwater at a well-characterized site where AFFF was released to the ground as part of fire-fighting activities during a catastrophic fire at a petroleum storage facility in the United Kingdom. Because the PFOS-containing AFFF was released concurrently with petroleum containing methyl-tert-butyl ether (MTBE) which has well-known fate and transport characteristics, the fate and transport of PFOS in a fractured chalk aquifer could be compared with that of MTBE. Based on mathematical fate and transport modelling results, they found that PFOS transport velocity was significantly lower than the average linear groundwater velocity and that the dual-porosity retardation factor for PFOS was lower than MTBE, indicating PFOS is more mobile than MTBE in this setting. The PFOS diffusion coefficient estimated through model calibration was significantly lower than the standard estimation method and it was hypothesized that PFOS transport was influenced by an anion exclusion effect associated with surface charge on the aquifer mineral surfaces.

One observation regarding the influence of surface sorption of PFAS to charged mineral surfaces during transport in water is that the results of the research in this area have been remarkably consistent, and demonstrate that surface sorption of PFAS to charged mineral surfaces during transport in water is an important mechanism controlling mobility of PFAS in water. However, very little research has been performed regarding this mechanism and what research has been published

has been focused on PFOS and PFOA. Clearly, more basic research is needed in this area.

Another observation regarding the influence of surface sorption of PFAS to charged mineral surfaces during transport in water is that site-specific information regarding soil mineralogy and groundwater geochemistry are required to understand and accurately predict PFAS mobility in water.

Apart from the two sorption mechanisms as discussed above, mobility of PFAS may also be influenced by the presence of co-contaminants (Lipson et al. 2013). Guelfo et al. (2013) studied the sorption of PFAS to multiple soils in the presence of (1) nonaqueous phase liquid (NAPL), which may be relevant at AFFF-impacted sites, and (2) non-fluorinated AFFF surfactants. PFAS with more than 6 CF2 groups demonstrated variable sorption properties affected by the presence of NAPL and non-fluorinated AFFF. Shorter chain PFAS generally showed an increase in the sorption due to the presence of co-contaminants. The authors concluded that "PFAS groundwater transport at AFFF-impacted sites will depend on the solid phase characteristics as well as the PFAS concentration and chain length". In another study (Pan et al., 2009) the influence of cationic and anionic surfactants on the mobility of PFOS was investigated. The results showed that in the presence of a cationic surfactant, the sorption of PFOS on sediments increased due to hydrophobicity partitioning to the sorbed surfactant. The anionic surfactant on the other hand, increased the mobilisation of PFOS (concentration dependent), meaning that both types of surfactants have contrasting impacts.

3.2.3. PFAS Transformations

Biotic Transformations

PFCAs and PFSAs are generally considered to be recalcitrant to biodegradation via naturally-occurring microorganisms in water or soil. Biodegradation studies in which PFOS or PFOA were monitored for loss of parent compound have been conducted using a variety of microbial sources and exposure regimes (Parsons, 2008). Under aerobic conditions with activated sludge, no loss or biotransformation of PFOS or PFOA was observed. Under anaerobic circumstances, some removal of PFOS and PFOA has been observed, but no metabolites nor increase of fluoride was measured. To date, no laboratory data exist that demonstrates that PFCAs or PFSAs undergo significant and complete biodegradation under environmental conditions.

Precursors are known to be transformed into PFCAs and PFSAs under natural circumstances. Biotransformation of the **8:2 Telomer Alcohol** (FTOH 8:2) is relatively well studied (Parsons et al., 2008). The aerobic degradation of FTOH 8:2 begins with oxidation of the alcohol to an acid moiety, and then a subsequent β-oxidation to the complete degradation of the non-fluorinated aliphatic portion of the molecule. As a result, a PFCA is created as a by-product, in this case, PFOA. The removal of only the non-fluorinated radical to form the corresponding PFCA, in this case PFNA, is minor. In another study, these compounds were not detected (Wang et al., 2009).

Degradation studies using radiolabelled compounds [^{14}C] on FTOH 8:2 molecules revealed a number of important results (Wang et al., 2009). After seven months of incubation, 35% of the ^{14}C molecules were irreversibly bound to the soil and could only be removed by combustion. This was confirmed by the fact that free fluoride (F) accounts for only a part of the mass loss (Dinglasan et al., 2004). A number of metabolites were identified, including:

- 3-OH-acid 7-3 F (CF_2) 7CHOH-CH_2COOH;
- 7-2 FT-ketone F (CF_2) 7$COCH_3$;
- 7-3 acid F (CF_2) 7CH_2CH_2COOH ;
- 2H-PFOA F (CF_2) 6CH_2-COOH (11% after 7 days).

The formation of some of these metabolites and the fact that the ^{14}C-labeling could be dismissed after the formation of $^{14}CO_2$ (6,8%) shows that multiple CF2-groups were reduced from FTOH 8:2. Three of the metabolites, PFOA (25%), 2H-PFOA (2%), and 7:3 acid (11%) were found to be stable. The remaining metabolites were detected only transiently. The ratio of PFOA to 7:3 acid (1,8 to 2,5) can be used as an indicator of the source of PFOS. PFOS was not observed as a transformation product from the degradation of FTOH 8:2 (Wang et al., 2009). Results also showed that degradation of FTOH 8:2 was relatively fast, with a half-life of approximately seven days. Partial mineralization of FTOHs to carbon dioxide during the study also shows that microorganisms can derive energy and grow from the removal of the non-fluorinated moiety.

Studies on the degradation of FTOH 8:2 in rat, mouse, trout, human hepatocytes, human liver microsomes and cytosol suggests that FTOH 8:2 in humans is converted only slightly, and that FTOH 8:2 is not a significant source of the formation of PFOA or other PFCAs (Nabb et al., 2007).

Microbial degradation of the **polyfluorinated alkyl phosphates** (PAPs) can occur by hydrolysis of the phospho-ester bond to form the respective FTOH as a by-product, which may then be converted according to further transformation processes (Lee et al., 2010). Short-chain PAPs were fully converted within ten days, but complete transformation of 2-mono-PAP after 90 days was not observed. PAPs can also be bio-transformed in higher organisms as demonstrated by experimental results with rats (D'Eon and Mabury, 2007).

To study the degradation of **industrial polymers**, a synthetic fluoroacrylate polymer was synthesized with different FTOH side chain lengths and incubated aerobically in soil over a period of two years (Russel et al., 2008). Terminal biotransformation by-products detected included PFOA, PFNA, PFDA, and PFUNa. However, a biodegradation half-life of 1.200 to 1.700 years was determined for these bio-transformations. Thus it is concluded that microbial degradation of fluoroacrylate polymers hardly plays a role in the fate and transport of these compounds in the natural environment.

Biotic transformations of PFAS can be associated with substantial changes in the physicochemical properties of the compounds.

Chemical Transformations

PFCAs and PFSAs have shown to be very persistent in the environment (Wang et al., 2015). One study of Taniyasu et al. (2013) provided the first experimental evidence from field studies (at altitudes more than 2.500 m) that PFAS including PFOS can undergo photolysis. Taniyasu et al. (2013) states: "Long chain PFAS (PFCAs, PFSAs, FTOHs) can be successively dealkylated to short chain compounds such as perfluorobutanoic acid (PFBA) and perfluorobutane sulfonate (PFBS), but the short chain compounds were relatively more resistant to photodegradation". However, Wang et al. (2015) clearly doubt these results looking at the lack of information provided in the research.

Prior to the above mentioned study, photolysis was already investigated by many scientists (e.g. Chen et al., 2006, Hori et al., 2007, Giri et al., 2011), demonstrating photolysis of PFCAs. These studies were mostly performed with relatively high concentrations of PFAS and partly under extreme reaction conditions (e.g. under pressure, in combination with photochemical oxidants), not representing natural environmental conditions. No other studies were found that showed photolytic degradation of PFOS and PFOA under natural circumstances.

Regarding chemical degradation of **precursors,** volatile compounds such as FTOHs may react in the atmosphere and be oxidized by chlorine atoms, oxygen molecules, or photochemically generated OH radicals (Houtz et al., 2012). These authors concluded that photo-oxidation of FTOHs with chlorine atoms mainly produces by-products including fluorotelomer carboxylic acids (FTCAs), fluorotelomer aldehydes (FTALs), perfluoraldehyde (PFAL), carbonyl, PFOA and PFNA. It was also concluded that photo-oxidation of FTOH with hydroxyl radicals leads to the production of FTAL, PFAL and carbonyl. Abiotic transformations of PFAS can also be associated with substantial changes in the physicochemical properties of the compounds.

4. TOXICITY

The available data on PFAS toxicity is dominated by PFOS, PFOA and also PFHxS due to the widespread detection of these compounds in humans and the environment, and concern that these could biomagnify to a level whereby humans consuming fish may be adversely affected. Much less data is available on the toxicology of other PFAS, and this is often inconsistent and fragmentary. For the less investigated polyfluorinated chemicals, toxicology is often estimated based on structure-activity relationships, or structural homologues.

Human exposure to PFAS is mainly by ingestion of contaminated food or water. These compounds are not metabolised, bind to proteins (not to fats) and are mainly detected in blood, liver and kidneys. Elimination of PFOS, PFHxS and PFOA from the human body takes some years, whereas elimination of shorter chain PFAS is in the range of days. The half life of PFOS and PFOA in rodents is in the range of months which can cause extrapolation issues in tests.

There is significant data available on the impact of (sub)chronic PFOS and PFOA exposure on reproductive and/or developmental and other types of effects in both humans and animals. However, the results from epidemiological studies are not always consistent. Animal studies show mainly effects from PFOS and PFOA on the liver, the gastrointestinal tract and on thyroid hormone levels. In general, PFOS is more toxic compared to PFOA.

In 2008, the European Food Safety Authority derived a TDI (Tolerable Daily Intake) for PFOS of 150 ng/kg bw/day and for PFOA of 1.500 ng/kg bw/day. Later, taking into account more recent toxicity data, the U.S. EPA has proposed much lower RfDs (Reference Doses) of 30 ng/kg bw/day for PFOS and 20 ng/kg bw/day for PFOA (2014, draft).

Carcinogenic effects of PFOS and PFOA have also been studied (human and animal studies, no focus on other PFAS). Several authorities, including ATSDR, U.S. EPA and IARC do not classify PFOS and PFOA as “proven carcinogens”, but instead as “suggestive carcinogens” or “possibly carcinogenic to humans” because of existing uncertainties.

PFOS has been categorised as moderately acute and slightly chronically toxic to aquatic organisms. The MAC EQS derived by the European Commission for European freshwater and saltwater are based on the lowest NOEC reported (NOEC of < 2,3 µg/l for Chironomus tentans) to protect the most sensitive species.

The Sections below provide more detailed information about the exposure, toxicity and the bioaccumulation potential of PFOS and PFOA (Section 4.1 to 4.3). Information of other PFAS is included in Section 4.4.

4.1. UPTAKE, DISTRIBUTION IN TISSUE, BIOACCUMULATION AND ELIMINATION OF PFOS AND PFOA

4.1.1. Uptake

Due to the physicochemical characteristics of perfluorinated compounds, exposure of PFAS is most likely via ingestion of contaminated food or water (dietary uptake/oral route) (Fromme et al., 2009, ATSDR, 2009). As PFAS have also been found in both

air and dust, exposure by breathing air, ingestion of dust, or dermal contact with dusts or aerosols of PFAS may also be a source of exposure (ATSDR, 2009).

Compared to data on ingestion, relatively little data are available on other paths of exposure, such as skin contact with PFAS-treated utensils or inhalation of indoor air (Stahl et al., 2011). The significance of these exposure pathways is unclear. ATSDR (2009) concluded that carpets treated with perfluoroalkyls can be a source of exposure for children.

4.1.2. Distribution in tissue

Perfluoroalkylated substances such as PFOS and PFOA have, contrary to most other persistent organic pollutants (POPs), a low affinity to lipids, but bind to proteins. PFOS is associated with cell membrane surfaces and accumulates in various, mainly high perfused, body tissues of exposed organisms (DEPA, 2013).

The highest concentrations are usually detected in blood, liver, kidneys, lung, spleen and bone marrow. Lower concentrations are detected in heart, testes, fat, brain and muscles. In the general public, PFOS concentrations in the blood range between sub-ppb levels up to the hundred ppb level. PFOA levels in blood are generally lower (sub-ppb levels up to tens of ppb levels, Loganathan et al., 2011). Although accumulation of PFAS in muscles is minimal (DEPA, 2013), accumulation in muscles may be an important exposure route when consuming fish and meat. Stahl et al. (2012) analysed PFOS and PFOA concentrations in liver and muscle tissue of wild boar to evaluate the potential health danger resulting from consumption of wild boar meat or liver. Both PFOS and PFOA were detected in liver and muscle tissue, whereas concentrations of PFOS were significantly higher in organs and tissues. Considering the TDI (see Section 4.2.2) for PFOS and PFOA, negative health effects from consumption of wild boar are not expected (Stahl et al., 2012). The very low Annual Average-Environmental Quality Standard EQS (see Section 5) however is based upon consumption of fish by humans.

Both in animals and humans, PFOS and PFOA cross the placenta, and are also excreted in breast milk (Stahl et al., 2011).

An unequivocal correlation between age and blood-PFAS concentrations is not evident. However, gender-dependent differences are as follows: men generally show higher concentrations of PFAS than women (Rylander et al., 2009). This gender related difference in concentration levels was also detected during other studies, such as the study of Calafat et al (2007), based on data of the U.S. population.

Neither PFOS nor PFOA are metabolized to any significant extent (Stahl et al., 2011).

4.1.3. Bioaccumulation

Conder et al. (2008) concluded that: “(1) bioconcentration and bioaccumulation of perfluorinated acids is directly related to the length of each compound’s fluorinated carbon chain; (2) PFSAs are more bioaccumulative than PFCAs of the same fluorinated carbon chain length”.

The numerical criterion under REACH defining that a substance is bioaccumulative is a bioconcentration factor (BCF) in aquatic species higher than 2000 l/kg. (Commission Regulation (EU) No 253/2011). Bioconcentration factors > 1 l/kg indicate bioaccumulative potential only from a scientific standpoint.

Information about bioconcentration, bioaccumulation and biomagnification for PFOS and PFOA is presented below.

Overall, it should be noted that bioaccumulation can differ significantly between aquatic and terrestrial organisms. As PFSAs and PFCAs are generally highly water soluble and have a low vapour pressure (Section 3), the efficiencies of biological depuration mechanisms (i.e. lungs vs. gill) and thus the values for bioaccumulation differ (PFOS depuration from fish is relatively rapid). As a consequence, studies may indicate a tendency for bioaccumulation based on data from terrestrial organisms while data from aquatic organisms may not be as conclusive, or even clearly indicate a lack of meaningful bioaccumulation (e.g., aquatic BAFs may be less than 2.000).

PFOS:
A selection of bioconcentration (BCF), bioaccumulation (BAF) and biomagnification (BMF) factors for PFOS is presented in **Table 4.1**[2].

Table 4.1: A selection of BCFs, BAFs and BMFs for PFOS

Bioconcentration Factor Ratio between the chemical concentration in an organism to the concentration in water (exclusion of dietary intake)		
Bluegill	1.866 – 4.312	Drottar et al., 2001
Rainbow Trout	1.100 – 5.400	Drottar et al., 2001
Catfish and largemouth bass (Decatur, Alabama)	830 – 26.000	Giesy and Newsted, 2001
Rainbow Trout	2.900 (liver) 3.100 (blood)	Martin et al., 2003
Bioaccumulation Factor (within a trophic level) Increase of a chemical concentration in certain tissues of an organism due to absorption from food/environment		
Zooplankton/water	240	Houde et al., 2008
Mysis/water	1.200	Houde et al., 2008
Sculpin/water	95.000	Houde et al., 2008
Lake trout/water	16.000	Houde et al., 2008
Biomagnification Factor (across trophic levels) Increase of a chemical concentration in an organism compared to the chemical concentration in its diet		
Arctic cod/zooplankton (Western Canadian Arctic)	8,7	Powley et al., 2008
Caribou/lichen (Canada)	2,0 – 9,1	Müller et al., 2011
Wolf/caribou (Canada)	0,8 – 4,5	Müller et al., 2011
Dolphin/seatrout (2 U.S. locations)	0,9	Houde et al., 2006
Seatrout/pinfish (2 U.S. locations)	4,6	Houde et al., 2006

[2] In case that more information on bioaccumulation of PFOS is desired, following publications (a not limitative list) can be considered for review: Asher et al., 2012, Awad et al., 2011, De Silva et al., 2011, De Solla et al., 2012, Inoue et al., 2012, Jeon et al., 2010, Kwadijk et al., 2010, Labadie et al., 2011, Liu et al., 2011, Pan et al., 2014, Sakurai et al., 2013. Many of these publications also contain information on the bioaccumulation potential of PFOA and other PFAS.

Walrus/clam (Eastern Arctic Food Web)	4,6	Tomy et al., 2004
Narwhal/Arctic cod (Eastern Arctic Food Web)	7,2	Tomy et al., 2004
Beluga/Arctic cod (Eastern Arctic Food Web)	8,4	Tomy et al., 2004
Beluga/redfish (Eastern Arctic Food Web)	4,0	Tomy et al., 2004
Polar bear/seal (Canadian Arctic)	177	Martin et al., 2004

Note: due to the continuous improvements of the analytical methods for PFAS, it could be difficult to compare recent with older analytical results. Studies performed before 2007 may have considerable analytical inaccuracies and should be viewed in that light.

The data in **Table 4.1** show bioconcentration factors (BCF) > 2.000 l/kg, demonstrating the bioaccumulation properties of PFOS.

The BMF in **Table 4.1** highlight that predatory animals are recorded with greater concentrations in their bodies compared to the concentrations in their diets, demonstrating the biomagnification properties of PFOS. As a result, concentrations of PFOS are likely to be elevated within organisms at higher trophic levels.

In general, the bioaccumulation potential in the soil environment has been shown to be significantly lower than in the marine environment (DEPA, 2013).

PFOA:
A selection of bioconcentration, bioaccumulation and biomagnification factors for PFOA is presented in **Table 4.2**.

Table 4.2: A selection of BCFs, BAFs and BMFs for PFOA

Bioconcentration Factor Ratio between the chemical concentration in an organism to the concentration in water (exclusion of dietary intake)		
Water breathing animals	1,8 – 8,0	ECHA, 2014
Rainbow Trout	12 (liver) 25 (blood)	Martin et al., 2003
Bioaccumulation Factor (within a trophic level) Increase of a chemical concentration in certain tissues of an organism due to absorption from food/environment (e.g. water and food)		
Water breathing animals	0,9 – 266	ECHA, 2014
Biomagnification Factor (across trophic levels) Increase of a chemical concentration in an organism compared to the chemical concentration in its diet		
Water breathing animals	0,02 – 7,2 (most data below 1)	ECHA, 2014
Caribou/lichen (Canada)	0,9 – 11	Müller et al., 2011
Wolf/caribou (Canada)	0,9 – 3,8	Müller et al., 2011
Walrus/clam (Eastern Arctic Food Web)	1,8	Tomy et al., 2004
Narwhal/Arctic cod (Eastern Arctic Food Web)	1,6	Tomy et al., 2004

Beluga/Arctic cod (Eastern Arctic Food Web)	2,7	Tomy et al., 2004
Beluga/redfish (Eastern Arctic Food Web)	0,8	Tomy et al., 2004
Beluga whale/Pacific herring (Western Canadian Arctic Food Web)	1,3	Tomy et al., 2009
Arctic cod/marine arctic copepod (Western Canadian Arctic Food Web)	2,2	Tomy et al., 2009
Dolphin/seatrout (2 U.S. locations)	1,8	Houde et al., 2006
Seatrout/pinfish (2 U.S. locations)	7,2	Houde et al., 2006
Polar bears/ringed seal (2 U.S. locations)	45 – 125	Butt et al., 2008
Polar bear/seal (Canadian Arctic)	8,6	Martin et al., 2004

Note: due to the continuous improvements of the analytical methods for PFAS, it could be difficult to compare recent with older analytical results. Studies performed before 2007 may have considerable analytical inaccuracies and should be viewed in that light.

The results in **Table 4.2** show that the reported BCFs for PFOA are far below 2.000 l/kg. Also BAFs are well below 2.000. These data show that based on the REACH definition for “bioaccumulation”, this criterion is not met for PFOA. In Annex XV “Proposal for a Restriction of PFOA” (ECHA, 2014), it is concluded that the bioaccumulation criterion defined in the REACH regulation cannot be used to assess the bioaccumulation potential of PFOA. However, due to the long half-live times in humans and BMFs > 1, there is evidence for bioaccumulation of PFOA.

The revised Annex XIII of the REACH regulation (March 2011) was expanded with criteria for assessing the bioaccumulation potential: results regarding biomagnification, bioaccumulation in terrestrial species and concentrations in human body fluids could also be considered in the evaluation of the “bioaccumulation” criterion.

The Proposal Document for a restriction of PFOA (ECHA, 2014) concludes the following: “The bioaccumulative property is proven by studies from aquatic and terrestrial food webs, which clearly indicate accumulation of PFOA and APFO. In addition, human data strongly indicate that PFOA and APFO bioaccumulate in humans. It is of special concern that PFOA and APFO biomagnify in endangered species as shown for the polar bear and in animals which are likely to become endangered in the near future (narwhal and beluga whale). Additionally, human gestational and lactational exposure are of special concern as the foetus and newborn babies are highly vulnerable to exposure to toxic substances. Based on a weight of evidence approach, it is considered that the data from environmental species and humans shows that the B criterion of REACH Annex XIII is fulfilled”.

4.1.4. Elimination

Both PFOS and PFOA are very slowly eliminated from the human body. The Toxicological Overview for PFOS and PFOA, published by the Public Health England (2009), documents a half life[3] from the human body of approximately 9 years for PFOS and 4 years for PFOA. Some data about half lives for PFOA and PFOS are summarized in **Table 4.3**.

