Perfluoroalkylated substances

Aquatic environmental assessment

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Preface

In January 2002, the University of Amsterdam, Institute for Biodiversity and Ecosystem Dynamics (IBED), Department of Environmental and Toxicological Chemistry (MTC) was contracted by the RIKZ to carry out a desk study of perfluoroalkylated substances. This study is directed to the whole track of perfluoroalkylated substances in the environment, i.e.. from production and emission to immission, waste and effects.
The project was coordinated by A.M.C.M. Pijnenburg and R.W.P.M. Laane from the RIKZ. The authors of the report are F.M. Hekster and P. de Voogt.

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Summary

General

Perfluoroalkylated substances (PFAS) is the collective name for a group of fluorinated chemicals, including oligomers and polymers. There are two major production routes for PFAS: Electrochemical fluorination and telomerisation. The products from the first process contain a sulfonyl group (the so-called *ECF-products*). The products from the second production process contain an ethylene group (*telomers*). POSF ($C_8F_{17}SO_2F$) is the most important production intermediate for electrochemical fluorination. 8:2 FTOH ($C_8F_