Table 4.3: Half Life Times for PFOS and PFOA

PFOS		
Cynomolgus monkeys	132 days (males) 110 days (females)	Noker and Gorman,2003
Cynomolgus monkeys (male and female)	200 days	Seacat at al., 2002
Rodents	1 – 2 months	Chang et al., 2012
Monkeys	4 months	Chang et al., 2012
Retired fluorochemical workers (U.S.A)	5,4 years	Olsen et al., 2007
PFOA		
Rats	5,63 days (males) 0,08 days (females)	Ohmori et al., 2003
Cynomolgus monkeys	33 days (males) 21 days (females)	Butenhoff et al., 2004
Retired fluorochemical workers (U.S.A)	2,3 – 3,8 years	Olsen et al., 2007
Population study (U.S.A)	2,9 – 8,5 years	Seals et al., 2011
Population study (U.S.A)	2,3 years	Bartell et al., 2010

In fluorochemical workers, PFHxS had the longest observed elimination half-life (8,5 years), followed by PFOS (5,4 years), and PFOA (2,3-3,8 years) (Olsen et al. 2007). Based on the studies listed above, the excretion of PFAS varies with the type of perfluorochemicals and also with the animal species and gender. The reason for the species and gender differences in elimination are not well understood (U.S. EPA, 2009).

In general, the blood half-lives of perfluorochemicals:

- are longer for sulfonates than for carboxylates;
- are shorter for branched isomers than straight chain;
- are often shorter in females than males. This may be due to the difference in renal clearance (and hormones) (DEPA, 2013). Sex differences documented for rats and monkeys are not always found in humans (DEPA, 2013);
- increase with chain length for carboxylates;
- vary a lot between species.

The primary clearance route for PFOS and PFOA is urine, rather than faecal elimination (Bull et al., 2014).

[3] Half life: the time required for a concentration to decrease by half compared to its initial concentration

4.2. HUMAN TOXICOLOGY OF PFOS AND PFOA

4.2.1. Health effects of acute exposure

The acute lethal toxicity of PFOS moderately corresponds to a classification as acute toxicity Category 4. In general, PFOS is more toxic compared to PFOA (DEPA, 2013).

Some data on acute toxicity of PFOS and PFOA are summarized in **Table 4.4**.

Table 4.4: A selection of acute toxicity data of PFOS and PFOA

PFOS				
Inhalation				
Rats		1,9 – 4,6 mg/l, 1 hour (PFOS dust in air)	Symptoms: Signs of emaciation Nasal discharge Stained urogenital region Breathing disturbances General poor condition	OECD, 2002
	LC50	5,2 mg/l (PFOS dust in air)		OECD, 2002
Ingestion				
Rat	Oral LD50	250 mg/kg bw	Symptoms: hypoactivity, stained urogenital region, decreased limb tone and ataxia, stomach distension, lung congestion	3M, 1999
Newborn mouse	Oral LD50	10 mg/kg bw/d		Lau et al., 2004
Rat	Oral LD50	Between 50 – 1500 mg/kg bw		OECD, 2002
Dermal Exposure				
No accurate data available. The only available dermal study is from Biesemeier and Harris (1974) (no detailed information available in this study)				
PFOA				
Inhalation				
No data about effects of acute exposure to humans and animals.				

Ingestion				
Rats	LD50	430 – 680 mg/kg bw	Symptoms: enlarged livers, gastrointestinal irritation, weight loss	PHE, 2009
Guinea Pig	LD50	200 mg/kg bw		PHE, 2009
Dermal Exposure				
New Zealand White rabbits	Dermal LD50	> 2000 mg/kg bw		Glaza, 1995
Rabbits	Dermal LD50	4300 mg/kg bw		Kennedy, 1985
Rats	Dermal LD50	7000 mg/kg bw (male) 7500 mg/kg bw (female)		Kennedy, 1985

LC: Lethal Concentration
LD: Lethal Dosis

There are no data to assess the acute toxicity following high exposure by means of inhalation, ingestion, dermal or ocular contact in humans (PHE, 2009). Also the extensive literature search by Bull et al. (2014) did not identify data on the acute toxicity of PFOS and PFOA.

Public Health England (2009) states: "Animal data suggest that PFOS and PFOA have moderate acute oral toxicity with effects on the gastrointestinal tract and liver. Animal data suggest that they are mild skin and eye irritants".

4.2.2. Health effects of (sub)chronic exposure

There is much data on the impact of (sub)chronic PFOS and PFOA exposure on reproductive and/or developmental and other types of effects in both humans and animals.

Epidemiological studies (humans)
During the past few years, several epidemiological studies were conducted to investigate relations between PFOS/PFOA exposure and various health effects like fertility, growth, and developmental biomarkers (e.g. studies from workers at different 3M plants, population studies of residents from Ohio, West Virginia, Quebec, among others). Several of the human epidemiological studies have recently reported associations with PFOS and cholesterol, birth weight changes and various thyroid parameters. However, these studies show inconsistent results. Therefore, the U.S. EPA's Science Advisory Board notes: "The results of existing epidemiology studies are not adequate for use in quantitative risk assessment" (U.S. EPA, 2014).

Animal Studies
Several studies have been carried out to examine chronic exposure[4] on animals, with focus on mice, rats and monkeys. The following toxic effects could been seen, following chronic exposure (PHE, 2009):

- Effects on the liver as primary target organ (Increase of the liver weight, liver cell hypertrophy)

[4] Chronic exposure experiments are long-term experiments in contrast to acute toxicity tests. Co-effecting factors may be influencing the results, i.e. lower stress-tolerance as compared to the reference animal

- Effects on the gastrointestinal tract
- Effects on thyroid hormone levels
- Body weight loss
- Effects on the lipid metabolism (Stahl et al., 2011)
- Reproductive and developmental toxic effects (e.g. reduction of foetal weight, oedema, delayed ossification of bones, cardiac abnormalities)

Some of the reported no-observed-effect-concentration (NOEC) and lowest-observed-adverse-effect-levels (LOAEL) are summarized in **Table 4.5**.

Table 4.5: Health effects of (sub)chronic exposure: NOEC and LOAEL for PFOS and PFOA exposure

PFOS				
Rats	Oral Diet, 14 weeks	NOEC: 0,4 mg/kg bw/d	Liver Effects	Seacat et al., 2003
Rats	Oral Gavage	NOEC: 1 mg/kg bw/d	Developmental Effects	Lau et al., 2003
Rats	Oral Diet, 90 days	LOAEL: 2 mg/kg bw/d	Liver Effects	Goldenthal, 1978
Rats	Oral gavage, 28 days	LOAEL: 5 mg/kg bw/d	Decrease in body weight	Cui et al., 2009
Rats	Oral gavage, 20 days	NOEC: 1,0 mg/kg bw/d	Maternal toxicity	Butenhoff et al., 2009
Rabbits	Oral gavage	NOEC: 0,1 mg/kg bw/day (maternal) NOEC: 1 mg/kg bw/day (foetal) LOAEL: 1 mg/kg bw/day (maternal) NOEC: 2,5 mg/kg bw/day (foetal)	Developmental maternal and foetal toxicity	Case et al., 2001
Cynomolgus Monkey	Oral Diet, 6 months	NOEC: 0,03 mg/kg bw/d LOAEL: 0,15 mg/kg bw/d	Effect on Thyroid hormone values	Seacat et al, 2002
PFOA				
Mice	Oral Gavage, 14 days	LOAEL: 0,3 mg/kg bw/day	Liver Weight	Loveless et al., 2006
Rats	Oral Gavage, 14 days	LOAEL :1 mg/kg bw/day NOEC: 0,3 mg/kg bw/day	Effect on hormone values	Loveless et al., 2006

Rats	Oral Diet, 14 days	LOAEL: 1,7 mg/kg bw/day (male) LOAEL: 76 mg/kg bw/day (female) NOEC: 0,6 mg/kg bw/day (male) NOEC: 22 mg/kg bw/day (female)	Liver Effects	Goldenthal, 1978
Rats	Oral Diet, 90 days	LOAEL: 0,6 mg/kg bw/day NOEC: 0,06 mg/kg bw/day	Liver Effects	Perkins et al., 2004
Mice	Oral Gavage	LOAEL: 1 mg/kg bw/day (maternal) LOAEL: 3 mg/kg bw/day (foetal) NOEC: 1 mg/kg bw/day (foetal)	Developmental Effects	Lau et al., 2006
Rats	Oral Gavage (Two generation study)	LOAEL: 1 mg/kg bw/day (F0, paternal) LOAEL: 1 mg/kg bw/day (F1, foetal) NOEC: > 30 mg/kg bw /day (F0, maternal)	Reproductive Effects	Butenhoff et al., 2004

Derivation of Reference Doses (RfDs[5]) / Tolerable Daily Intakes (TDIs)

U.S. EPA

In October 2009, the U.S. EPA issued provisional subchronic Reference Doses (RfDs) for PFOS and PFOA (U.S. EPA, 2009). The subchronic RfD for PFOS was 800 ng/kg bw/day and the subchronic RfD for PFOA was 200 ng/kg bw/day. The PFOS RfD was based on increases in liver weight in mice (Lau, et al., 2006), and the PFOA RfD was based on increased levels of thyroid stimulating hormone, reduced triiodothyronine, and reduced high density lipoproteins in monkeys (Seacat, et al., 2002).

In February 2014, the U.S. EPA released Draft Health Effects Documents for PFOS (U.S. EPA, 2014a) and PFOA (U.S. EPA, 2014b) which proposed chronic RfDs for these compounds of 30 ng/kg bw/day and 20 ng/kg bw/day, respectively.

For PFOS, the proposed RfD is based on a rat developmental neurotoxicity study by Butenhoff et al. (2009) that found increased motor activity and decreased habituation

[5] A Reference Dose (RfD) is the maximum amount of a substance that can be ingested daily over a lifetime without causing adverse non-cancer health effects

on Post Natal Day 17 in male offspring following a maternal dose of 1 mg/kg/day. No effects on pup body weight were reported. The selected proposed PFOS RfD is based on a pharmacokinetic approach that models human serum levels associated with developmental neurotoxicity in rat (Butenhoff et al. 2009) and is supported by the slightly higher 50 and 60 ng/kg bw/day RfD values for increases in liver weight and other developmental effects. Thus, co-occurring critical endpoints are protected by the chosen PFOS RfD.

For PFOA, the proposed RfD is based on modelled serum values from four different points of departure doses based on two rat studies (Palazzolo et al., 1993, York et al., 2002) and one mouse study (Lau et al., 2006) that showed consistent responses across studies. Reduced liver weight was used as a common denominator for loss of homeostasis and protection against co-occurring adverse developmental or kidney effects observed in two of the studies (York et al., 2002, Lau et al., 2006).

These proposed RfDs were subjected to peer review by independent scientists in August of 2014. The peer reviewers questioned the U.S. EPA's rationale for choosing reduced liver weight as the basis for the RfD for PFOA, and they requested further justification for the use of animal data as the basis for the RfD when human data are currently available. The proposed chronic RfD values will not be added to the U.S. EPA IRIS database until the Health Effects Documents are finalized.

Europe

European Food Safety Authority (2008): The Scientific Panel on Contaminants in the Food Chain (CONTAM) established a TDI for PFOS of 150 ng/kg bw/day. This TDI was based on the NOEC of 0,03 mg/kg bw/day from a subchronic study with Cynomolgus monkeys (Seacat et al., 2002. See **Table 4.5**). The TDI for PFOA of 1500 ng/kg bw/day was linked with the two-generation reproductive study with rats by Butenhoff et al. (2004, see **Table 4.5**).

4.2.3. Carcinogenic effects

Human studies
The cancer incidence related to PFOS and PFOA exposure in worker-based populations was studied in several studies (e.g. at several 3M plants in U.S.A and Europe, DuPont's Washington Works Plant). In most cases, these human epidemiological studies could not find a direct correlation between the PFOS exposure and carcinogenicity, mainly due to the lack of information on other types of exposure (e.g. lifestyle information, influence from the use of other chemicals at the plants). Only in the DuPont's study (West Virginia Washington Works Plant, 2003) was a significant increase observed for cancer of kidney, bladder and urinary track organs, due to exposure to PFOA.

Studies within the general population (without occupational exposure to PFAS) did not reveal any direct correlation between PFOS/PFOA exposure and carcinogenity (U.S. EPA, 2014a).

Animal studies - PFOS
Thomford et al. (2002) performed a study on carcinogenicity in which male and female rats were administered different concentrations of PFOS over a period of 104 weeks. A significant positive correlation was detected between PFOS exposure and the incidence of hepatocellular adenoma (liver) in male and female rats.

A comparable study was performed by Butenhoff et al. in 2012. Also in this study a significant increase in hepatocellular adenoma was observed in males and females. It was only in the female, 20 ppm dose group that a hepatocellular carcinoma was observed. There were no significant effects on kidney or bladder.

It has not been determined whether these results can also be extrapolated to humans.

Animal studies - PFOA
The studies of Butenhoff et al. (2012) and Biegel et al. (2001), both with rats, showed that PFOA exposure was correlated with liver adenomas or carcinomas, testicular Leydig cell adenomas and pancreatic acinar cell tumors (the latter, only showed in Biegel et al., 2001). In addition, ovarian tubular hyperplasia and adenomas were observed in the female rats in the Butenhoff et al. study (2012). In both studies, effects were detected in the 20 mg/kg/day-dose-group. Only the Leydig cell adenomas demonstrated a dose-response relationship.

There are no carcinogenicity studies using other animals than rats.

General conclusions on carcinogenity
In regards to carcinogenesis, Stahl et al. (2011) concludes: “a genotoxic mechanism cannot be assumed for PFOS and PFOA, but rather a tumour promoting effect and/or epigenetic process comes into question”.

ATSDR (2009) states: “The information available does not prove that perfluoroalkyls cause cancer in humans, but the evidence is not conclusive”.

The U.S. EPA concludes that evidence of carcinogenicity of PFOS is “suggestive”, but not definitive, because the tumour incidence does not indicate a dose response (U.S. EPA, 2014a). Based on the risk assessment study performed in 2005 (U.S. EPA, 2005), PFOA’s carcinogenicity was also categorized as “suggestive”. In the U.S. EPA 2014b study, a Human Equivalent Dose (HED) of 0,58 mg/kg bw/day and a slope factor of 0,07 $(mg/kg\ bw/day)^{-1}$ was calculated (the basis for this calculation was the dose-response data of the Leydig cell tumours in rats, Butenhoff et al., 2012).

In June 2014, the International Agency for Research on Cancer (IARC), as part of the World Health Organization, assessed the carcinogenicity of PFOA. PFOA was classified as follows: “possibly carcinogenic to humans (Group B), based on limited evidence in humans that exposure to PFOA is associated with testes and kidney cancer and limited evidence in experimental animals” (IARC, 2014). Currently, PFOS is not yet classified by IARC.

4.3. TOXICITY OF PFOS AND PFOA TO ECOLOGICAL RECEPTORS

Ecotoxicity data were primarily identified for aquatic organisms such as algae, aquatic plants, invertebrates and fish, and birds. Ecotoxicity tests of PFAS are mostly limited to PFOS and PFOA, and the dataset is small in comparison to established pollutants, but also to many other emerging chemicals of concern (Funkhouser, 2014).

PFOS
A good overview of PFOS’ key acute and chronic aquatic ecotoxicological tests was provided in the “PFOS EQS Dossier” (2011), prepared for the revision of the Environmental Quality Standards Directive” (Directive 2013/39/EU), a daughter Directive of the Water Framework Directive (WFD), and it is shown in the tables in **Appendix 3**.

Based on this information, the EC_{50} for freshwater algae and aquatic plants (acute tests/96h) ranges between 48 and 283 mg PFOS/l. The EC_{50} for freshwater invertebrates (acute tests/48h) ranges between 4 and 124 mg PFOS/l. The NOEC for freshwater invertebrates ranges between < 0,002 and 12 mg PFOS/l. The differences in the measured EC and NOEC values are species dependent (for more information, see **Appendix 3**).

The following general conclusions can be derived from the PFOS aquatic ecotoxicological studies:

- Based on laboratory toxicity studies, PFOS can be generally categorized as "moderately acute and slightly chronically toxic to aquatic organisms" (Giesy et al., 2010);
- The most sensitive genus to PFOS exposure is the invertebrate (midge) *Chironomus tentans*. This genus is approximately 40-fold more sensitive compared to the next most sensitive genus (*Pimephalus*) (Giesy et al., 2010);
- Acute invertebrate toxicity data show that marine invertebrates are more sensitive to short-term PFOS exposure than freshwater invertebrates (Giesy et al., 2010).

Funkhouser (2014) states: "One considerable uncertainty with regard to PFOS ecotoxicity is a general lack of longer-term exposure studies. As an example, the vast majority of studies on PFOS toxicity to aquatic invertebrates have been less than a generation of particular study organisms and overall, less than 28 days. Because many PFAS and especially PFOS are persistent, longer-term exposures may occur in the environment".

The MAC EQS derived by the European Commission for European freshwater and saltwater are based on the lowest NOEC reported (NOEC of < 0,0023 mg/l for *Chironomus tentans*) to protect the most sensitive species. The derived EQS are described in Section 5.2.

PFOA

Following general conclusions can be derived from the PFOA aquatic ecotoxicological studies:

- Acute toxicity testing with aquatic species indicates that PFOA is generally less toxic than PFOS. There is a difference of about a factor 10 (DEPA, 2013). As an example, these effects were clearly shown in a marine species study with three different trophic levels, conducted by Mhadhbi et al. (2012);
- The most sensitive pelagic organism is *Pseudokircheneriella subcapitata* (a freshwater alga), with a 96-hour LOEC of 2,0 mg/l (Environment Canada, 2012);
- There are studies in aquatic organisms showing potential of PFOA to affect endocrine function. In minnows at PFOA concentrations of 3-30 mg/l, thyroid hormone biosynthesis was inhibited, vitellogenin expression was induced in males, oocytes developed in the testes of male fish, and ovary degeneration occurred in females. Other studies show hepatotoxicity, immunotoxicity and chemosensitivity in other different organisms such as mussels, seals, dolphins, turtles and rats (Environment Canada, 2012, cited from DEPA, 2013);
- PFOA exhibits low chronic toxicities in benthic organisms (> 100 mg/l) (Environment Canada, 2012).

A study with white leghorn chickens showed that PFOA had no effect on embryonic pipping success at concentrations up to 10 µg/g of embryos. However, there was a significant accumulation of PFOA in the liver of the embryos, compared to the initial whole-egg concentration (Environment Canada, 2012).

Currently, there is no EQS derived for PFOA by the European Commission.

Ecotoxicological effects to higher trophic level wildlife

Due to the multiple global sources of PFOS and PFOA and the persistency of these compounds (and therefore the wide-scale fate and transport pathways), both compounds are detected across the globe, even in remote places. Concentrations are detected in a variety of wildlife, such as seals, walrus, polar bears, dolphins, eagles, amongst others in all continents. PFOA concentrations in the liver of Canadian polar bears are about 13 µg/kg bw (Environment Canada, 2012). PFOA concentrations increase yearly by 2,3% in central East Greenland polar bears. In adult female sea otters, concentrations increased significantly over a 10-year period (Environment Canada, 2012).

Information about the accumulation and biomagnification potential of PFOS and PFOA is included in Section 4.1.3.

4.4. TOXICITY, HALF LIFE TIMES AND BIOACCUMULATION POTENTIAL OF OTHER PFAS

As mentioned previously, the most detailed studies of toxic and adverse health effects have been carried out for PFOS and PFOA. These two compounds, alongside PFHxS, are the compounds which are usually detected at the highest concentrations in human matrices (U.S. EPA, 2009). However, their use is currently being phased out and shorter-chain compounds are increasingly being used as replacements.

The data presently available regarding the toxicology of PFAS other than PFOS and PFOA is in comparison meagre, inconsistent, and fragmentary, particularly in light of the diversity of PFAS found in biological matrices. However, data for fluorotelomers and shorter chain homologues continue to be published. For the less investigated polyfluorinated chemicals, preliminary properties may be estimated based on their structure or from homologues.

A recent study of the Danish Environmental Protection Agency (DEPA, 2015c) describes the human toxicity of short-chain PFAS as follows: “The toxicokinetics and toxicity in humans for short-chain PFAS are mainly investigated for PFHxS, and that substance has rather similar properties as PFOS” and further “The other short-chain PFAS seem to be less toxic than PFOS/PFOA but the available data is insufficient for a final evaluation”.

Another good overview of the toxicity of various long- and short- chain PFAS is included in the extensive literature review of Bull et al., 2014.

Short-chain PFAS

- Generally no or lower bioaccumulation potential in comparison to PFOS and PFOA although there may be some exceptions. The BCFs of PFBS and PFBA are about a factor 3 lower compared to the BCFs of PFOS and PFOA, respectively (based on modelling exercises) (Rayne et al., 2009). On the other hand, Lasier et al. (2011) states that “sulfonates with four to seven carbons may be as likely to

bioaccumulate as PFOS". In addition, it is difficult to extrapolate bioaccumulation data from animal studies to humans, as stated by DEPA (2015c) as follows: "The high presence of short-chain PFAS, especially PFBA, in human tissue including brain from deceased people is worrying, and it shows that the short-chain PFAS and a fluortelomer metabolite may be much more bioaccumulative in humans than the studies with experimental animals conclude".

- Persistent
- No data on carcinogenity for PFBA, PFHxA, PFBS, PFHxS
- Summary of information for the most common short-chain PFAS:
    - PFBA
        - Half-life in fluorochemical workers: 1,2 – 4,6 days (Chang et al., 2008)
        - Half-life in retired fluorochemical workers: 1,9 – 6,3 days (Chang et al., 2008)
        - Half-life in male monkeys: 40,3 hours (Chang et al., 2008)
        - Half-life in female monkeys: 41,0 hours (Chang et al., 2008)
        - Urine is the main route of elimination of PFBA (Chang et al., 2008)
        - General low level of toxicity (Rickard, 2009)
    - PFHxA
        - Half-life in male monkeys: 5 hours (Gannon et al., 2011)
        - Half-life in female monkeys: 2 hours (Gannon et al., 2011)
        - Half-life in rats: 2,5 hours, after oral dosing and 1 hour after in vitro administration (Gannon et al., 2011)
        - Urine is the main route of elimination of PFHxA (Gannon et al., 2011)
        - NOEC for subchronic toxicity: 20 mg/kg bw/day (rats) (Rickard, 2009)
        - NOEC for reproductive toxicity: 500 mg/kg bw/day (rats) (Rickard, 2009)
        - NOEC for developmental toxicity: 100 mg/kg bw/day (rats) (Rickard, 2009)
        - Not genotoxic (Rickard, 2009)
    - PFBS
        - Half-life in retired fluorochemical workers: 13,1 – 45,7 days, with an average of 27,7 days) (Olsen et al., 2007)
        - Half-life in male rats: 2,1 hours (Chengelis et al., 2009)
        - Half-life in female rats: 0,64 hours (Chengelis et al., 2009)
        - Urine is the main route of elimination of PFBS (Chengelis et al., 2009, Olsen et al., 2007)
        - Based on the results of multiple acute ecotoxicity tests, PFBS is classified as an insignificant hazard by the U.S. National Institute of Occupational Safety and Health (NIOSH). No labelling required by the European Union (3M, Technical Data Bulletin)
        - PFBS acute oral LD50 (> 2000 mg/kg) in rat toxicity studies is classified by the U.S. EPA as "slightly toxic", by the European Union as "no hazard" (3M, Technical Data Bulletin)
        - Based on a NOEL of > 1000 mg/kg bw/day in a two-generation reproduction study with rats, PFBS is considered practically non-toxic in multi-generation reproduction (3M, Technical Data Bulletin)
        - BCF in Rainbow Trout (liver and blood): < 1 (no bioconcentration) (Martin et al., 2003)

- PFHxS
  - In a study with Swedish women, serum PFHxS concentrations (4,7 ng/ml) are lower than PFOS (20,7 ng/ml), but higher than PFOA (3,8 ng/ml) (Karman et al., 2007)
  - Half-live in retired fluorochemical workers: 8,5 years (Olsen et al., 2007)
  - Half-life in mice: 25 – 30 days (Sundström et al., 2012)
  - Half-life in male monkeys: 141 days (Sundström et al., 2012)
  - Half-life in female monkeys: 87 days (Sundström et al., 2012)
  - Urine is the main route of elimination of PFHxS (Sundström et al., 2012)
  - Studies that looked at the effects of maternal exposure levels during pregnancy and anthropometry of their new-born babies have been inconsistent (cited in Bull et al., 2014)

Long-chain PFAS

- Bioaccumulation potential: high (U.S. EPA, 2009)
  - Perfluorohexadecanoic acid (C16): BCF = 4.700 – 4.800 (Carp)
  - PFODA (Perfluorooctadecanoic acid) (C18): BCF = 320 – 430 (Carp)
- Environmental Toxicity testing: The acute toxicity of C9 –C20 PFCAs is low to moderate with acute EC/LC50 values between 8,8 – 285 mg/l (Environment Canada, 2012)
- Biochemical responses due to exposure to long-chain PFCAs in environmental toxicity testing: vitellogenin induction, oxidative stress and chemical sensitization in species such as marine mussels, rainbow trout and Baikal seals (Environment Canada, 2012)
- No data on carcinogenicity for the long-chain PFAS
- Summary of information for some long-chain PFAS:
  - PFNA (Perfluorononanoic acid) (C9)
    - Half-life in male mice: 34-68 days (Tatum-Gibbs et al., 2011)
    - Half-life in female mice: 25-68 days (Tatum-Gibbs et al., 2011)
    - Half-life in male rats: 29-30 days (Tatum-Gibbs et al., 2011)
    - Half-life in female rats: 1,4-2,4 days (Tatum-Gibbs et al., 2011)
  - PFDA (perfluorodecanoic acid) (C10)
    - Half-life in male rats: 40 days (Ohmori et al., 2003)
    - Half-life in female rats: 58 days (Ohmori et al., 2003)
  - PFDS (Perfluorodecane sulfonic acid) (C10)
    - No data available

Others (Precursors, Fluorotelomers)

- 8:2 FTOH (8:2 Fluorotelomer alcohol) (precursor of PFOA) (information from Bull et al., 2014):
  - Half-life in rats: < 5 hours
  - Excretion primarily via the faeces (> 70%)
  - Metabolism to PFOA, PFNA, PFDA, and other long chain PFCAs
  - Presence of the FTOH metabolites in blood following occupational exposure suggests metabolism of FTOHs to high levels of PFOA and PFNA in humans
  - NOEC (oral gavage, 90 days, rats, repeat dose toxicity): 5 mg/kg bw/day
  - NOEC(oral diet, 74 days, rats, reproductive toxicity): 25 mg/kg bw/day
  - NOEC (oral diet, 74 days, rats, developmental toxicity): 200 mg/kg bw/day

DEPA (2013) states: “Results from analyses of PFAS in polar bears indicate that fluorotelomers also contribute to the total bioaccumulation of per- and polyfluorinated compounds in these animals because perfluorononaic acid (PFNA) was almost only found in its linear form while both linear and branched isomers were observed for PFOA”.

5. REGULATION

Concern around the environmental effects of PFAS use began in the late 1990s when it was realised that, due to their resistance to biodegradation, PFOS and PFOA were ubiquitous in various biological (wildlife and humans) and environmental (water bodies) matrices, and could biomagnify. The degree of biomagnification is proportional to perfluorocarbon chain length and so regulatory initiatives to restrict the use of PFAS have focussed on the long chained PFAS. With global restrictions now in place for PFOS, further regulation is proposed in Europe and elsewhere to restrict the manufacture and use of any PFAS substance that contains a C7 or C8 perfluorocarbon moiety in its molecular structure. As there is a growing understanding of the properties of PFAS, it is clear that further information on their toxicology, persistence and bioaccumulation ptotential is required to further define which specific PFAS compounds pose a potential for risk to human health and the environment.

In 2009, PFOS was added to Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs), meaning that measures must be taken to restrict its production and use. In Europe, the use of PFOS is banned, although there are some exemptions. Substances or mixtures may not contain PFOS above 0,001 wt% (EU 757/2010). A derogation for the use of legacy fire-fighting foam stocks containing >0,001 wt% PFOS ended on June 27th 2011.

Since 26th June 2013, PFOA and its ammonium salt (APFO) have been identified as chemicals of “very high concern” and added to the candidate list of the European Chemicals Agency (ECHA). Since that time, four further long-chain PFCA (11 to 14 carbon atoms) have been identified as substances of very high concern. In a restriction proposal submitted to The European Chemicals Agency (ECHA) in 2014, Germany and Norway requested that the concentration of PFOA and possible PFOA precursors in products placed on the market be limited to <2 ppb, which is 5.000 times lower than the current limit for PFOS (0,001 wt%, or 10.000 ppb). The restriction proposal also covers substances having linear or branched perfluoroheptyl derivatives with the formula C7F15- as a structural element (ECHA, Annex XV Restriction Report, 2014). At the time of writing (Nov 2015), the second public consultation was ongoing (public consultation of the draft SEAC opinion). While the manufacture and use of short chain PFAS is still permitted, their persistence in the environment increases the risk of future use restrictions.

In 2013, PFOS and its derivatives were included in the EU Directive on Environmental Quality Standards (2013/39/EU amending 2008/105/EC). The EU annual average environmental quality standard (EQS) for PFOS in surface freshwater is set at a very low criterion of 0,00065 µg/l, based on the potential for secondary poisoning in humans due to fish consumption. The EQS of 0,00065 µg/l is derived from starting points that are considered by many as very conservative, and is lower than background levels typically recorded in surface waters (see Section 6). It is also lower than the LOQ typically achieved by commercial laboratories. The date set for EU-wide compliance with the EQS is 22nd December 2027, with member states required to submit to the Commission a supplementary monitoring programme and a preliminary programme of measures to achieve compliance by 22nd December 2018.

Provisional drinking water standards developed by EU member states are generally around 0.1 to 0.5 µg/l PFOS, which is 3 orders of magnitude higher than the Annual Average EQS. In those countries where target values for groundwater have been derived these are within a similar range. Environmental standards may also encompass a range of other PFCAs and PFSAs, with limits set both for individual

substances and also the total PFAS concentration. The available provisional drinking water, groundwater and soil guidelines are summarized in **Table 5.1**.

Table 5.1: Overview of (provisional) guidelines for drinking water, groundwater and soil in European countries and abroad

Drinking Water Criteria in µg/l in European Countries															
	PFOS	**PFOA**	**PFOSA**	**PFBS**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFNA**	**PFDA**	**6:2 FTS**	**PFHpS**	**PFHxS**	**PFPeS**	**Remark**
Denmark	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	-	(0,1)	-	Sum of these 12 parameters: 0,1 µg/l
Germany	0,3	0,3	-	-	-	-	-	-	-	-	-	-	-	-	
The Netherlands	0,53	-	-	-	-	-	-	-	-	-	-	-	-	-	Values not included in legislation, but can be used in case of a PFOS contamination
Sweden	0,09	(0,09)	-	(0,09)	-	-	-	-	-	-	-	-	-	-	This limit is also applied for the sum of PFOS, PFHxS, PFBS, PFOA, PFHpA, PFHxA and PFPeA
U.K.	0,3	0,3	-	-	-	-	-	-	-	-	-	-	-	-	Tiered approach (concentrations of Tier 1 included)
Drinking Water Criteria in µg/l abroad															
	PFOS	**PFOA**	**PFOSA**	**PFBS**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFNA**	**PFDA**	**6:2 FTS**	**PFHpS**	**PFHxS**	**PFPeS**	**Remark**
Minnesota	0,3	0,3	-	7	7	-	-	-	-	-	-	-	-	-	
New Jersey	-	0,04	-	-	-	-	-	-	0,013	-	-	-	-	-	
U.S. EPA	0,2	0,4	-	-	-	-	-	-	-	-	-	-	-	-	
Canada	0,3	0,7	-	-	-	-	-	-	-	-	-	-	-	-	

Groundwater Criteria in µg/l in European Countries															
	PFOS	**PFOA**	**PFOSA**	**PFBS**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFNA**	**PFDA**	**6:2 FTS**	**PFHpS**	**PFHxS**	**PFPeS**	**Remark**
Denmark	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	(0,1)	-	(0,1)	-	Sum of these 12 parameters: 0,1 µg/l
Germany	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
State of Bavaria	0,23	-	-	3,0	7,0	3,0	1,0	0,3	0,3	0,3	-	-	-	-	PFOS + PFOA + PFHxS: 0,3 µg/l
State of Baden-Württemberg	0,23	0,3	-	3,0	7,0	3,0	1,0	0,3	0,3	0,3	0,3	0,3	0,3	1	(1) In the case that PFOS, PFOA, H4PFOS, PFNA, PFDA, PFHpS, PFHpA, PFHxS, PFHxA, PFPeS, PFPeA, PFBS and PFBA occur at the same time: Concentration/limit value <1 (2) Each additional per- and polyfluorinated compound: 1 µg/l, each

Groundwater Criteria in µg/l in European Countries															
The Netherlands	0,023	-	-	-	-	-	-	-	-	-	-	-	-	-	Values not included in legislation, 4 different target values were derived for different site use scenarios. 0,023 is the most stringent value.
Groundwater Criteria in µg/l abroad															
	PFOS	**PFOA**	**PFOSA**	**PFBS**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFNA**	**PFDA**	**6:2 FTS**	**PFHpS**	**PFHxS**	**PFPeS**	**Remark**
New Jersey	-	-	-	-	-	-	-	-	0,02	-	-	-	-	-	
Soil Criteria in mg/kg in European Countries															
	PFOS	**PFOA**	**PFOSA**	**PFBS**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFNA**	**PFDA**	**6:2 FTS**	**PFHpS**	**PFHxS**	**PFPeS**	**Remark**
Denmark	(0,4)	(0,4)	(0,4)	(0,4)	(0,4)	(0,4)	(0,4)	(0,4)	(0,4)	(0,4)	(0,4)	-	(0,4)	-	Sum of these 12 parameters: 0,4 mg/kg ts
Germany	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
State of Bavaria	Evaluation for pathway Soil -> Groundwater is based on Leachate Concentrations (µg/l) Evaluation for recycling of Soils is based on LAGA M20 Criteria														
The Netherlands	0,003	-	-	-	-	-	-	-	-	-	-	-	-	-	Values not included in legislation, 4 different target values were derived for different site use scenarios. 0,023 is the most stringent value.

More information about the global treaties and conventions, European legislation and national setting of guidelines is discussed in the sections below.

5.1. GLOBAL TREATIES AND CONVENTIONS

In May 2009, the parties of the Stockholm Convention - an international environmental treaty - decided to add PFOS to Annex B of the Stockholm Convention on POPs. This means that the parties must take measures to restrict the production and use of PFOS to those deemed acceptable purposes and/or specific exemptions listed in the Annex (Stockholm Convention, 2009). Acceptable purposes mean that there was no time limit put to the use, whereas specific exemptions meant that the exemption was only valid for 5 years after 2009:

- Acceptable purposes: Photo-imaging, photo-resistance and anti-reflective coatings for semi-conductors, etching agent for compound semi-conductor and ceramic filters, aviation hydraulic fluids, metal plating (hard metal plating) only in closed-loop systems, certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio-opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters), fire-fighting foams, insect baits for control of leaf-cutting ants from *Atta spp*. and *Acromyrmex spp*.

- Specific exemptions: Photo masks in the semiconductor and liquid crystal display (LCD) industries, metal plating (hard metal plating, decorative plating), electric and electronic parts for some colour printers and colour copy machines, insecticides for control of red imported fire ant, and termites, chemically driven oil

production, carpets, leather and apparel, textiles and upholstery, paper and packaging, coatings and coating additives, rubber and plastics.

In June 2015, the European Union has submitted a proposal to list PFOA, its salts (e.g. APFO) and PFOA-related compounds (e.g. 8:2 FTOH) in Annexes A, B and/or C[6] of the Stockholm Convention. The POPs review Committee (POPRC) will evaluate the proposal and will make recommendations to the Conference of the Parties. It will take at least 5 years to complete the procedures to list PFOA, its salts and PFOA-related compounds under the Stockholm Convention (Stockholm Convention, 2015).

5.2. EUROPEAN UNION LEGISLATION

5.2.1. EU Regulations regarding PFAS use

Legislation within the European Union (EU) is focused mainly on the use of PFOS and its derivatives. PFOS is currently classified under REACH (registration, evaluation, authorisation and restriction of chemicals) as a “PBT” substance (persistent, bioaccumulative and toxic).

The EU in effect banned the use of PFOS in finished and semi-finished products in 2006 (Directive 2006/122/EC). The maximum allowed concentration of PFOS in these products was 0,005%. Exemptions were made for certain industrial applications (e.g. photolithography, chromium plating industry, hydraulic fluids for aviation). In 2009 (Regulation EC 552/2009), this was incorporated into the existing REACH regulation (Annex XVII of REACH Regulation no. 1907/2006).

As described in Section 5.1, the parties of the Stockholm Convention decided in 2009 that the application and use of PFOS had to be restricted (Stockholm Convention, 2009). This was enforced through Regulation 850/2004/EC (relating to POPs) with PFOS added in 2010 (EU regulation 757/2010 dated 24 August 2010), and the threshold value lowered to or below 10 mg/kg (0,001 wt%) when it occurs in substances or in preparations.

Therefore, the following restrictions currently apply in the EU for PFOS and its derivatives ($C_8F_{17}SO_2X$, X=OH, metal salts, halide, amide and others, including polymers):

- Substances or mixtures may not contain PFOS above 0,001 wt%;
- Semi-finished products or articles or components containing PFOS 0,1 wt% or greater are not allowed to be brought into circulation;
- New textiles or other coated new materials with a content of 1 µg/m² or more are not allowed to be brought into circulation.

Exemptions apply for the following applications as long as no alternatives are available:

- Photo-resistive or anti-reflective coatings for photolithographic processes;
- Photographic coatings applied to films, papers, or printing plates;

[6] Annex A: measures must be taken to eliminate the production and use of these chemicals, Annex B; measures must be taken to restrict the production and use of these chemicals, Annex C: measures must be taken to reduce the unintentional releases of these chemicals.

- Mist suppressant for non-decorative hard chromium (VI) plating systems in closed loop systems;
- Hydraulic fluids for aviation and aerospace;
- PFOS-based wetting agents for controlled electroplating systems may still be used until August 26, 2015;
- Aqueous Firefighting Foams sold before December 27, 2006, could have been used until June 27, 2011. Currently firefighting foams have to contain less than 0,001 wt% PFOS.

For other PFAS, there are still no specific manufacturing or application restrictions in the EU, with the exception of Norway (see Section 5.3).

PFOA and its ammonium salt (APFO, perfluoro-ammoniumoctanate) recently have been identified as chemicals of "very high concern", as defined under the European chemicals regulation, REACH (http://echa.europe.eu/candidate-list-table). From 26 June 2013 these substances were added to the candidate list of the ECHA.

Germany and Norway proposed a restriction that covers the following substances:

- PFOA, including its salts;
- Any other substance having linear or branched perfluoroheptyl derivatives with the formula C_7F_{15}- as a structural element, including its salts, except those derivatives with the formula C_7F_{15}-X where X= F, Cl, Br;
- Any other substance having linear or branched perfluorooctyl derivatives with the formula C_8F_{17}- as a structural element, including its salts, except those derivatives with the formula C_8F_{17}-X, where X= F, Cl, Br or, C_8F_{17}-SO_2X', C_8F_{17}-C(=O)OH or C_8F_{17}-CF_2-X' (where X'=any group, including salts).

The proposed restriction covers the manufacturing, use and placing on the market of the above mentioned substances (derivatives of C8 and C7) as a substance, as a constituent of other substances, or in mixtures, if the concentration is equal or greater than 2 ppb (2 µg/kg). Articles containing these substances in concentrations equal to or greater than 2 ppb are also proposed to be restricted (ECHA, Annex XV Restriction Report, 2014).

Currently, the second public consultation is ongoing (public consultation of the draft SEAC opinion).

The German Federal Environmental Agency (UBA), together with the Norwegian Environmental Authority (Klif, now Miljødirektoratet), identified four more perfluorinated compounds as substances of very high concern: long-chain perfluorocarbonic acids with 11 to 14 carbon atoms (henicosafluoroundecanoic acid, tricosafluorodecanoic acid, pentacosafluorotridecanoic acid, heptacosafluorotetradecanoic acid). These compounds were added to the REACH candidate list on 19 December 2012 because of their very persistent and very bio-accumulating properties (vPvB). Consequently manufacturers and distributors must notify the ECHA, if their products contain more than 0,1 weight percent of these substances.

5.2.2. EU Environmental quality standards

The Directive on "Environmental Quality Standards" (EQSD) (Directive 2008/105/EC) is a daughter directive of the Water Framework Directive (WFD) and sets environmental quality standards for certain priority and priority hazardous substances. The list of these substances will be reviewed at regular intervals (currently set at six years) on the basis of scientific data and risk assessments. In Directive 2013/39/EC (12 August 2013) new priority hazardous substances were added, including PFOS and its derivatives, and a number of EU-wide environmental quality standards (EQS) were set. The EQS presented in the Directive were derived by RIVM (Dutch National Institute for Public Health and the Environment / Rijksinstituut voor Volksgezondheid en Milieu) in 2010 (RIVM, 2010).

The EQS for PFOS and derivatives are summarized in **Table 5.2**. The annual average EQSs (AA-EQS) set by the European Commission of 0,00065 µg/l (surface freshwater) or 0,00013 µg/l (coastal and transitional waters) are regarded as extremely challenging considering the current PFOS-levels recorded in European waters (see Section 6).

The derivation of the EQS is discussed in the PFOS EQS Dossier of 2011, prepared by the Sub-Group on Review of the Priority Substances List (under Working Group E of the Common Implementation Strategy for the Water Framework Directive).

The Maximum Allowable Concentration-EQS (MAC-EQS) was derived using a pooled freshwater-marine acute toxicity data set. The MAC-EQS for the freshwater environment ("Inland surface waters") is based on an acute toxicity test result using the marine mysid *Mysidopsis bahia* (96h LC50: 3,6 mg/l, with an assessment factor of 100). For the marine environment ("Other surface waters") the MAC-EQS is based on the same data point to which an additional assessment factor of 5 is applied (96h LC50: 3,6 mg/l, with an assessment factor of 500).

The AA-EQS was calculated based on 3 methodologies: (1) based on ecotoxicity, (2) based on secondary poisoning and (3) based on fish consumption by humans. The lowest calculated AA-EQS, in this case the one based on fish consumption by humans, was proposed as the AA-EQS for inland surface waters.

The following data were considered during derivation of the AA-EQS (based on fish consumption by humans): a TDI of 150 ng/kg bw/day (EFSA. 2008, see also Section 4.2.2), a human body weight of 70 kg, a daily consumption of 115 g fish, a maximum contribution of fish to the TDI of 10% and a BCF and BMF of 2.800 l/kg and 5 kg/kg (from water to fish), respectively.

For secondary poisoning (EQS Biota), the Cynomologus monkey subchronic study (6 months, chronic effects are not known) of Seacat et al. (2002) was used.

Table 5.2: EQS of the European Commission for PFOS and its derivatives

Name of substance	AA-EQS* (µg/l)		MAC-EQS** (µg/l)		EQS (µg/kg)
	Inland surface waters	Other surface waters	Inland surface waters	Other surface waters	Biota
Perfluoro octane sulfonate and its derivatives (PFOS)	0,00065	0,00013	36	7,2	9,1

* AA: Annual average
** MAC: Maximum allowable concentration

The new EU Directive 2013/39/EC entered into force on 9 September 2013, and must be transposed into Member State legislation by 14 November 2015. The new EQS in the directive should be taken into account during the establishment of supplementary monitoring programmes during implementation of the Water Framework Directive. The 'programmes of measures' have to be submitted to the European Commission by the 22 December 2018. Based on the aim of achieving good surface water chemical status, in theory the EQS of the newly identified priority substances have to be met by 22 December 2027.

Remarks on the EQS
The AA-EQS for PFOS in surface water 0,00065 µg/l is considerably lower than the (provisional) drinking water standards (roughly between 0,1 and 0,5 µg/l for PFOS, see next paragraphs). There is a difference of nearly 3 orders of magnitude.

The low level of the AA-EQS is driven by the starting point for the calculation being the consumption of fish. Wilson (2015) demonstrated that with alternative (also defendable) values for: TDI (0,3 vs. 0,15 µg/kg day), contribution of fish to dietary uptake (73% vs. 10%), average fish consumption rate (0,028 kg/day vs. 0,115 kg/day), bioconcentration and biomagnification factors (1.124 vs 2.800 and 2 vs 5), the AA-EQS could have been derived 375 times higher (0,24 µg/l).

5.3. NATIONAL LEGISLATION AND GUIDANCE IN EUROPEAN COUNTRIES

In most EU countries no additional national legal levels have been set. Most limits are still provisional and are being used as screening levels.

5.3.1. Denmark

The Danish Ministry of the Environment (DEPA, 2015) proposed the following health-based quality criteria in drinking water:

PFOS: 0,1 µg/l
PFOSA: 0,1 µg/l
PFOA (and salts e.g. APFO): 0,3 µg/l

Where PFOS, PFOA and PFOSA occur in the drinking water at the same time, the following criteria can be used (Concentration/Limit value < 1):

PFOA (conc. µg/l) / 0,3 µg/l + PFOS (conc. µg/l) / 0,1 µg/l + PFOSA (conc. µg/l) / 0,1 µg/l < 1

In the case that groundwater is directly used for drinking water consumption, the same criteria as for drinking water should be used for groundwater. In cases where contaminated soil affects the groundwater, the same health based drinking water quality criteria can be applied for the groundwater affected by the contamination (cited from DEPA, 2015).

DEPA (2015) has derived the following health-based soil quality criteria:

PFOS: 0,39 mg/kg soil
PFOSA: 0,39 mg/kg soil
PFOA: (and salts, e.g. APFO): 1,3 mg/kg soil

In the case that PFOS, PFOA and PFOSA occur in the soil at the same time, the following criteria can be used (Concentration/Limit value < 1):

PFOA (conc. mg/kg) / 1,3 mg/kg + PFOS (conc. mg/kg) / 0,39 mg/kg + PFOSA (conc. mg/kg) / 0,39 mg/kg

More recently, on 27 April 2015, DEPA proposed new drinking water, groundwater and soil criteria for the sum of 12 PFAS (DEPA, 2015b). **Table 5.3** gives an overview.

Table 5.3: Most recent provisional drinking water, groundwater and soil criteria from DEPA (27 April 2015)

Sum of:	Provisional drinking water and groundwater criterion (µg/l)	Provisional soil criterion (mg/kg TS)
PFBS	0,1	0,4
PFHxS		
PFOS		
PFOSA		
6:2 FTS		
PFBA		
PFPeA		
PFHxA		
PFHpA		
PFOA		
PFNA		
PFDA		

5.3.2. Germany

The only national legal set value in Germany is related to the use of soil fertilizers. The legal limit for the use of soil fertilizers set in the German Fertilizer Ordinance (Düngemittelverordnung, DüMV, December 2012) is 100 µg/kg dry matter for the Sum of PFOS and PFOA.

The Umweltbundesamt (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 PFAS (adults, long life exposure). They regard a maximum yearly average value of 0,1 µg/l – as a precautionary value – for the sum total of highly accumulating PFAS as adequate (Umweltbundesamt, 2006). The above mentioned criteria are currently also used for the protection of groundwater.

There are no federal regulated values for discharge water or soil.

State of Bavaria

The Bavarian State office for Environment (Bayerische Landesamt für Umwelt, LfU) has published provisional evaluation criteria for selected PFAS in groundwater, surface water and soil (LfU, 2015). These provisional criteria, applicable in the State of Bavaria are discussed below.

The provisional threshold values for groundwater are summarized in **Table 5.4**.

Table 5.4: Provisional threshold values for groundwater (LfU, 2015)

Parameter	Provisional threshold value (µg/l)
PFOS	0,23
PFOS + PFOA + PFHxS	0,3
PFBA	7,0
PFBS	3,0
PFPeA	3,0
PFHxA	1,0
PFHpA	0,3
PFNA	0,3
PFDA	0,3

These threshold values were derived based on the HRIV-Concept of the Drinking Water Commission of the Federal Ministry of Health and are also based on the criteria of LAWA (Länder-Arbeitsgemeinschaft Wasser) to derive the “no-effect-levels” (called “Geringfügigkeitsschwellenwerte”). An exceedance of the groundwater threshold values highlights an adverse change of the groundwater status according to the Water Resources Law.

As long as the EU Directive 2013/39/EU is not implemented, $PNEC_{aquatic}$ (Predicted No Effect Concentrations) values shall be used to evaluate PFAS impacts in surface water. LfU derived PNEC values based on investigations with rainbow trout and are summarized in **Table 5.5**.

Table 5.5: $PNEC_{aquatic}$ values for surface water (LfU, 2015)

Parameter	PNEC (µg/l)
PFOS	0,05
PFOA	570

To calculate the risk potential for the pathway Soil → Groundwater, leachate values (elution according to DIN 38414-S4, water-solid ratio 10: 1) are to be used, as the sole determination of solids content is not meaningful, due to the mobility behaviour of the PFAS. The PFAS concentration in the eluate is transferred to the leachate at the sampling location. The assessment is based on the preliminary Level-1 and Level-2 values, as listed in **Table 5.6**, in accordance with the procedure described in LfU leaflet 3.8/1.

Table 5.6: Preliminary Level-1 and Level-2 values for PFAS for the Pathway Soil → Groundwater (LfU, 2015)

Parameter	Preliminary Level-1 Value (µg/l)	Preliminary Level-2 Value (µg/l)
PFOS	0,23	1,0
PFOS + PFOA + PFHxS	0,3	1,0
PFBA	7,0	28,0
PFBS	3,0	12,0
PFPeA	3,0	12,0
PFHxA	1,0	4,0
PFHpA	0,3	1,0
PFNA	0,3	1,0
PFDA	0,3	1,0

The preliminary Level-1-values correspond to the threshold values for groundwater (see **Table 5.4**). Further investigation or additional evaluation is triggered in the case that these levels are exceeded. The preliminary Level-2 values are used directly as a criterion for groundwater and leachate at the sampling location. When the Level-2 value is exceeded, risks cannot be excluded and remedial measures are usually required.

For the recycling/reuse of mineral residues / wastes outside of landfills only clean soil (Class Z0) may be used. For this scenario, for a number of PFAS concentration values were set according to LAGA M 20 (Länder-Arbeitsgemeinschaft Abfall (LAGA), 2003). Recycling/reuse is only allowed if the eluate concentrations do not exceed the levels as indicated in **Table 5.7**.

In case of recycling/reuse of soil material in “unrestricted incorporation” in technical buildings according to LAGA M 20 (Status of 6 November 1997), the concentrations shall fulfill the criteria of Class Z0. Any use of soil material in “restricted open installations” in technical buildings according to LAGA M 20 is only allowed if the PFC-concentrations fulfill the criteria of Class Z1.1.

Table 5.7: Criteria for the S4-Eluate (based on LAGA M 20) (LAGA, 2003)

Parameter	Z 0 (µg/l)	Z 1.1 / Z 1.2 (µg/l)	Z 2
Σ PFHxS, PFOS, PFOA, $PFC_{C>8}$	0,1	0,3	1,0
PFHxA	0,3	1,0	4,0
PFPeA	1,0	3,0	12,0
PFBS	1,0	3,0	12,0
PFBA	3,0	7,0	28,0

The adsorption of PFAS to soil is highly dependent on the soil matrix (see also Section 3). Therefore threshold concentrations for soil were not calculated.

According to a letter from the Bavarian Ministry of 7th January 2008 (updated on 23 June 2014), all sewage sludge with potential use on agricultural land or for landscape planning and a capacity of water treatment plants of 1.000 population equivalent, shall be analyzed for PFAS. A precautionary value of 100 µg/kg dry matter (+ 25% measurement tolerance) is applicable (LfU, 2015) (Germany, 2009).

State of Baden-Württemberg

On 17 June 2015, the State of Baden-Württemberg (Ministerium für Umwelt, Klima und Energiewirtschaft) published provisional threshold values for groundwater. These provisional levels are summarized in **Table 5.8**.

Table 5.8: Provisional threshold values for Groundwater (Baden-Württemberg, 2015)

Nr	PFAS	Provisional Groundwater threshold (µg/l)
	PFOS	0,23
1	PFOS	0,3 [1]
2	PFOA	0,3
3	H_4PFOS [2]	0,3
4	PFNA	0,3
5	PFDA	0,3
6	PFHpS	0,3
7	PFHpA	0,3
8	PFHxS	0,3
9	PFHxA	1,0
10	PFPeS	1,0
11	PFPeA	3,0
12	PFBS	3,0
13	PFBA	7,0
	Other per- und polyfluorinated compounds	Each 1,0

[1]: For the case that the compounds with Nr. 1 to 13 are present at the same time, following criterion shall be used: Concentration/Limit value < 1. For PFOS, the Limit Value of 0,3 µg/l shall be used, instead of the Limit value of 0,23 µg/l for the single compound.
[2]: H_4PFOS = 6:2 Fluorotelomer sulfonic acid (6:2 FTS)

Most of the threshold values are taken from the UBA, TWK and LAWA.

5.3.3. The Netherlands

Following an accidental spillage of PFOS-contaminated AFFF in the Netherlands, the RIVM has derived risk based action levels for PFOS contamination (RIVM, 2011). These values have not been adopted into legislation, but can be used should an incident involving PFOS contamination take place.

A range of potential action levels have been defined based on background levels, and risk-based protection of ecology and human health. The four standards have been developed based on:

1. Reporting limit or (if higher) the background level of PFOS in soil and groundwater;
2. Eliminating ecological risks (based on evaluation being used in other frameworks, such as the Water Framework Directive). The values have been derived using two commonly used methods (**Table 5.2**);
3. Eliminating ecological effects (based on concentrations that effects have been observed in (ecotoxicological) experiments) and protection of groundwater as a drinking water resource;
4. Sustainable soil use (upper values based on risks to ecology and humans, based on evaluations used in other legislation such as re-use soil and sediment, including use for drinking water).

The RIVM-derived values are provided in **Table 5.9**:

Table 5.9: Risk based scenarios with derived action levels for PFOS

Scenario	Risk based value soil (µg/kg)	Risk based value groundwater (µg/l)
2a. Eliminating ecological risks (via established method preventive policy)	3,2	0,023
2b. Ecological protection (via sensitivity distribution species)	3,2	0,094
3. Ecological protection (ecotoxicological experiments) and quality of drinking water meets drinking water criteria	10	0,53
4. Permanent sustainable use of the soil (fit for use), groundwater quality meets drinking water criteria	100	4,7
	Reporting Limit / Background Level	
1. Reporting Limit /Background Level	0,1	0,010

One of the scenarios above could be used to determine risk based target levels, depending on the site setting and presence of receptors.

5.3.4. Norway

Norway is the only European Country where PFOA-containing consumer products are prohibited. The Environmental Agency of Norway restricted the use of PFOA in the Consumer Product Regulations (FOR 2004-06-01 nr 922, Section 2-32) as follows:

- Limit of PFOA in substances and mixtures with a maximum 0,001% PFOA, starting 1. June 2014
- Limit of PFOA in textiles, carpets and other coated consumer products with maximum 1 µg/m², starting 1. June 2014.
- Further restrictions on adhesives, foil, or tape in semiconductors, and photographic coatings for film, paper, or screen are extended on 1 January 2016.

The Norwegian guideline value for PFOS in soil is 100 µg/kg dry weight (Norwegian Pollution Control Agency).

5.3.5. Sweden

In 2014, Livsmedelsverket derived a maximum tolerable drinking water level of 0,09 µg/l for PFOS. As a precautionary measure, this limit was further applied for the sum of seven PFAS: PFOS, PFHxS, PFBS, PFOA, PFHpA, PFHxA and PFPeA (from DEPA, 2015).

5.3.6. United Kingdom

In 2009, the Drinking Water Inspectorate published guidance on the levels of PFOS and PFOA that water companies should act upon to fulfil their statutory obligations to ensure the safety of drinking water. The guidance is based on a multi-tiered approach and summarized in the table below (from Drinking Water Inspectorate, 2009):

Table 5.10: Guidance for PFOS and PFOA (from Drinking Water Inspectorate, UK)

Item	Regulatory requirement	Guidance value (concentration)	Minimum action to be taken
Perfluorooctane sulphonate (PFOS)			
Tier 1	Regulation 27 (Risk assessment)	potential hazard	• ensure considered as part of statutory risk assessment
Tier 2	Regulation 10 (Sampling: further provisions)	> 0,3µg/l	• consult with local health professionals; • monitor levels in drinking water.
Tier 3	Regulation 4(2) (Wholesomeness)	> 1,0µg/l	As tier 2 plus: • put in place measures to reduce concentrations to below 1.0µg/l as soon as is practicable.
Tier 4*	Water Industry (Suppliers' Information Direction) 2009 (Notification of events)	> 9,0 µg/l	As tier 3 plus: • ensure consultation with local health professionals takes place as soon as possible; • take action to reduce exposure from drinking water within 7 days.
*Note - notification to the Inspectorate may also be triggered at lower levels due to Tier 1, 2 or 3 activities			
Perfluorooctanoic acid (PFOA)			
Tier 1	Regulation 27 (Risk assessment)	potential hazard	• ensure considered as part of statutory risk assessment
Tier 2	Regulation 10 (Sampling: further provisions)	> 0,3 µg/l	• consult with local health professionals; • monitor levels in drinking water.
Tier 3	Regulation 4(2) (Wholesomeness)	> 5,0µg/l	As tier 2 plus: • put in place measures to reduce concentrations to below 5.0µg/l as soon as is practicable.
Tier 4*	Water Industry (Suppliers' Information Direction) 2009 (Notification of events)	> 45,0µg/l	As tier 3 plus: • ensure consultation with local health professionals takes place as soon as possible; • take action to reduce exposure from drinking water within 7 days.
*Note - notification to the Inspectorate under the Information Direction may also be triggered at lower levels due to Tier 1 2 or 3 activities			

5.4. LEGISLATION OUTSIDE EUROPE

For comparison reasons, further risk based values from outside of the European Union are included below.

5.4.1. U.S. EPA

In 2009, the U.S. EPA set the following drinking water guidance values (advisory levels):

- PFOA: 0,4 µg/l
- PFOS: 0,2 µg/l

If these provisional health advisory levels are exceeded, the use of water for drinking or cooking should be stopped. They reflect an amount of PFOS and PFOA that may cause adverse effects in the short term (weeks to months).

Currently, PFOS and PFOA are included by the U.S. EPA on the Draft Contaminant Chemical List 4 (CCL 4) (http://www2.epa.gov/ccl/chemical-contaminants-ccl-4), meaning that in the future regulation may be required under the Safe Drinking Water Act (SDWA).

Minnesota
More than ten years ago the Minnesota Department of Health (MDH) commenced the development of drinking water criteria for some PFAS. MDH published the following Health Risk Limits (HRLs) which are considered safe for people, including sensitive subpopulations (http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcshealth.html):

- PFOA: 0,3 µg/l
- PFOS: 0,3 µg/l
- PFBS: 7 µg/l
- PFBA: 7 µg/l

http://www.pca.state.mn.us/index.php/view-document.html?gid=2869

New Jersey
The Department of Environmental Protection of the State of New Jersey (NJ DEP) developed in 2009 a preliminary drinking water guidance value for PFOA, set at 0,04 µg/l (NJ DEP, 2009). This guidance level is the first phase of an ongoing process to establish a drinking water standard (MCL) for PFOA.

Related to this low drinking water guidance criteria, NJ DEP writes the following: “This value is the lower end of the range of values derived based on several non-cancer and cancer endpoints in different species, most of which cluster within a factor of two of this value. This drinking water concentration is expected to be protective of both non-cancer effects and cancer at the one in one million risk level. The recommendations provided here will be re-evaluated as additional data on PFOA’s effects and kinetics in humans and animals become available”.

In July 2015, the New Jersey Drinking Water Quality Institute proposed a drinking water maximum contaminant level (MCL) for PFNA (perfluorononanoic acid) of 0,013 µg/l, which is a protective level for chronic drinking water exposure and

technically feasible (NJ Drinking Water Quality Institute, 2015). The New Jersey Drinking Water Institute recommends “that NJ DEP propose and adopt an MCL of 13 ng/l for PFNA in drinking water”.

In 2014, NJ DEP developed a draft interim groundwater criterion for PFNA, set at 0,02 µg/l (NJ DEP, 2014).

Preliminary guidance values for PFOS are not available.

5.4.2. Canada

In 2010, Health Canada set the following provisional drinking water guidance values for PFOA and PFOS:

- PFOA: 0,7 µg/l
- PFOS: 0,3 µg/l

In 2013, Environment Canada developed draft Federal Environmental Quality Guidelines (FEQGs) for PFOS. These FEQGs are summarized in **Table 5.11**.

Table 5.11 Draft Federal Environmental Quality Guidelines for PFOS in the environment in Canada (from Environment Canada, 2013)

Air	Sediment	Water (ng/l)	Fish Tissue (ng/g wet weight)	Wildlife Diet (ng/g wet weight food)		Bird Egg (ng/g wet weight)
				Mammalian	Avian	
N/A		6.000	8.300	4,6	8,2	1.900

These draft FEQGs are based on laboratory toxicity studies. If concentrations are detected above the FEQGs, Environment Canada conclude that adverse effects in the environment may occur.

6. CURRENT CONDITIONS OF EUROPEAN WATERS

Monitoring data from across the EU show the widespread occurrence of PFAS in surface water, with the very low EQS for PFOS in freshwater (0,00065 ug/l) often exceeded.

In an EU-wide survey, 122 water samples were collected in streams and rivers of 27 European countries (sampling in 2007, Loos et al., 2009). PFOS was detected in 93% of the samples with the highest concentration (1,371 µg/l) in the River Krka in Slovenia. PFOA was detected in 97% of the samples at a maximum concentration of 0,174 µg/l. In addition to PFOS and PFOA, a wide range of other PFCAs and PFSAs were also detected.

A survey of 40 PFAS in surface water along the River Rhine watershed from Lake Constance to the North Sea found that total PFAS concentrations ranged from 0,00035 µg/l in the North Sea to 0,621 µg/l in the River Scheldt. PFOS, PFOA, PFBS and PFBA were usually the major compounds, with the C4-PFAS compounds PFBS and PFBA, accounting for up to 94% of the total.

In a recent European study of PFAS concentrations in 90 waste water treatment plant effluents (Loos et al., 2013), PFOA, PFHpA and PFOS were detected in more than 90% of the waters, with PFOA at the highest median concentration (0,0129 µg/l).

More information about the sources of PFAS in European waters and the occurrence of PFAS in European surface waters is included in the following sections. It highlights the wide spread occurrence of PFAS in the environment but is not intended to give a complete overview.

6.1. SOURCES OF PFAS TO EUROPEAN WATERS

The sources which can release significant quantities of perfluorinated alkyl acids to the environment are industrial and municipal wastewater treatment plants (e.g. from textile industry, chrome-plating industry, among others), landfill leachate treatment plants, fire-fighting incidents and fire-fighting training areas (e.g., at airports, fuel production and storage facilities) and landfills. Furthermore, indirect emissions are caused by atmospheric degradation of precursor compounds, which is likely the major source of pollution in remote areas, causing local “background” concentrations of PFAS.

Municipal wastewater treatment plant effluents and infiltration of urban runoff and leaching piping are probably the major source of diffuse pollution to rivers and aquifers (Eschauzier et al., 2012). Loos et al. (2013) stated: “Often PFAS concentrations increase in wastewater treatment plants as a result of biodegradation of precursors during the activated sludge process. PFOA is generally fully discharged into receiving rivers, while about half of PFOS is retained in the sewage sludge”.

Loos et al. (2013) investigated the sources of PFAS contamination in European rivers. They assessed the effluents of 90 European waste water treatment plants and their effect on emerging polar organic contaminants. The study primarily focused on municipal wastewater treatment plants, but some plants treated industrial wastewaters. The research was a follow-on study for the surveys for organic contaminants carried out previously by the European Commission’s Joint Research Centre (Loos et al., 2009, 2010). The results are summarized in the **Table 6.1**.

Table 6.1: PFAS Concentrations and Detection Frequency in 90 European Waste Water Treatment Plants (Loos et al., 2009, 2010)

	Detection Frequency (%)	Median Concentration (ng/l)	Highest (single) Maximum Concentration (mg/l) [1]
PFOA	99	12,9	15,9
PFHpA (C7)	94	5,1	3,0
PFOS	93	12,2	2,1
PFNA (C9)	89	2,3	2,7
PFDA (C10)	81	2,9	1,7
PFHxA (C6)	71	5,7	23,9
PFHxS (C6)	70	3,4	0,922

[1] These concentrations are relevant in relation to the MAC-EQS under the Water Framework Directive (see Section 5.2.2).
Note: No data are available about the waste water treatment plants participating in the sampling campaign (no data on waste water source, country, capacity, exact sampling procedure, etc.), although the data are considered representative for the EU.

Loos et al. (2013) stated: "Despite the voluntary phasing out of the production of perfluorooctane sulfonyl-based chemicals in the USA in 2002 (by the main producers), and European restrictions on marketing and use of products containing PFOS coming into force in 2006 (EC, 2006), the detection of PFOS in WWTPs indicates that products containing PFAS are still releasing these substances into the environment". Low PFOS concentrations are still allowed (see Section 5.2.1), meaning that release of PFOS into the environment cannot be solely classified as "historical".

6.2. PRESENCE IN EUROPEAN SURFACE WATERS

In an EU-wide survey, a range of polar organic persistent pollutants were analysed in unfiltered water samples collected in 2007 at 122 sampling locations in streams and rivers in 27 European countries (Loos et al., 2009). PFOS was detected in 93% of the samples (reporting limit 1 ng/l). The PFOS concentrations reported by Loos et al. (2009) are summarized in the table below.

Table 6.2: PFOS Concentrations in some European Rivers, studied by Loos et al., 2009

River	Country	Maximum PFOS Concentration (µg/l)
Krka	Slovenia	1,371 [1]
Scheldt	Belgium	0,154
Scheldt	The Netherlands	0,110
Seine	France	0,097
Rhine	Germany (Wesel)	0,032

[1] Average PFOS concentration: 39 µg/l, Median PFOS concentration: 0,006 µg/l

PFOA was detected in 97% of the samples. The maximum level was 0,174 µg/l. The average and median were 0,012 and 0,003 µg/l.

Eschauzier and coworkers investigated data concerning the presence of perfluoroalkyl acids in European surface waters, groundwater and drinking waters (Eschauzier et al., 2012). Additional data from a monitoring programme of the European Commission Joint Research Centre are given on their website. It gives an overview of concentrations of (emerging) contaminants measured in 2007 (JRC, 2007). The monitoring data confirm the widespread occurrence of PFAS in surface water. PFOS concentrations often exceed the new environmental quality standards for freshwater (see Section 5.2.2) meaning that an environmental risk especially to fish-eating birds and mammals at the highest trophic levels of the food chain could in theory be present.

An overview of the occurrence of PFAS in the different regions of Europe is given in the following sections.

6.2.1. Scandinavia

Relatively low concentrations of PFAS have been found in the Nordic surface waters in comparison to the rest of Europe (Eschauzier 2012). This could be explained by the lower population density and reduced industrial activities. At locations near the larger cities (Oslo, Stockholm, Helsinki), higher values up to 0,050 µg/l have been measured (JRC, 2007).

Filipovic et al. (2015) investigated the distribution of some PFAS related to the usage of AFFFs at a military airport in Stockholm, Sweden. PFAS concentrations (as a sum-parameter) in the nearby groundwater ranged between 0,738 to 51 µg/l. Concentrations up to 0,079 µg/l were detected in surface water.

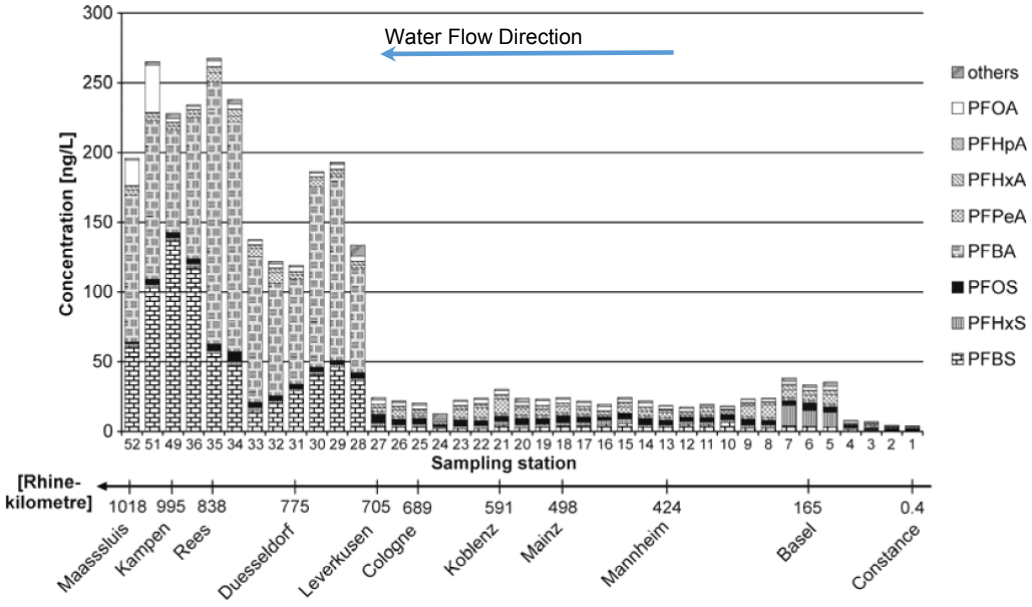
6.2.2. River Rhine and other big central European Rivers

The central European rivers have higher concentrations and mass discharges of PFAS than those in the Northern European countries. The rivers Rhine, Rhone, Danube, Po and Scheldt have been studied extensively (e.g. Eschauzier et al., 2012, Moeller et al., 2010).

Moeller and co-workers studied the concentration profile of 40 PFAS in surface water along the River Rhine watershed from Lake Constance to the North Sea (Moeller et al., 2010). In the study, 75 water samples were taken along the course of the River Rhine as well as several major tributaries such as the Rivers Neckar, Main, Ruhr and waters from the Rhine-Meuse delta (Rivers Meuse and Scheldt). In this research, the concentrations of PFAS (total), measured in 2008, ranged from 0,00035 µg/l in the North Sea to 0,621 µg/l in the River Scheldt. PFOS, PFOA, PFBS and PFBA were usually the major compounds. The C4-based compounds, PFBS and PFBA, were found to be the predominating PFAS, with a percentage contribution of up to 94%.

In the River Rhine the concentrations of PFAS increase from 0,005 to 0,260 µg/l as the water flows downstream. Two large increases in concentrations have been measured, as can be seen in **Figure 6.1**.

Figure 6.1: PFAS concentration profile in surface water along the River Rhine (Moeller et al., 2010)



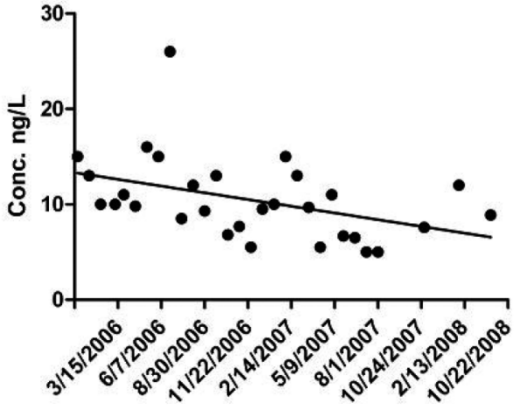
The first sharp increase occurs between station 4 and 5 by a factor of approximately 10 for PFHxS. The source could not be identified, but was likely caused by direct industrial emissions or indirectly via wastewater treatment plant effluents.

The second sharp increase occurs between station 27 and 28. This increase was found to be originating from the effluent of a wastewater treatment plant treating industrial wastewaters near the city of Leverkusen. By the end of 2008 measures had been taken to reduce the discharge of PFBS and PFBA at this wastewater treatment plant, which resulted in concentrations decreasing to about 0,010 µg/l at Station 28 in 2009 (Moeller et al., 2010).

In general, the concentrations PFOS and PFOA were lower in this study compared to earlier studies, but the concentrations of PFBS and PFBA were higher. This might be a result of the decreasing usage of PFOA and PFOS and the replacement of these compounds by the C4-based compounds PFBS and PFBA, although the difference may also be due to a variation in the time of sampling and the exact sampling locations.

Downstream along the River Rhine, at Nieuwegein (NL) (between Kampen and Maassluis in **Figure 6.1**), in the period of 2006-2009, the concentrations of PFOS and PFOA were below 0,030 µg/l for each compound. In this period, the concentrations of PFOS and PFOA show a decreasing trend (**Figure 6.2**).

Figure 6.2: Concentration of PFOA (ng/l) in the River Rhine at Lekkanaal, Nieuwegein (NL), sampled in the period of 2006 to 2008 (Eschauzier, 2012).



The River Moehne (Germany), which is a tributary of the River Ruhr, showed the highest concentrations of PFAS. The source of this contamination is related to the accidental release of PFAS via contaminated soil improvers applied on agricultural areas in the Moehne catchment in 2006 (Moeller et al., 2010).

In the River Scheldt (Belgium), the total PFAS concentration increased by a factor of 2.5 downstream of Antwerp (from 0,233 to 0,621 µg/l). Industrial plants located in the harbour area of Antwerp, including a fluorochemical manufacturing facility, have been reported as the likely sources (Moeller et al., 2010).

The mass discharge of PFAS into the European rivers was shown to correlate with the population of the catchment and thus (partly) explains the higher concentrations encountered in populated areas (Eschauzier, 2012).

Ahrens and coworkers (2010) examined the spatial distribution of 15 PFAS in surface water in the North Sea. The highest concentration was found near the coast, whereas the concentrations decreased rapidly from 0,018 to 0,00007 µg/l towards the open North Sea (past the coastal sampling points).

6.2.3. Italy

High concentrations of PFOA, with mean concentrations of 0,089 µg/l (Loos et al., 2008) and 0,200 µg/l (McLachlan et al., 2007), have been reported in the River Po, Italy. In a more recent study (Castiglioni, 2014), nine PFCAs and three PFAS have been monitored in the area of Milano. The mass balance of the emissions in the River Lambro basin showed continuously increasing contamination as the water moves downstream. The contamination originated mainly from industrial sources (90%) compared to urban sources. In the Veneto area, high concentrations have been measured, with total PFAS concentrations exceeding 1 µg/l (written question to the European Parliament, 2013).

6.2.4. United Kingdom

A UK study on the prevalence of PFOS, PFOA and related compounds in 2008 showed that PFOS and PFOA do not appear to be widespread background contaminants of drinking water in England. At sites where specific pollution incidents have occurred, contamination of environmental waters with PFOS has been encountered (Atkinson, 2008).

One of the known incidents in the U.K. occurred on 11 December 2005 at the Hertfordshire Oil Storage Terminal (known as the Buncefield Fire). More than 250.000 liter of AFFF was used to extinguish the fire, resulting in a considerable impact of soil and groundwater with PFAS and oil compounds.

Furthermore in the River Wyre high concentrations of PFOA (0,100 µg/l) have been encountered, and in the River Severn, high concentrations of PFOS have been encountered (0,238 µg/l) (Loos et al., 2009 / JRC).

Generally, minimal work has been done in the UK to understand background levels in groundwater or surface water.

6.2.5. Poland

A study in Poland reported concentrations of PFOS in rivers, lakes, streams in Poland and in the coastal region of the Baltic Sea. The concentrations varied between < 0,0005 and 0,150 µg/l. PFHxS was also reported (< 0,00025 – 0,110 µg/l) and PFOA occurred in concentrations of <0,0005 to 0,018 µg/l. Long-chained carboxylates could only be found in water of a drainage ditch close to an industrial area (Rostokowski et al., 2009).

7. CHEMICAL ANALYSIS METHODS

While a range of standard methods are available for the analysis of PFSAs and PFCAs, many PFAS cannot be analysed readily due to the lack of appropriate reference materials. To address this difficulty analysis techniques have been developed whereby PFAS are quantitively oxidized to fluoride (AOF method), or a mixture of PFSAs and PFCAs (TOP method). The TOP method is most sensitive, with a detection limit around 1 ng/l range, vs 1 ug/l for AOF).

Whereas the target levels in groundwater for PFOS can sufficiently and reliably be measured and are above background levels, the AA-EQS of 0,00065 µg/l is so low that it lies beyond the operational range of commercial (and most other) laboratories.

In the subsequent sections a short overview of analytical possibilities and challenges is given. In **Appendix 4** more detail is given on this subject.

7.1. OVERVIEW OF STANDARD METHODS

Worldwide there are a variety of standard methods available applicable for the analysis of PFSAs and PFCAs, including the international standard ISO 25101:2009(E) for the analysis of PFOS and PFOA. Most of the international available standards are based on liquid chromatography with a tandem MS/MS detector. Since the preparation of the samples starts with sorption of the compounds on an ion exchanger, only compounds with a polar group like the perfluorinated carboxyl acids (PFCAs) and perfluorinated sulfonic acids (PFSAs) are captured. The German DIN procedure (HPLC-MS-MS) currently allows for the quantification of the highest number of compounds, and covers the analysis of PFOS and PFOA, and 8 other simple PFAS in soil and groundwater. However, currently (as of 2015) the analysis of up to 23 PFAS based on the DIN standard is offered by various commercial laboratories. The most challenging problem in extending this list is the availability of appropriate standards. In the scientific arena a number of other analytical methods are applied, such as the GC-MS-MS method for the determination of volatile facilitated telomers.

In commercial laboratories, the detection limit is in the range of 0.01 µg/l per compound. Only highly specialized laboratories are able to analyze the PFAS with one order of magnitude lower detection limit.

7.2. AOF AND TOP, TWO NEW SUM PARAMETERS

Many compounds used especially in fire extinguishing foams, but also in other industrial branches, are derivatives of the PFCAs or PFSAs. Since many PFAS cannot be analysed readily, it is appropriate to consider analysing a “sum parameter”, similar to adsorbable organic halogenated compounds (AOX)[7].

To determine the total PFAS content, the sum parameter AOF (absorbable organic fluorine compounds) has been developed. This analytical method, based on Combustion Ion Chromatography, is currently undergoing standardization. Because of the relatively high detection limit (1 µg/l fluoride) and the fact that the individual PFAS cannot be separated but show a substantially different toxicological potential, the AOF can only be used as guideline value and cannot be used to replace the

[7] The AOX (absorbable organic halogens) do not comprise any fluorinated compounds.

analysis of individual compounds. Furthermore, up to now, the correlation which could exist between AOF and PFAS has not been determined.

The other method (total oxidisable precursor, TOP) is an alternative which involves the oxidation of the precursors present in a sample during sample preparation to form PFCAs and PFSAs, which can then be quantified by a conventional analysis. An analysis of the sample with and without these oxidative pretreatment allows an estimate of the precursor content of the sample (Houtz, 2012)

7.3. SAMPLING

Specific precautions have to be taken in the sampling of environmental media since PFAS adsorb strongly to glass. Teflon-containing materials can lead to increased blank values if AOF is analysed, and may also interfere with the analysis by adsorbing PFAS. Currently the most appropriate material for sampling seems to be polyethylene or polypropylene. However, it is not yet clear whether screening at sub- ng/l level is feasible using currently available field sampling techniques.

8. SOIL AND GROUNDWATER REMEDIATION

The remedial options available to address PFAS contamination are limited by the unique physico-chemical properties of these compounds. Many remediation methods utilized to address hydrocarbon contamination, such as air stripping, sparging, soil vapour extraction and bioremediation, are ineffective due to the low volatility of these compounds and their resistance to microbial degradation

Technologies currently used for the remediation of PFAS contaminated sites include soil incineration or excavation to landfill (where authorized) and groundwater extraction with PFAS adsorption onto activated carbon or resins. Landfilling or adsorptive techniques do not include a destruction of the PFAS molecules and may lead to leachate issues in the future

Groundwater abstraction volumes may be high if remediation is required to very low environmental quality standards (e.g. for PFOS). Although the degree of sorption of PFAS to sediment is generally low, it can be significant if organic material is present. Sorption of PFAS to sediment, leading to retardation of transport in groundwater, increases with perfluorocarbon chain length and may extend the duration of groundwater extraction. Possible alternative techniques include soil washing, soil solidification and the use of in-situ permeable reactive barriers or funnel and gate systems.

Current best practice disposal routes for spent PFAS adsorption media are high temperature incineration at >1000˚C, or regeneration at a specialist facility.

Emerging water treatment technologies for PFAS, such as photolysis/ photocatalysis, reductive decomposition, advanced oxidation and sonolysis, require high energy input per unit water volume and long residence times. Careful monitoring of treatment performance is also required to ensure complete breakdown of the various PFAS substances that may be present. Consequently, these technologies are unlikely to be feasible for high flowrate, low concentration applications

The following sections provide more information about remediation technologies with proven success or potential for success in the future.

8.1. PFAS-IMPACTED SOILS, SUB-SOILS AND SOLID MATERIALS

Currently there are no proven biological or chemical techniques which can cause mineralization of all PFAS. The most recalcitrant PFAS are reported to be PFSAs such as PFOS, for which there are no proven methods causing mineralization *in situ*. Precursors and telomers (polyfluorinated compounds) may be broken down by microbial action or using certain chemical oxidants to form perfluorinated compounds as terminal “dead end” daughter products.

Excavation is the most commonly applied treatment method for PFAS impacts in the vadose zone. The excavated soil subsequently has to be placed into a landfill, or to be treated by other technologies. Looking to the future, excavation is not the preferred option for contaminated soil given the challenges faced with managing potential leachate generation or the high costs (financial, environmental) associated with other viable *ex situ* treatment options if the soils are not sent directly to landfill.

8.1.1. Landfills

While contaminated soil excavation and disposal to landfill is a remediation option, there may be challenges for the receiving landfill, because PFAS subsequently will become constituents of leachate (due to the high solubility of many PFAS) whereas the standard leachate treatment plants may not be able to effectively treat these substances. This is because they do not biodegrade (Oliaei et al., 2013). Landfills are already a source for release of PFAS to the environment since many consumer products are being placed into landfills at the end of their product life (e.g. impregnated carpets, textiles). Therefore, before sending soil contaminated with PFAS to landfills, checks should be undertaken to confirm that they are appropriately designed and managed so as to prevent further release into the environment.

8.1.2. Incineration

Excavated soil could also be treated by high temperature incineration. However, this can have significant cost implications alongside a large energy use requirement. Although PFOS was used as a fire suppressant, its thermal stability is limited (Giesy, 2010). This is based on the ease of cleavage of C-S bonds. However a very stable backbone remains with only C-F and C-C bonds (other PFAS). At 600°C, incineration of PFOS-contaminated material results in many by-products (Yamada and Taylor, 2003). In the same study, at higher temperatures (750 and 900°C) these by-products were not observed. Another study showed that a variety of reaction products can be formed at temperatures below 1.000°C (Yamada et al., 2005). For complete degradation, PFOS has to be destroyed with high temperature incineration at 1.000 – 1.200°C (Schultz, 2003; Yamada et al., 2005).

8.1.3. Immobilization (Solidification / Stabilization)

There is another alternative for vadose zone treatment. PFAS-contaminated soils can also be treated *in situ*. In this case, the contaminant will not be removed, but the leachability is reduced by immobilizing the contaminant(s). This can be done via stabilization and/or solidification. To stabilize the contaminant, additives such as activated carbon or other commercial products can be added, e.g. RemBind™ and MatCare™. Das et al., 2013 investigated the adsorption kinetics of PFOS on MatCARE™. This material displayed much faster kinetics (60 minutes) to reach adsorption equilibrium and significantly higher PFOS adsorption capacity (0,093 mmol g^{-1}) when compared to a commercially-available activated carbon. Subsequent release of PFOS over an incubation period of 1 year was negligible (0,5-0,6%) (Das et al., 2013). Das et al. 2013 did not investigate the effectiveness of the methodology for other PFAS.

It is also possible to solidify soil with different cement mixtures. Obviously the outcome is no longer a granular geology but a monolith, and the leachate depends upon the type of cement and mixing ratios.

Immobilizing solid materials prior to landfill disposal might also be an option to reduce leachate concentrations.

8.1.4. Soil Washing

There is anecdotal evidence that Soil Washing is a possible technique for concentrating PFAS into sludge or washing water. Since the sorption of PFAS is low to moderate, PFAS tend to move to the aqueous phase. A non-reported trial from

DEC contractors (presented during the NICOLE meeting on unconventional contaminants in Manchester, June 2015 www.nicole.org), indicated that a significant part of the soil fraction was cleaned below target levels after two washing cycles. The amount of sludge or GAC that needed to be incinerated or transported to a landfill and the costs were not evaluated.

8.2. PFAS-IMPACTED GROUNDWATER

8.2.1. Pump and treat

Currently, groundwater extraction is the only viable *in situ* remediation technique to treat PFAS-contaminated water. The technique relies on extraction of water, with subsequent treatment of the water.

Water treatment techniques such as granular activated carbon (GAC), ion exchange and nanofiltration or reverse osmosis have been shown to be effective in removing selected PFAS from water as part of a pump & treat system. A subsequent destruction step such as incineration is required for complete remediation. Of these water treatment techniques, GAC is currently the most commonly applied technology.

Granular Activated Carbon (GAC)

This technique has been shown to be effective in removing PFOS and PFOA at parts per billion levels from relatively clean water (see **Figure 8.1**). GAC consistently removes PFOS at µg/l concentrations with an efficiency of more than 90% (Ochoa-Herrera, 2008, Eschauzier, 2011). However, GAC can be inefficient at removing PFOA and other PFAS (Oliaei, 2006). PFAS sorption is lower than organics with similar molecular weights (Qui, 2007), and other co-contaminants will compete for, and preferentially utilize, the adsorptive potential of the GAC media. The sorption velocity is faster for longer-chained PFAS and smaller diameter GAC particles; therefore, GAC that is optimized for PFOS removal will not optimally remove other PFAS (Qui, 2007, Eschauzier, 2011). Adsorption loadings for GAC are relatively low compared to other contaminants, and competition occurs when other contaminants are present.

Other types of adsorbents that have been used for PFAS include powdered activated carbon, polymers, maize straw derived ash, alumina and montmorillonite (Yu et al., 2011; Senevirathna et al., 2010; Hansen et al., 2010; Qu et al., 2009, Yu et al., 2009; Chen et al., 2011; Zhou et al., 2010). Commercial products have been developed for PFAS adsorption claiming better performance for shorter PFAS than conventional GAC. Spent adsorptive media are typically incinerated at high temperature (>1000^{o}C) or thermally regenerated at a specialist facility, thereby adding to the overall management cost.

Ion Exchange Resins

Ion exchange resins or ion exchange polymers provide a large surface area onto which PFOS can attach. The contaminant removal from water is achieved by the attraction of the negatively charged functional to positively charged functional groups within the resin. The removal is stoichiometric, unlike sorption. A variety of resins containing different functional groups are available. Ion exchange resins are considered suitable for low concentration and high volume water treatment applications. Upon reaching maximum capacity of the resin, regeneration with NaCl solution, ethanol or hot water is possible and would produce a low volume concentrated PFOS waste stream ready for incineration. (Ochoa-Herrera 2008, Du et al., 2014).

For PFOS, different ion exchange resins can be suitable. Sorption using ion-exchange polymers is based on the attraction of the negatively charged functional group of PFOS, and also on the relatively negatively charged tail (due to electron negativity of the fluorine atoms). Non-ion exchange polymers usually show weaker bonding between the adsorbent and adsorbate, which makes regeneration easier and regeneration can occur, for example by solvent washing (Senevirathna et al., 2010). Anion-exchange resins exhibit higher adsorption capacity (Du et al., 2014).

In general sorption capacities decrease in the following order:

ion-exchange polymers > non-ion-exchange polymers > GAC

However, at lower concentrations (100 ng/l) non-ion exchange polymers showed higher adsorption capacity than other adsorbents. Adsorption kinetics highlight that GAC and ion-exchange polymers show fast sorption kinetics, much faster than non-ion exchange polymers (Senevirathna et al., 2010).

Chitosan beads have a high adsorption capacity of about 5.5 mmol/g for PFOS mainly due to the formation of micelles in porous materials. Anion-exchange resins show an adsorption capacity of about 4-5 mmol/g for PFOS (Du et al., 2014).

Nano Filtration and Reverse Osmosis

Nano filtration (NF) and reverse osmosis (RO) are relatively similar processes. Both allow the selective passage of a solvent, while the solutes are retained partially or completely. In a study the NF membranes in general had lower rejections than RO membranes. This was expected as NF membranes have larger pores and thinner rejection layers. Removal efficiencies for NF ranged from 90-99% (Tang, 2007; Schröder, 2010).

The use of RO membranes is a widely accepted filtration technique. Tang (2007) reports on a study of thin film composite polyamide RO membranes, where 99% removal of PFOS was achieved with several types of membranes at concentrations >1 mg/l. RO is normally used in the drinking water industry for removal of PFAS and other contaminants (Tang, 2007).

8.2.2. Permeable Reactive Barriers

There is no experience available with Permeable Reactive Barriers (PRB) or Funnel and Gate systems, but there is no reason why some of the water treatment techniques, as described in the previous paragraph (GAC, Ion Exchange Resins) should not work in a GAC-sand PRB or a Funnel and Gate with exchangeable cassettes. Also other sorbtive media like e.g. RemBind™ and MatCare™ might work in these systems. Currently research is being conducted about the applicability of several PRB technologies (e.g. SERDP/ESTCP dossiers ER-2423 and ER-2425).

8.3. DEGRADATION OF PFAS

Research is currently being conducted on methods to achieve degradation of PFAS. A number of the key methods are summarized in this section. However there are still a number of concerns:

- Contaminated media often contain a complex mix of multiple PFAS. Often the amount of precursors is more than significant. Incomplete breakdown may result in an increase in PFCAs or PFSAs, an adverse effect.

- Most research is being conducted using demineralized water instead of environmental samples. Matrix effects can play a large role in the efficiency of treatment processes;
- Research is focused mainly on PFCAs (e.g. PFOA) but less on PFSAs (e.g. PFOS), whilst degradation of PFSAs is more difficult than PFCAs
- The studies mainly focus on the disappearance of the parent products (e.g. PFOS or PFOA), with less attention given to the reaction products and yield of fluoride.

Oxidation

According to Vecitis (2009), PFOS and PFOA oxidation is slow due to the high electronegativity of the fluorine atoms surrounding the carbon chain. They are recalcitrant towards oxidation due to the complete substitution of fluorine (C-F bond) for hydrogen (C-H bond). The perfluorinated backbone of PFOS and PFOA will also reduce the oxidizability of the ionic functional group ($-SO_3^-$ for PFOS and $-CO_2^-$ for PFOA), since it inductively reduces functional group electron density. Thus the perfluorination of PFOS and PFOA renders these compounds very difficult to degrade by advanced oxidation techniques. The presence of any other dissolved organic compound besides aqueous PFOS and PFOA will competitively inhibit degradation by oxidation, due to its low reaction rate (Buxton, 1988).

Nevertheless, several laboratory studies attest to the feasibility and varying degrees of effectiveness of chemical oxidation for PFOA destruction (Hori et al., 2005, 2008; Ahmad 2012; Hao, 2014). Several variations of oxidation processes using persulfate show promising results for degrading PFOA (Hori et al., 2005, 2008). PFOA was also effectively destructed by ultraviolet-activated Fenton oxidation (Tang et al., 2012). Although the hydroxyl radical does not degrade PFOA, chemical oxidation systems can be effective in treating PFOA via alternative radical species (Ahmad, 2012). However, these studies focus mainly at treatment of PFOA and have not been validated for treatment of other PFAS too.

A challenge may be the complex composition of contaminated media and the presence of precursors which have large organic functional groups that can be oxidized via conventional oxidative processes (e.g. hydroxyl radical mediated) leaving PFCAs or PFSAs.

Reduction

Perfluorinated compounds are difficult to defluorinate due to the low reduction potentials of fluorine ($E < -2,7$ V). Only the aqueous electron and alkaline metals have lower standard reduction potentials. Sub-critical elemental iron reduction (high temperature, high pressure) has been reported to degrade PFOS. However this is not feasible for *in situ* application.

The solvated electron is a powerful reductant ($E = -2,87$ V). Other reduction possibilities include alkaline 2-propanol photolytic reduction and vitamin B12 mediated reduction, however these options are costly (Vecitis, 2009).

Sonochemistry

Sonochemistry is the generation of chemical reactions by application of an acoustic field to a solution. High intensity ultrasound creates waves of compression and rarefaction, leading to the production and subsequent collapse of sub-microscopic bubbles. If the bubbles collapse within 1 microsecond and vapour temperatures near 4.700 °C and high pressures are generated, then PFAS will pyrolytically decompose at the bubble-water interface (Moriwaki et al., 2005; Cheng et al., 2008, 2009). The

proposed reaction mechanism is degradation of PFOS due to oxidation after dissociation of the SO3-group, which generates PFOA. The PFOA will then undergo shortening of the perfluorocarbon chain caused by repetition of the COO-dissociation (Moriwaki et al., 2005).

In environmental media, in which more compounds are present than in demineralized water, lower degradation rates were observed for sonochemical degradation. For example, in landfill groundwater the degradation rate was reduced by 61% and 56% for PFOS and PFOA respectively, due to the presence of other organic constituents. (Cheng et al., 2008). The lower degradation rate was caused by other organic contaminants, rather than dissolved organic matter. A combined process of ozonation and sonolysis has shown to recover the rate loss for PFOS and PFOA.

Inorganic groundwater constituents also negatively affect PFAS sonochemical kinetics. Cheng and co-workers evaluated the effects of several inorganic species on sonochemical kinetics. It showed that the rate of reduction in the groundwater was primarily due to the presence of bicarbonate. Common cations had negligible effects (Cheng et al., 2009).

Photolysis

PFCAs and PFSAs have shown to be very persistent in the environment, there is no solid evidence that these compounds degrade photolytically under natural light conditions. There are references present that show that PFOS, PFOA and PFDA can degrade in the laboratory under circumstances in the UV-C range (Wang et al., 2015). The adsorption is weak up to 220 nm and even lower from 220 to 600 nm.

Adding $FeCl_3$ increases the applicable absorption region (Jin et al., 2014). In this research, PFOS concentrations decreased below the detection limit within 48 hours. A reaction mechanism was proposed, with intermediates of mainly C2-C8 PFCAs. After 72 hours, 74% of the fluorine could be accounted for, with 58% as free fluoride.

9. CONCLUSIONS

- Poly- and perfluoroalkyl substances (PFAS) have been used since the 1970s in a wide range of industrial and commercial products as oil, water and stain repellents and surfactants. Relevant to the refining industry is the use of PFAS in class B (flammable liquid) fire-fighting foams, including Aqueous Film Forming Foam (AFFF), Fluoroprotein (FP) and Film Forming Fluoroprotein Foam (FFFP).
- The unique physical and chemical properties of PFAS mean they are difficult to replace with equally effective substitutes in many products, including class B fire-fighting foams.
- Limited physicochemical and toxicological data is available for many poly- and perfluoroalkyl substances (PFAS) and properties can vary greatly with respect to head group and chain length. Some PFAS have been identified as PBT; persistent, bio accumulative and toxic for humans and wildlife. PFOS and PFOA are the most well-known and studied compounds within this group.
- PFOS was added in 2009 to the Stockholm Convention on Persistent Organic Pollutants. While some PFAS can degrade in the environment, many end-products (including PFOS and PFOA) do not mineralize, making them very persistent. In addition, several PFAS bio-accumulate and many are highly soluble and mobile in the environment.
- PFAS sources to the environment include landfills, waste-water treatment plants, fire-fighting training areas and PFAS manufacturing plants. There are also numerous diffuse sources associated with the use of PFAS in consumer products.
- While there is ongoing debate around the toxicity of PFAS and whether they are carcinogens, there is sufficient evidence to trigger increasing regulatory focus in many parts of the world, including Europe.
- The European Union has set a very low annual average environmental quality standard (AA-EQS) for inland surface water of 0,00065 µg/l, based on the potential for secondary poisoning in humans due to fish consumption. The date set for EU-wide compliance with the AA-EQS is 22nd December 2027, with member states required to submit to the Commission a supplementary monitoring programme and a preliminary programme of measures to achieve compliance by 22nd December 2018
- Background PFOS concentrations in many European surface water bodies are higher than the AA-EQS, which presents major challenges for compliance. In addition, the analytical methods currently used by commercial laboratories yield quantification limits above or close to the AA-EQS.
- Environmental quality standards vary across EU member states and may encompass a range of other both short and long chain poly- and perfluorinated compounds, with limits set for both individual substances and also the total PFAS concentration.
- Commercial products (including AFFF) may contain PFAS substances for which commercial analysis methods are not yet available, and which may biotransform into PFAS of concern. The potential contribution from such precursor substances can be assessed by pre-treating environmental samples to convert unknown PFAS into a suite of readily analysable PFSAs and PFCAs.
- PFAS in soil and groundwater are currently difficult and expensive to remediate. Options include excavation to landfill for soil (where authorised), and abstraction combined with activated carbon or resin treatment for groundwater. Current best practice disposal routes for PFAS adsorption media are high temperature incineration at >1000°C, or regeneration at a specialist facility. Alternative water treatment techniques, such as sonolysis and advanced chemical oxidation, are being developed that may be more widely used in the future.

The information provided in the body of the report can be used for risk assessment and evaluation of management options. It must be stressed that this is an active field of research, with regular advances in the science around PFAS toxicity, fate, transport and remediation technologies.

10. GLOSSARY

AA-EQS	Annual Average Environmental Quality Standard
AFFF	aqueous-fire-fighting-foam
AOF	adsorbable organic fluorinated compounds
AOX	adsorbable organic halogens
APFO	perfluorooctanoic acid ammonium salt
BAF	bioaccumulation factor
BCF	bioconcentration factor
BMF	biomagnification factor
CIC	combustion ion chromatography
COM	Committee on Mutagenicity of Chemicals in Food, Consumer Products and the Environment
COPC	constituents of potential concern
ECF	electrochemical fluorination
ECHA	European Chemicals Agency
EPA	Environmental Protection Agency
EQS	environmental quality standards
FTA	fluorotelomer acid
FTOH	fluorotelomer alcohol
FTS	fluorotelomer sulfonic acid (6:2 FTS = H_4PFOS)
GAC	granular activated carbon
HED	human equivalent dose
HF	hydrogen fluoride
HFA	hexafluoroacetone
Kd	soil distribution coefficient
Koc	organic carbon-water partition coefficient
Kow	octanol-water partition coefficient
IARC	International Agency for Research on Cancer
LOAEL	lowest observed adverse effect level
LOD	limit of detection
LD	lethal dosis
MAC	maximum allowable concentration
MCL	maximum contaminant level
MTBE	methyl-tert-butyl ether
NF	nano filtration
NOEC	no observed effect concentration
PAP	polyfluorinated alkyl phosphate
PBT	persistent, bioaccumulative and toxic
PFAS	poly- and perfluoroalkyl substance
PFBA	perfluorobutanoic acid/ perfluorobutanoate
PFBS	perfluorobutane sulfonic acid/ perfluorobutane sulfonate
PFC	perfluorinated compound
PFCA	perfluoroalkyl carboxylic acid
PFDA	perfluorodecanoic acid/ perfluorodecanoate
PFDS	perfluorodecane sulfonic acid/ perfluorodecane sulfonate
PFHpA	perfluoroheptanoic acid/ perfluoroheptanoate

PFHxS	perfluorohexanoic acid/ perfluorohexane sulfonate
PFNA	perfluorononanoic acid/ Perfluorononanoate
PFOA	perfluorooctanoic acid/ perfluorooctanoate
PFOS	perfluorooctanesulfonic acid/ perfluorooctane sulfonate
PFOSA	perfluorooctane sulfonamide
PFPA	perfluorinated phosphonic acid
PFPeA	perfluoropentanoic acid
PFSA	perfluoroalkyl sulfonic acid
pKa	dissociation constant
PNEC	predicted no effect level
POP	persistent organic pollutant
POSF	perfluorooctane sulfonylfluoride
PTFE	polytetrafluoroethylene
REACH	registration, evaluation, authorization and restriction of chemicals
RfD	reference dose
RIVM	Dutch National Institute for Public Health and the Environment
RO	reverse osmosis
RP	reversed phase
SEAC	Committee of Socio-economic Analysis
SPE	solid phase extraction
TDI	total daily intake
TM	telomerization
TOP	total oxidisable precursor
vPvB	very persistent and very bio-accumulating properties
WFD	Water Framework Directive
WWTP	waste water treatment plant

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APPENDICES CONTENT

APPENDIX 1 HISTORICAL USES OF PFAS

Compound	AFFF	Paper industry (food packaging)	Textile industry	Chemical industry	Galvanic industry	Photolithograpic industry	Electro industry (semiconductor)
POSF (perfluoro-octanesulfonyl fluoride) Starter compound for the production of PFOS	X	X	X	X			
PFOS	X AFFF-foam	X Food packaging	X Textile, Carpets, furniture, outdoor clothing, leather Impregnation	X Oil and gas industry Polish Dispersion media Ink Paint Varnish	X Metal and plastic coating, comprising; Chromium, zinc, gold, copper, nickel, tin, brass, etc.	X Coating of photographic films, papers, printing plates	X
PFOA	X	X		X Polymer-production, Dyes Polishes Adhesives Lubricants		X	
APFO Ammoniumsalt of PFOA						X	
FOSE Perfluorsulfonamidethanol		X	X Fiber finishing	X Electro fluorination	X	X Photographic paper	
FOSA (perfluoroctanesulfonamido)	X	X Paper equipment	X Leather equipment	X Electro fluorination	X Metal surface treatment Electroplating		X
PFOSE (N-alkylsulfonamido-ethanol)		X Coating of food packaging	X Coating of carpeting, clothing				
PFOSA (Perfluoroctyl-sulfonic acid)		X Paper, cardboard packaging	X Stain repellant Water repellant Textiles, carpet, leather	X Oil repellant			
PTFE (Teflon)				X			
FTOH (Fluorotelomer alcohols)		X	X Water repellant	X Polymers Paints Impregnating agents	X		
PAP (Polyfluorinated Alkyl Phosphates)		X Fastfood packaging					
Fluorcarbon resins		X	X				
N-alkyl-substituted perfluorooctane-sulfonamide						X Photographic paper	
NEtFOSA (N-Ethyl perfluorooctane sulfonamide)							
NEtFOSE (N-ethyl perfluoroctane sulfonamido-ethanol)		X					

	Medical technology	Cleaning agents	Pesticide industry	Cosmetical industry	Cookware (non-stick)	Aviation industry
POSF (perfluorooctane-sulfonyl fluoride) Starter compound for the production of PFOS						
PFOS	X Manufacture of video endoscopes	X Alkaline cleaning agents Detergents Carpet cleaner	X Insecticides	X Cleaning fluids Shampoos Handcremes		X Hydraulic fluids
PFOA			X Insecticides Herbicides	X	X Teflon production	
APFO Ammoniumsalt of PFOA						
FOSE Perfluorsulfonamifethanol			X Pesticides			
FOSA (perfluoroctanesulfonamido)		X Alkaline cleaning agents Floor polish				
PFOSE (N-alkylsulfon-amido-ethanol)						
PFOSA (Perfluoroctyl-sulfonic acid)						
PTFE (Teflon)	X Implantates				X	
FTOH (Fluorotelomer alcohols)		X			X	
PAP (Polyfluorinated Alkyl Phosphates)						
Fluorcarbon resins						
N-alkyl-substituted perfluorooctane-sulfonamide	X		X			
NEtFOSA (N-Ethyl perfluorooctane sulfonamide)			X Insecticides			
NEtFOSE (N-ethyl perfluoroctane sulfonamido-ethanol)						

APPENDIX 2 PHYSICOCHEMICAL PROPERTIES

Name	Acronym	CAS Registry Number	Molecular Formula	Molecular Weight [g/mol]	Density[a] (20 - 25 °C) [g/ml]	Water Solubility[b] (20 - 25 °C) [g/L]	Melting Point[a] [°C]	Boiling Point[a] [°C]	Vapor Pressure[b] [Pa]	Henry-Coefficient [Pa·m³·mol⁻¹]	log Kow[b] [-]	log K_{OC} [L/kg]	Kd (pH 7)	Dissociation Constant (pKa)
Perfluoroalkyl Carboxylates / Perfluoroalkyl Carboxylic Acids	**PFCAs**													
Perfluorobutanoic Acid	PFBA	375-22-4	$F(CF2)_3COOH$	214.04	1.65	Miscible	-17.5	121	1307	--	2.82	1.88	--	-0.2 to 0.7
Perfluoropentanoic Acid	PFPeA	2706-90-3	$F(CF2)_4COOH$	264.05	1.70	112.6	--	124.4	1057	--	3.43	1.37	--	-0.06
Perfluorohexanoic Acid	PFHxA	307-24-4	$F(CF2)_5COOH$	314.05	1.72	21.7	14	143	457	--	4.06	1.91	--	-0.13
Perfluoroheptanoic Acid	PFHpA	375-85-9	$F(CF2)_6COOH$	364.06	1.79	4.2	30	175	158	--	4.67	2.19	0.4 - 1.1	-0.15
Perfluorooctanoic Acid	PFOA	335-67-1	$F(CF2)_7COOH$	414.07	1.80	3.4 - 9.5	37 - 60	188 - 192	4 - 1300	0.04 - 0.09	5.30	1.31 - 2.35	0 - 3.4	-0.16 to 3.8
Perfluorononanoic Acid	PFNA	375-95-1	$F(CF2)_8COOH$	464.08	1.75	9.50	59 - 66	218	1.3	--	5.92	2.39	2.6 - 5.9	-0.17
Perfluorodecanoic Acid	PFDA	335-76-2	$F(CF2)_9COOH$	514.09	1.76	9.50	77 - 88	218	0.2	--	6.50	2.76	2.0 - 31	-0.17
Perfluoroundecanoic Acid	PFUnA	2058-94-8	$F(CF2)_{10}COOH$	564.09	1.76	0.004	83 - 101	160 - 230	0.1	--	7.15	3.30	12 - 103	-0.17
Perfluorododecanoic Acid	PFDoA	307-55-1	$F(CF2)_{11}COOH$	614.10	1.77	0.0007	107 - 109	245	0.01	--	7.77	--	24 - 269	-0.17 to 0.8
Perfluorotridecanoic Acid	PFTrdA	72629-94-8	$F(CF2)_{12}COOH$	664.11	1.77	0.0002	--		0.3	--	8.25	--	--	--
Perfluorotetradecanoic Acid	PFTeDA	376-06-7	$F(CF2)_{13}COOH$	714.12	1.78	0.00003	--	276	0.1	--	8.90	--	--	--
Perfluoropentadecanoic Acid	PFPeDA	141074-63-7	$F(CF2)_{14}COOH$	764.12	--	--	--	--	--	--	--	--	--	--
Pentadecafluorooctanoic Acid Ammonium Salt (Ammonium Pentadecafluorooctanoate)	APFO	3825-26-1	C8 H4 NF15 NO2	445.11	--	14.2	157 - 165	--	0.01	--	--	--	--	2.5
Perfluoroalkyl Sulfonates / Perfluoroalkyl Sulfonic Acids	**PFSAs**													
Perfluorobutane Sulfonate	PFBS	375-73-5	$F(CF2)_4SO_3H$	300.10	1.81	46.2 - 56.6	76 - 84	211	631	--	3.90	1.00	--	-6.0 to -5.0
Perfluorohexane Sulfonate	PFHxS	432-50-8	$F(CF2)_6SO_3H$	400.11	--	2.3	--	--	58.9	--	5.17	1.78	0.6 - 3.2	-6.0 to -5.0
Perfluoroheptane Sulfonate	PFHpS	357-92-8	$F(CF2)_7SO_3H$	450.12	--	--	--	--	--	--	--	--	--	--
Perfluorooctane Sulfonate	PFOS	1763-23-1	$F(CF2)_8SO_3H$	500.13	--	0.52 - 0.57	54	> 400	6.7	<2e-6 to 3e-4	6.43	2.5 - 3.1	0.1 - 97	-6.0 to -2.6
Perfluorodecane Sulfonate	PFDS	333-77-3	$F(CF2)_{10}SO_3H$	600.14	--	0.002			0.71	--	7.66	3.53	--	--
Perfluoroalkyl Phosphonic Acids	**PFPAs**													
Perfluorobutyl Phosphonic Acid	PFBPA	52299-24-8	$F(CF2)_4P(O)(OH)_2$	350.02	--	14259.1	--	--	0.18	--	2.19	--	--	--
Perfluorohexyl Phosphonic Acid	PFHxPA	40143-76-8	$F(CF2)_6P(O)(OH)_2$	400.03	--	515.3	--	--	0.04	--	3.48	--	--	--
Perfluorooctyl Phosphonic Acid	PFOPA	40143-78-0	$F(CF2)_8P(O)(OH)_2$	500.05	--	24.5	--	--	0.01	--	4.73	--	--	--
Perfluorodecyl Phosphonic Acid	PFDPA	52299-26-0	$F(CF2)_{10}P(O)(OH)_2$	600.06	--	0.5	--	--	0.0002	--	5.98	--	--	--
Perfluorooctane Sulfonamide and Derivatives														
Perfluorooctane Sulfonamide	PFOSA	754-91-6	$F(CF2)_8SO_2NH_2$	499.14	--	-	154 - 155	--	--	--	-	2.5 - 2.62	35 - 56	--
Perfluorooctane Sulfonamidoethanol	FOSE	10116-92-4	$F(CF2)_8SO_2NH(CH_2)_2OH$	543.19	--	0.0009	--	--	0.00	--	5.78	--	--	--
N-Methyl-Perfluorooctane Sulfonamide	N-MeFOSA	31506-32-8	$F(CF2)_8SO_2NHCH_3$	513.17	--	0.0002	--	--	0.30	--	6.07	3.14	--	--
N-Ethyl-Perfluorooctane Sulfonamide	N-EtFOSA	4151-50-2	$F(CF2)_8SO_2NHCH_2CH_3$	527.20	--	0.0001	--	--	0.12	--	6.71	3.23	--	--
N-Methyl-Perfluorooctane Sulfonamidoethanol	N-MeFOSE	24448-09-7	$F(CF2)_8SO_2N(CH_3)(CH_2)_2OH$	557.22	--	0.0003	--	--	0.0004	--	6.00	--	--	--
N-Ethyl-Perfluorooctane Sulfonamidoethanol	N-EtFOSE	1691-99-2	$F(CF2)_8SO_2N(CH_2CH_3)(CH_2)_2OH$	571.25	--	0.0001	55 - 60	--	0.002	--	6.52	--	--	--

Name	Acronym	CAS Registry Number	Molecular Formula	Molecular Weight [g/mol]	Density[a] (20 - 25 °C) [g/ml]	Water Solubility[b] (20 - 25 °C) [g/L]	Melting Point[a] [°C]	Boiling Point[a] [°C]	Vapor Pressure[b] [Pa]	Henry-Coefficient [Pa·m³·mol⁻¹]	log Kow[b] [-]	log K_{OC} [L/kg]	Kd (pH 7)	Dissociation Constant (pKa)
Fluorotelomer sulfonic acids	**FTSs**													
1H, 1H, 2H, 2H-Perfluorobutanesulfonic Acid	H4-PFBS (2:2 FTS)	149246-63-9	$F(CF_2)_2CH_2CH_2SO_3H$	228.13	--	-	--	--	-	--	--	--	--	--
1H, 1H, 2H, 2H-Perfluorohexanesulfonic Acid	H4-PFHxS (4:2 FTS)	757124-72-4	$F(CF_2)_4CH_2CH_2SO_3H$	328.15	--	27.9	--	--	0.33	--	3.21	--	--	--
1H, 1H, 2H, 2H-Perfluorooctanesulfonic Acid	H4-PFOS (6:2 FTS)	27619-97-2	$F(CF_2)_6CH_2CH_2SO_3H$	428.17	--	1.3	--	--	0.11	--	4.44	--	--	1.31
1H, 1H, 2H, 2H-Perfluorodecanesulfonic Acid	H4-PFDeS (8:2 FTS)	39108-34-4	$F(CF_2)_8CH_2CH_2SO_3H$	528.18	--	0.06	--	--	0.01	--	5.66	0.01	--	1.32
1H, 1H, 2H, 2H-Perfluoroundecanesulfonic Acid	H4-PFUdS (10:2 FTS)	120226-60-0	$F(CF_2)_{10}CH_2CH_2SO_3H$	628.20	--	0.002	--	--	0.001	--	6.91	--	--	--
1H, 1H, 2H, 2H-Perfluorotetradecanesulfonic Ac	H4-PFTeS (12:2 FTS)	149246-64-0	$F(CF_2)_{12}CH_2CH_2SO_3H$	728.21	--	0.0002	--	--	0.001	--	7.94	--	--	--
Fluorotelomer Alcohols	**FTOHs**													
Perfluormethylethanol 2:2	2:2 FTOH	54949-74-5	$F(CF2)_2CH_2CH_2OH$	164.08	--	--	--	--	--	--	--	--	--	--
Perfluorethylethanol 4:2	4:2 FTOH	2043-47-2	$F(CF2)_4CH_2CH_2OH$	264.09	--	0.98	--	--	214	--	3.30	0.93	--	--
Perfluorhexylethanol 6:2	6:2 FTOH	647-42-7	$F(CF2)_6CH_2CH_2OH$	364.11	--	0.02	-33	172	18.2	5726	4.54	2.43	--	--
Perfluorocylethanol 8:2	8:2 FTOH	865-86-1	$F(CF_2)_8CH_2CH_2OH$	464.12	--	0.0001	45	114	3.98	5039	5.58	3.84	--	--
Perfluordecylethanol 10:2	10:2 FTOH	678-39-8	$F(CF2)_{10}CH_2CH_2OH$	564.14	--	0.00001	--	--	0.20	7776	6.63	6.20	--	--
Perfluordodecylethanol 12:2	12:2 FTOH	39239-77-5	$F(CF2)_{12}CH_2CH_2OH$	664.15	--	--	--	--	--	--	--	--	--	--
Polyfluorinated Alkyl Phosphates	**PAPs**													
Monoester	monoPAP													
4:2 Fluortelomerphosphatemonoester	4:2 monoPAP	150065-76-2	$F(CF2)_4CH_2CH_2OP(O)(OH)_2$	344.07	--	11.9	--	--	0.000	--	1.99	--	--	--
6:2 Fluortelomerphosphatemonoester	6:2 monoPap	57678-01-0	$F(CF2)_6CH_2CH_2OP(O)(OH)_2$	444.09	--	2.6	--	--	0.000	--	3.39	--	--	--
8:2 Fluortelomerphosphatemonoester	8:2 monoPAP	57678-03-2	$F(CF2)_8CH_2CH_2OP(O)(OH)_2$	544.10	--	0.16	--	--	0.000	--	4.67	--	--	--
10:2 Fluortelomerphosphatemonoester	10:2 monoPAP	57678-05-4	$F(CF2)_{10}CH_2CH_2OP(O)(OH)_2$	644.12	--	0.01	--	--	0.000	--	5.92	--	--	--
12:2 Fluortelomerphosphatemonoester	12:2 monoPAP	57678-07-6	$F(CF2)_{12}CH_2CH_2OP(O)(OH)_2$	744.13	--	0.0003	--	--	0.000	--	7.21	--	--	--
Diester	**diPAP**													
4:2 Fluortelomerphosphatediester	4:2 diPAP	135098-69-0	$F(CF2)_4CH_2CH_2OP(OH)OCH_2CH_2$-	590.15	--	0.0004	--	--	0.000	--	6.16	--	--	--
6:2 Fluortelomerphosphatediester	6:2 diPAP	57677-95-9	$F(CF2)_6CH_2CH_2OP(OH)OCH_2CH_2$-	790.18	--	8.E-07	--	--	0.000	--	8.41	--	--	--
8:2 Fluortelomerphosphatediester	8:2 diPAP	678-41-1	$F(CF2)_8CH_2CH_2OP(OH)OCH_2CH_2$-	990.21	--	5.E-10	--	--	0.000	--	10.93	--	--	--
10:2 Fluortelomerphosphatediester	10:2 diPAP	1895-26-7	$F(CF2)_{10}CH_2CH_2OP(OH)OCH_2CH_2$	1190.24	--	2.E-12	--	--	0.000	--	12.88	--	--	--
12:2 Fluortelomerphosphatediester	12:2 diPAP	57677-99-3	$F(CF2)_{12}CH_2CH_2OP(OH)OCH_2CH_2$	1390.27	--	3.E-15	--	--	0.000	--	15.15	--	--	--
Polytetrafluoroethylene (Teflon)	PTFE	9002-84-0	$(CF_2)_{2n}$	--	--	--	327°C (Decomposes at 260°C)	--	--	--	--	--	--	--

Notes

Blank font indicates information from published literature sources.

Blue font indicates chemical formulas.

Red font indicates parameters estimated with published equations. Calculated parameters are based on the neutral form of the substances (and not the conjugate base, which predominates for some PFAS at neutral pH)

-- No data or not applicable.

[a] CAS database at http://www.chemicalbook.com

[b] Wang, et al., 2011.

Unless otherwise indicated, all parameter values obtained from literature sources listed separately.

APPENDIX 3 ACUTE AND CHRONIC AQUATIC ECOTOXICITY OF PFOS (TABLES FROM THE PFOS EQS DOSSIER, 2011)

ACUTE EFFECTS			Master reference
Algae & aquatic plants (mg.l^{-1})	**Freshwater**	*Selenastrum capricornutum* /96 h EC_{50} : 71mg/l and 126mg/l	Environment Agency,2004
		Selenastrum capricornutum/96h EC_{50}: 48.2mg/l *	Environment Agency,2008
		Pseudokirchneriella subcapitata / 72 h EC_{50}: 120 mg/l	OECD, 2002 in RIVM 2010
		Navicula pelliculosa / 96 h EC_{50}: 283 mg/l	OECD, 2002 in RIVM 2010
		Chlorella vulgaris/96h EC_{50}: 81.6 mg/l	Environment Agency,2004 Boudreau et al, 2003b in RIVM 2010
		Anabaena flos-aquae / 96h EC_{50}: 176 mg/l	Environment Agency,2004 OECD, 2002 in RIVM 2010
		Lemna gibba / 7d EC_{50}: 31.1mg/l	Environment Agency,2004 Boudreau et al, 2003b in RIVM 2010
	Marine	*Skeletonema costatum*/96 h EC_{50} : >3.2mg/l	Environment Agency,2004
Invertebrates (mg.l^{-1})	**Freshwater**	*Daphnia magna* / 48 h EC_{50} : 27 mg/l	Environment Agency,2004
		Daphnia magna / 48 h EC_{50}: 4 mg/l **	Environment Agency,2008
		Daphnia magna / 48 h EC_{50}: 48 mg/l (geometric mean of 6 values)	OECD, 2002, Boudreau et al, 2003b, Ji et al 2008, and Li, 2009 in RIVM 2010
		Daphnia pulicaria / 48 h EC_{50}: 124 mg/l	Boudreau et al, 2003b in RIVM 2010
		Moina macrocopa / 48 h EC_{50}: 18 mg/l	Ji et al, 2008 in RIVM, 2010
		Neocaridina denticulate / 96 h EC_{50}: 9.3 mg/l	Li, 2009 in RIVM 2010
		Dugesia japonica / 96 hr LC_{50}: 18 mg/l (geometric mean of two values)	Li, 2008 and Li, 2009 in RIVM 2010
		Physa acuta / 96 hr LC_{50}: 165 mg/l	Li, 2009 in RIVM 2010
		Unio complamatus / 96 hr LC_{50}: 59 mg/l	Environment Agency,2004 OECD, 2002 in RIVM 2010
	Marine	*Mysid shrimp (Americamysis bahia)* / 96 h EC_{50} : 3.6mg/l	Environment Agency,2004 OECD, 2002 in RIVM 2010
		Brine shrimp (Artemia spp) / 48hr LC_{50}: 8.9 mg/l	Environment Agency,2004
		Artemia spp / 48 hr LC_{50}: 8.3 mg/l	OECD, 2002 in RIVM 2010
		Crassostrea virginica (Eastern oyster) 96hr EC50 >3.0mg/l (Shell deposition)	Wildlife international (2000) referenced in OECD 2002
	Sediment	No data	

Fish (mg.l^{-1})	**Freshwater**	*Fathead minnow (Pimephales promelas* /96 h EC_{50} : 4.7mg/l ***	Environment Agency,2004
		Fathead minnow (Pimephales promelas/96h LC50: 9.5mg/l	Environment Agency,2008
		Pimephales promelas / 96 h LC_{50}: 6.6 mg/l (geometric mean of two values)	OECD, 2002 in RIVM 2010
		Bluegill sunfish (Lepomis macrochirus) / 96 h LC_{50}: 6.9 mg/l	Environment Agency,2004
		Lepomis macrochirus / 96 h LC_{50}: 6.4 mg/l	OECD, 2002 in RIVM 2010
		Oncorhynchus mykiss / 96h LC_{50}: 7.8mg/l	Environment Agency,2008
		Oncorhynchus mykiss / 96 h LC_{50}: 13 mg/l (geometric mean of two values)	OECD, 2002 in RIVM 2010
	Marine	*Sheepshead minnow (Cyprinodon variegatus*/ 96hr EC_{50} : >15mg/l	Environment Agency,2004
		Oncorhynchus mykiss / 96h LC50: 13.7mg/l	Environment Agency,2004 OECD, 2002 in RIVM 2010
Other taxonomic groups			

* Noted that this study should be considered with care as it is based on nominal concentrations and the study duration is longer than the recommended test duration.

** This value was generated in a static system with nominal concentrations and therefore the data should be treated with care.

*** This study was conducted in a static system with nominal test concentrations and should therefore be treated with care.

CHRONIC EFFECTS			Master reference
Algae & aquatic plants (mg.l^{-1})	**Freshwater**	*Selenastrum capricornutum*/96h EC_{10}: 5.3mg/l *	Environment Agency, 2008
		Lemna gibba/7d NOEC: 15.1mg/l	Environment Agency,2004
		Lemna gibba/42d EC_{10}: 0.2mg/l **	Environment Agency,2008
		Chlorella vulgaris / 96h EC_{10}: 8.2mg/l	Environment Agency,2008 Boudreau et al, 2003b in RIVM, 2010
		Navicula pelliculosa / 96 h NOEC: 44mg/l	Environment Agency,2004 OECD, 2002 in RIVM 2010
		Rhapidocelis subcapitata /96h EC_{10}: 53mg/l	OECD, 2002 in RIVM, 2010
		Anabaena flos-aqua /96h NOEC: 44mg/l	OECD, 2002 in RIVM, 2010
		Lemna gibba/7d EC_{10}: 6.6mg/l	Environment Agency,2008 Boudreau et al., 2003b in RIVM, 2010
		Myriophyllum sibiricum / 42 d NOEC: 0.092mg/l	Hanson et al, 2005 in RIVM 2010
		Myriophyllum spicatum / 42 d NOEC: 3.2mg/l	Hanson et al, 2005 in RIVM, 2010
	Marine	*Skeletonema costatum* /96h NOEC : >3.2mg/l	Environment Agency,2004 OECD, 2002 in RIVM, 2010
Invertebrates (mg.l^{-1})	**Freshwater**	*Daphnia magna* / 21 d NOEC : 12 mg/l	Environment Agency,2004
		Daphnia magna/28d NOEC: 7mg/l ***	Environment Agency,2004
		Daphnia magna/21d NOEC: 5.3mg/l ***	Environment Agency,2004
		Daphnia magna / 21/28 d NOEC: 7.0 mg/l (geomean of 4 values)	Boudreau et al, 2003b, OECD, 2002 and Ji et al, 2008 in RIVM, 2010
		Moina macrocopa / 7 d EC10: 0.40mg/l	Ji et al, 2008 in RIVM 2010
		Chironomus tentans / 10d NOEC: 0.049mg	Environment Agency,2008
		Chironomus tentans / 36d NOEC: 0.049mg <0032mg/l LOEC with 32% effect	MacDonald et al, 2004 in RIVM, 2010
		***Chironomus tentans* / 36d** **NOEC: <0.002mg** LOEC 0.002mg/l	MacDonald et al, 2004 in RIVM, 2010
		Enallagma cyathigerum / 120 d NOEC: <0.01mg/l LOEC with 18% effect	Bots et al, 2010 in RIVM 2010

	Marine	*Mysidopsis bahia* / 35 d NOEC : 0.25mg/l	Environment Agency,2004 OECD, 2002 in RIVM 2010
	Sediment	No data	
Fish **(mg.l^{-1})**	**Freshwater**	Fathead minnow (*Pimephales promelas* / 42d NOEC : 0.3mg/l	Environment Agency,2004
		Fathead minnow (*Pimephales promelas*) / 21d NOEC: 0.028mg/l	Environment Agency,2008 Ankley et al, 2005 in RIVM, 2010
		Oryzias latipes / 14 d NOEC: <0.01mg/l LOEC with 80% effect	Ji et al, 2008 in RIVM, 2010
		Bluegill sunfish (*Lepomis macrochirus* / 62d NOEC: <0.87mg/l	
	Marine	No data	
Other taxonomic groups		*Xenopus leavis* / 96 h NOEC: 5.0mg/l	

*Noted that the algal study needs to be treated with care as based on nominal concentrations and also of 96hr duration rather than the test recommendation of 72 hrs.

** Noted that this data generated in an outdoor microcosm study and the study details are incomplete

*** Noted that these studies were undertaken with nominal concentrations and therefore should be treated with care. Lowest valid datapoint is 12 mg/l.

APPENDIX 4 ANALYICAL METHODS

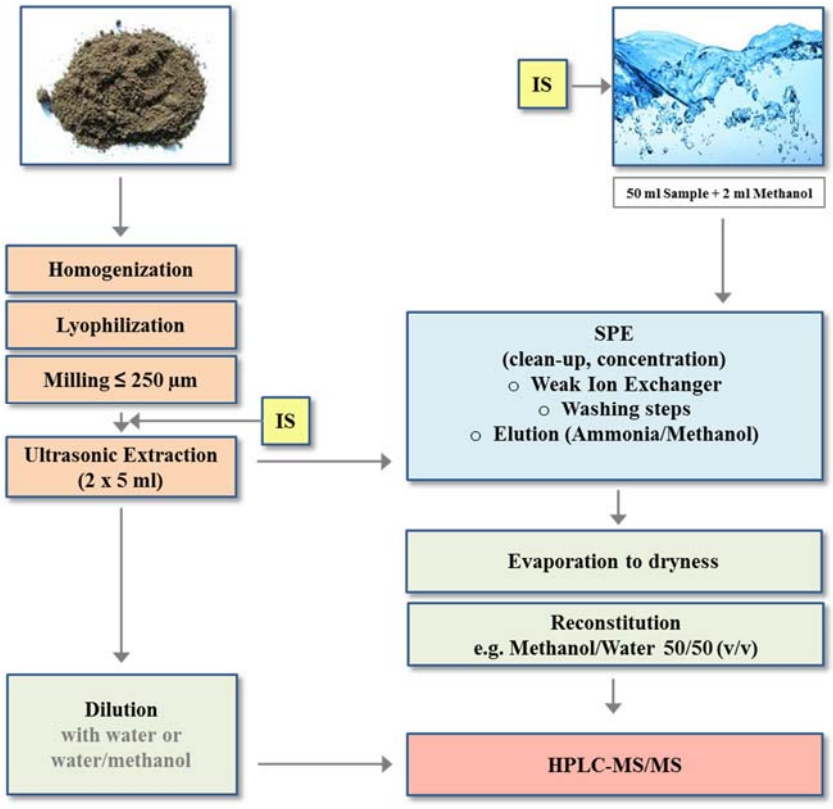
Overview of standard methods

Worldwide there are a variety of methods available applicable for the analysis of PFAS including the international standard ISO 25101:2009(E) (Water quality – Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) - Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry). However, this method is applicable exclusively for the analysis of PFOS and PFOA. The US-standard (Method 537: Determination of selected perfluorinated alkyl acids in drinking water by solid phase extraction and liquid chromatography / tandem mass spectrometry (LC/MS/MS); EPA/600/R08/092) is applicable to analyse a large number of perfluorinated carboxyls and sulfonates. All methods are based on liquid chromatography with a tandem mass selective detection. The German standard (DIN-Method) currently allows the quantification of the highest number of contaminants:

- Water: DIN 38407-42:2011-03 (F 42) Analysis of selected perfluorinated compounds (PFC) in water – Method via high performance liquid chromatography – tandem mass spectrometry (HPLC-MS/MS) after solid phase extraction (DIN, 2011a);
- Soil: DIN 38414-14 (S14) Analysis of selected perfluorinated compounds (PFC) in sludge, compost and soil – Method via high performance liquid chromatography – tandem mass spectrometry (HPLC-MS/MS) (S14) (DIN, 2011b).

The S14-method is suitable for sediments, sewage sludge, compost, and soil.

Figure 1. Analysis procedure according to DIN 38407-42:2011-03 (IS = Internal Standard)



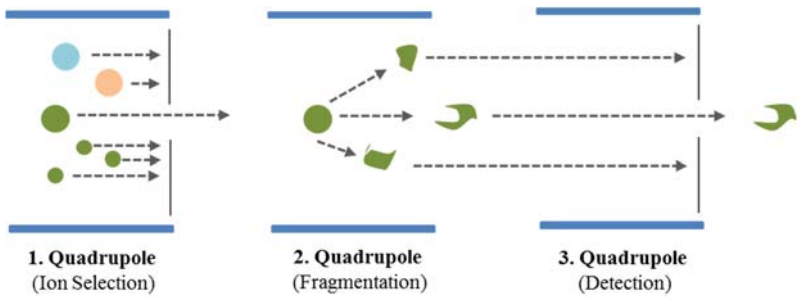
The general analytical procedure is shown in **Figure 1**. It consists in three steps: SPE-enrichment (*Solid Phase Extraction*), HPLC-separation and MS-MS-detection (DIN, 2011a). It is designed for the analysis of polar, low concentrated contaminants.

By selecting the appropriate solid (here: weak anion exchanger) for the SPE, it is possible to restrict the analysis to polar, negatively charged non-volatile substances, which bind to the ion exchange cartridge. The SPE serves to select and concentrate the contaminant and reduce matrix interference by dirty matrices. Other PFAS with no polar groups in the molecule cannot be detected with this analysis because they do not sorb to the ion exchanger during sample preparation.

It should be remarked that milling and ultrasonic extraction during sample preparation for solids analysis could destroy the PFAS. While this process is time-dependent (the destruction rate increases with time) and may not be significant, it may result in an underestimation of the true PFAS concentration.

The separation happens by Reversed Phase (RP) fluid-chromatography. The RP consists of alkyl chains covalently bonded to silica gel. The retention time of a substance depends on the retention in the stationary phase. The factor that limits the velocity of the process is the desorption back into the mobile phase. The branched isomers - especially occurring in PFOA, PFHxS and PFOS - usually elute just before the unbranched substances. For PFOS, several branched isomers are detected (DIN, 2011a).

Figure 2. MS-MS-coupling principle

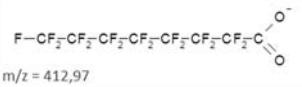
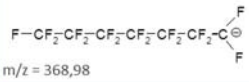
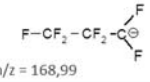
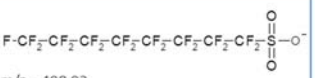


The identification and quantification is conducted using the very selective and sensitive Negative-Ions Electrospray Tandem Mass spectrometry (ESI-MS-MS) (**Figure 2**) (Theobald et al., 2007). Mass spectrometry is a method to measure the mass/charge ratio (m/z) of ions.

The ESI-Interface is the connection between the standard HPLC-system and the Tandem-MS. The mixed sample (liquid) is nebulized and becomes ionized in an electrical high voltage field. The Tandem-MS usually comprises three quadrupoles, although the measurement is done only in the first and the third. The central quadrupole (collision cell) is used for the fragmentation of the selected analyte. The quadrupole separation systems consist of four bar magnets. By applying electrical potential, the molecules with a precise mass (here: the molecules to be analysed) are accelerated, guided through the gap between the bars and filtered out. By doing so, undesired ions can be neutralized and therefore will not be detected. By changing the electrical field, the whole spectrum can be scanned using the first of the two MS systems. The ion to be analysed is then led to a collision cell, in which the molecule is energized by colliding with an inert gas like N_2 or argon. In this process, the ion is split into lighter, very specific ions, which are identified in the second mass spectrometer.

It is possible to reconstruct the structure of the analyte from the pattern of the different mass fragments. **Figure 3** shows the parental compounds and the most important product ions generated in each ionization step for two examples (PFOA and PFOS). Only one product ion is obtained for the compound PFBA and the intensity of the second product ion for the compounds PFPeA and PFHxA is too low for reliable identification. The first production step serves to identify, the second to quantify the product ions.

Figure 3. Example of typical fragmentation of PFOA and PFOS (DIN, 2011a)

Compound	Initial Ion	1. Product-Ion	2. Product-Ion
PFOA	 m/z = 412,97	 m/z = 368,98	 m/z = 168,99
PFOS	 m/z = 498,93	 m/z = 79,96	 m/z = 98,96

The HPLC-MS/MS method is suitable to analyse the PFAS (shown in blue in **Table 4**) in drinking water, groundwater, and surface water with a detection level of 0.01 to 0.015 µg/l per compound. In treated wastewater the detection limit for PFAS analysed in commercial laboratories analysed is 0.025 µg/l. The detection limit is based on the health protection precautionary values for drinking water. In soil samples, detection limits of 2 µg/kg dry weight are reached in most cases. This value is substantially below the threshold value for the sum of PFOA and PFOS in sewage sludge (100 µg/kg DW), which cannot be exceeded in case of agricultural use.

The method can potentially be used for other water types - for example untreated water - but the applicability needs to be checked for each individual case (DIN, 2011a). The same applies to the solid analysis. While the method could be suitable for other sample materials, for example fertilizers, but this needs to be tested for the individual case.

In association with the solid phase extraction, the method can basically be used for other materials with a polar functional group in the molecule, for example the compounds PFUnA, PFDoA, PFHpS, PFDS and H4PFOS. At present, the 23 compounds listed in **Table 1** can be analysed in commercial laboratories.

In addition, several other polar compounds can be analysed with this method. One example are the Telomer acids (degradation metabolites of Telomer alcohols) (Bayerisches Landesamt für Umwelt, 2012). However, this application has not yet been used as a commercial analysis method.

Table 1. Analysed compounds (HPLC-MS/MS-method), available standards and limit of detection (LOD) HLPC-MS/MS and GC-MS (DIN, 2011a) (Bayerisches Landesamt für Umwelt, 2012). (the compounds explicitly named in the DIN norm are shown in blue, compounds where no internal standards are applicable are shown in red)

Compound	Symbol	Internal/External Standard	LOD (Water) [µg/L]	LOD (Soil) [µg/kg]
Perfluoro-n-butanoic acid	PFBA	$^{13}C_4$-PFBA	0,01	2
Perfluoro-n-pentanoic acid	PFPeA	$^{13}C_4$-PFHxA	0,01	2
Perfluoro-n-hexanoic acid	PFHxA	$^{13}C_2$-PFHxA	0,01	2
Perfluoro-n-heptanoic acid	PFHpA	$^{13}C_4$-PFOA	0,01	2
Perfluoro-n-octanoic acid	PFOA	$^{13}C_4$-PFOA	0,01	2
Perfluoro-n-nonanoic acid	PFNA	$^{13}C_4$-PFOA	0,01	2
Perfluoro-n-decanoic acid	PFDA	$^{13}C_2$-PFDA	0,01	2
Perfluoro-n-undecanoic acid	PFUnA	$^{13}C_2$-PFUnA	0,01	2
Perfluoro-n-dodecanoic acid	PFDoA	$^{13}C_4$-PFOA	0,01	2
Perfluoro-n-tridecanoic acid	PFTrA	$^{13}C_4$-PFOA	0,01	2
Perfluoro-n-tetradecanoic acid	PFTA	$^{13}C_4$-PFOA	0,01	2
Perfluoro-n-butansulfonoic acid	PFBS	$^{13}C_4$-PFBA	0,015	3
Perfluoro-n-hexansulfonoic acid	PFHxS	$^{13}C_4$-PFOS	0,015	3
Perfluoro-n-heptansulfonoic acid	PFHpS	$^{13}C_4$-PFOS	0,01	2
Perfluoro-n-octansulfonoic acid	PFOS	$^{13}C_4$-PFOS	0,01	2
Perfluoro-n-decansulfonoic acid	PFDeS	$^{13}C_4$-PFOA	0,01	2
1H,1H,2H,2H-Perfluoro-n-octansulfonoic acid	H4PFOS (6:2FTS; H.H PFOS)	$^{13}C_4$-PFOS	0,01	2
Perfluorooctansulfonamide	PFOSA	^{13}C-MeFOSA	0,01	2
1H,1H,2H,2H-Perfluoro-n-decansulfonoic acid	H4-PFDeS (8:2FTS)	$^{13}C_4$-PFOS	0,01	2
2H,2H-Perfluorodecanoic oic acid	H2PFDA	$^{13}C_4$-PFOS	0,01	2
7H-Dodecafluoroheptanoic acid	HPFHpA	$^{13}C_4$-PFOA	0,01	2
Perfluoro-3,7-dimethyloctanoic acid	PF37DMOA	$^{13}C_4$-PFOA	0,01	2
2H,2H,3H,3H-Perfluoroundecanoic acid	H4PFUnA	$^{13}C_4$-PFOA	0,01	2
2H,2H-Perfluorohexanoic acid	4:2 FTCA	$^{13}C_2$-4:2-FTCA	n.s.	n.s.
2H,2H-Perfluorooctanoic acid	6:2 FTCA	$^{13}C_2$-6:2-FTCA	n.s.	n.s.
2H,2H-Perfluorodecanoic acid	8:2 FTCA	$^{13}C_2$-8:2-FTCA	n.s.	n.s.
2H,2H-Perfluorododecanoic acid	10:2 FTCA	$^{13}C_2$-10:2-FTCA	n.s.	n.s.
2-Perfluorohexylethanol	6:2 FTOH	$^{13}C_2D_2$-6:2-FTOH	n.s.	n.s.
2-Perfluorooctylethanol	8:2 FTOH	$^{13}C_2D_2$-8:2-FTOH	n.s.	n.s.
2-Perfluorodecylethanol	10:2 FTOH	$^{13}C_2D_2$-10:2-FTOH	n.s.	n.s.
2H,2H-Perfluorodecylacylate	8:2 FTA	8:2 FTA	n.s.	n.s.
2H,2H-Perfluorodecylmethacylate	8:2 FTMA	8:2 FTMA	n.s.	n.s.
2H,2H-Perfluorooct-1-en	6:2 FTen	6:2 FTen	n.s.	n.s.
2H,2H-Perfluorodec-1-en	8:2 FTen	8:2 FTen	n.s.	n.s.

n.s. = not specified

Analysis methods for fluorinated precursors

Today, a number of precursors that have been identified in AFFF can be analyzed by HPLC-MS/MS-Method. However, the biggest challenge for any precursor analysis is the availability of standards. Once they are available, this methods will be the best way to analyse most of the PFAS (Backe et la, 2013).

On the other hand, telomer alcohols and other nonpolar PFAS cannot be analysed with the HPLC-MS/MS-Method, because they cannot be concentrated using solid phase extraction. For these compounds gas chromatography (GC-MS) is suitable, as previous experiences with wastewater have demonstrated. The extraction and concentration can be achieved with a good recovery rate by using high purity MTBE (liquid/liquid-extraction). The detection limits were 0,06 µg/l (6:2 FTOH), 0,3 µg/l (8:2 FTOH) und 0,6 µg/l (10:2 FTOH). With a sensitive mass spectrometer these detection limits can be further improved. The lower detection limits refer to the evaluation of mass fragments 31 m/z, which represent the highest signal in the mass spectrum. The disadvantage is that the fragment is less selective for the fluorotelomere alcohols than bigger fragments or fragments containing fluorine. Therefore, in case of particularly complex matrices, it is recommended to choose a different fragment. Since the matrix of a wastewater sample can have very different characteristics depending on its origin, a mass labelled "standard" should be used to correct analyte material losses during the sample preparation (Marzinkowski et a., 2013).

In addition to this, a Headspace-GC-MS-method has been developed, which can be used without an enrichment step. The detection limit is 0,01 µg/l for each compound. The GC-PCI-MS (gas chromatography positive chemical ionization and tandem mass spectrometry) is also suitable as a robust analytical method for volatile compounds, like FTOH, PFOSE and PFOSA (Reagen 2009). After extraction with DCM (or with methanol) the sample clean-up can be performed vie SPE. Concentration of the sample should be avoided. If necessary, the sample should be filtered with a cellulose filter (0,45 µm) (Reagen 2009). Some of the compounds which can be analysed by GC-PCI-MS are listed below:

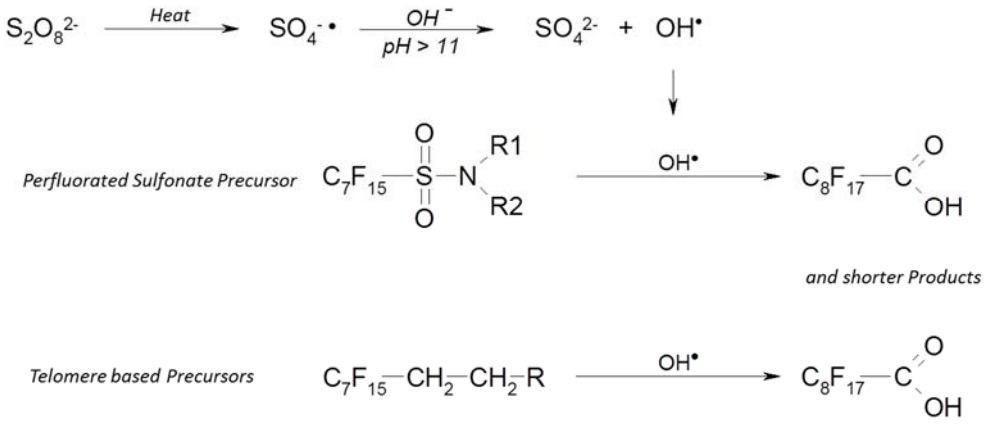
N-MeFOSA	(N-Methylperfluoro-1-octansulfonamide)
N,N-Me2FOSA	(N,N-Dimethylperfluoro-1-octansulfonamide)
4:2 FTOH	2-Perfluorobutylethanol
6:2 FTOH	2-Perfluorohexylethanol
8:2 FTOH	2-Perfluorooctylethanol
10:2 FTOH	2-Perfluorodecylethanol
7:2sFTOH	(1-Perfluoroheptylethanol)

Volatile PFAS - for example telomere alcohols - may also be present in the soil vapour. Up to now, no analytical methods for gas analysis were published. These could be developed based on the sampling method "*low flow sampling on Polyurethane foam in conjunction with a glass fiber filter in a stainless steel cartridge*". This procedure is described for the measurament of perfluorinated acids (Bayerisches Landesamt für Umwelt, 2012).

Precursor Oxidation

A precursor by definition is a compound that has the potential to form PFCAs or PFSAs.
Precursor oxidation with hydroxyl radicals is a sample preparation step that allows for quantification of unknown precursors (Houtz and Sedlak, 2012). The hydroxyl radicals are generated by thermolysis of persulfate in a basic medium. The generated radicals lead to the elimination of all functional groups and non-fluorinated residuals to form perfluorocarboxylic acids, which are readily analysed using standard methods.

Figure 4. Analysis of the total mass of oxidizable precursors



The sample is analysed before and after oxidation and the change in concentration of PFCAs is indicative of the total precursor composition. Additional research is needed to determine if all precursors are transformed to perfluorocarboxylic acids during the high temperature oxidation; however, 62-100% of precursors in known formulations of AFFF are converted (Houtz and Sedlack, 2012). It may be possible to check the effectiveness of the preparation step using analysis of total fluorine.

Adsorbable organic fluorinated compounds

Since many PFAS cannot be analysed with a reasonable effort, it is particularly interesting to analyse a "sum parameter", similar to adsorbable organic halogenated compounds (AOX)[8]. The AOF-method (AOF: adsorbable organic fluorinated compounds), currently undergoing the standardisation process, is based upon the sorption of the fluorinated compounds on synthetic activated carbon with low fluorine content. The carbon is completely burnt without any soot production in presence of water at a temperature of 950 – 1000°C (hydropyrolysis). The combustion gases (HF, CO_2 and others) are adsorbed in a neutral or basic solution, which is injected into an ion chromatograph. The analysis is performed on fluoride. This method, called *Combustion Ion Chromatography* (CIC) (Wagner et al, 2013; Lange, 2014), achieves a detection limit of 1,0 µg/l Fluorine. This corresponds to a detection limit of 0,64 µg/l, with respect to PFOS only. Currently this method cannot be used for soil samples, but can be applied to extracts of soil samples.

It is assumed that the new AOF-Method, once published, will rapidly be established in the commercial laboratories, even though few laboratories have the required analytical instrumentation. Once established, the analysis price will likely drop, and this method could become a routine screening analysis. At present this analysis is probably going to be performed on selected samples only, with the intent to check if further PFAS are present in addition to the 23 commercially analysable compounds.

Up to now it could still not be determined if a correlation between AOF and PFAS actually exists. Furthermore, since not all PFAS can be analysed, verification of a potential correlation is only possible to a limited extent.

[8] The AOX (absorbable organic halogens) do not comprise any fluorinated compounds.

It should be noted that for the corresponding sum parameter AOX the halogenides bind to the organic polymer matrix in water with a high organic load (e.g. landfill leachate) . As a consequence, the total AOX-value is very high, but this value does not correspond to the sum of the single compounds. A similar behaviour is expected for PFAS.

Furthermore, several other analytical methods for the quantification of fluorinated compounds exist. However, these are applied only in the research field (Gruber, 2011).

sampling

Sample Collection
For water sampling, teflon tubing should be avoided. Although high purity teflon tubing does not cause “blank contamination” in contrast to common teflon tubing, some researchers have found that Teflon could sorb PFAs. Usually polypropylen bottles rinsed with methanol and with PE screw caps are suitable for sampling; a minimum of 50 ml sample is needed to conduct the analysis.

If samples are taken for the of AOF it is very important to verify that the blank samples are clean. Therefore all materials containing PTFE are excluded, since suitable materials have not only to be PFAS-free, but also fluorine free. The use of silicone tubing for sampling and as gasket material is recommended.

The samples should be stored at the most for two weeks at a temperature of approximately 4°C. A longer storage time could lead to adsorption of compounds to the container and thus to losses (DIN, 2011a). By adding 5 Vol.-% Methanol to the samples, the losses by adsorption can be reduced. The sample dilution caused by the addition of methanol needs to be considerd in the results interpretation.

For volatile compounds (e.g. FTOH) gas tight lockable glass bottles should be used and completely filled, avoiding a gas phase to be present in the full bottle. The samples have to be stored at a temperature of 4°C. Tests have shown that already after 24 hours of storage 10% loss could occure. (Bayerisches Landesamt für Umwelt, 2012). If possible, the sampling containers should be opened only once.

The soil samples should be liner samples or taken by core drilling and collected in wide-necked polyethylene (PE) or polypropylene (PP) bottles with screw cap and polyethylene gasket. It should be checked that the rim of the glasses is clean before closing them. The sample quantity necessary for the analysis depends on the grain size and has to be sufficient to allow the laboratory to conduct the preparation steps and store a back-up sample. Apart from that, the usual prescriptions for sampling of contaminated water and soil apply.

Sample Preparation
For the preparation of the soil samples, the PFAS are extracted from the dry, homogenized sample via ultrasound-assisted extraction. Samples with high water content (sediments, sewage sludge) should preferably be dried by lyophilization. As an alternative, the drying can also be conducted at 40°C (more time consuming). To homogenize the sample, the dry material is crushed using an analytical mill to achieve a 95% throughput of the milled material through a 250 µm sieve. This allows obtaining a homogeneous sample from which representative samples for the analysis can be taken. Ultrasounds are applied (1 h, 40°C) (DIN, 2011b) to conduct the methanol extraction more efficiently. The extract is used for the next steps.

Coloured or turbid extracts (in most cases from sewage sludge, compost or sediments) or those, in which the contaminants have a very low concentration, are treated using solid phase extraction. The PFAS from the soil extracts (see **Figure 1**) or the water samples are concentrated on a weak anion-exchanger by performing a SPE on the unfiltered water sample (pH 6-8).

The solid phase is rinsed with water and solvents to separate the products that could interfere with the analysis. The adsorbed compounds are then eluted with methanol containing ammonia. Colourless extracts are analysed directly after dilution with water (Methanol: water 4:6). The leachate can be concentrated and dried by blowing off the solvent with nitrogen at a temperature of 40°C. The residual is dissolved again with a methanol-water mixture. The solution to be analysed can be filtered, if needed. Filtering will not cause losses. (DIN, 2011b).

The analysis of the nonpolar PFAS in water samples starts with the preparation using liquid-liquid extraction with MTBE. The extract is dried with sodium sulfate and concentrated in a rotary evapourator at 40°C and 400 mbar with acceptable losses (Bayerisches Landesamt für Umwelt, 2012).

For the concentration of Telomer acids, the rinsing step is usually avoided, because the losses are too high in this phase .

The volatile Telomer alchols can theoretically be found in soil vapour, but operating procedures for the sampling do not yet exist. They might be adapted from the ambient air sampling protocol. Here, Perfluoralcanoic acids in the ambient air are adsorbed on Polyurethane foam in conjunction with a glass fiber filter in a stainless steel cartridge and then leached in the laboratory (Bayerisches Landesamt für Umwelt, 2012).

Separation

According to the standard, colourless and clear soil extract or very concentrated water samples can be analysed without further pre-treatment. Part of the extract has to be diluted with water without allowing the methanol content to drop below 40%. It should be considered that the direct injection method is only allowed as an alternative. Documentation and a demonstration that this method is equivalent to the standard methods are necessary.

If the only solvent for the solution to be analysed is water, high losses occur, especially in the case of PFOS, PFNA and PFDA (DIN, 2011a). In case of relevant matrix interference, the samples have to be cleaned via SPE.

There are no particular requirements regarding the chromatography. A complete separation of the single substances is not necessary, because they can be differentiated by their mass.

Calibration and Quantification

During analysis, analyte losses occur during different steps. The recovery rate is therefore much lower than 100%. Especially in soil analysis the recovery rate varies very strongly depending on the soil type. Therefore, a comparison standard[9] (internal standard) carrying heavier isotopes, e.g. $^{13}C_4$-PFBA, is usually added to the sample. This means that four carbon atoms of the molecule are exchanged with ^{13}C-Isotopes. Since this contains an extra neutron in comparison to the more common ^{12}C this isotope, the masses of the not-marked compounds are 4 u (u; unified atomic mass unit) lower than the masses of the marked compounds. Both behave in the same way as far as losses in the preparation, chromatography and ionization are concerned. They can be differentiated clearly in the detection because of the different molecular weights. The retention times of the resulting peaks are compared to those of the standards to identify the substance. For

[9] According to the standard only the internal standardization is allowed for the sample analysis. To conduct the analysis, ^{13}C-marked standards have to be used at least for PFBA, PFHxA, PFOA und PFOS. If no internal standard is available for a substance, other internal standards can be considered, if the recovery rates are in the same range as the internal standards. This requirement is not always achieved, so that the use of additional standards, especially for substances that are often present, is basically recommended.

a reliable confirmation of the positive analysis results, the correspondence of the MS/MS Spectra of the sample to the standard should checked.

For the quantification, the area ratio of the analyte in the sample to the corresponding internal standards is calculated. This means that for each compound to be analysed an internal standard marked with an isotope has to be available. However, for many PFAS this is not the case. To allow the determination of the recovery rate, another mass labelled standard is used, which behaves like the selected analyte as much as possible as far as sample preparation and analysis are concerned. An “external standard” is used in this case for the quantification. This is the same compound, but not mass labelled. In the worst case, even external standards are missing for the quantification (Gruber, 2011). For example, for PFPeA and PFBS there are no mass labelled standards available. ^{13}C-PFBA is therefore used as internal standard for PFPeA and PFBS. PFBS measurement is based on ^{13}C-PFHxS.

For the important metabolites 5:3 FTCA and 7:3 FTCA there are no comparison substances, but ^{13}C-labelled Perfluorcarboxylic acids with an appropriate chain length are suitable as internal standards. According to the standard, only unbranched PFAS[10] can be used for calibration (DIN, 2011a). In the interpretation, the peak area of the linear and all the detected branched isomers is measured and evaluated on the basis of the calibration of the respective unbranched compounds. In the quantification it is assumed that the nonlinear isomers, which eluate just before the linear PFOS, show the same response-factor as the linear PFOS, although this is not completely correct. The analytical error is approx. 20%. This convention was agreed upon to allow the quantification of branched isomers. The reason is that their percentage, especially in the case of PFOS, can be significant and a chromatographic separation of all isomers is not possible in the usual conditions.

Moreover, the pure compounds for the calibration are not available for most of the isomers (DIN, 2011a). The indicated mass concentrations (in µg/l or µg/kg DW) are based on the respective anions.

APPENDIX 4 REFERENCES

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[10] Branched Isomers occur especially in the PFOA, PFHxS and PFOS analysis.

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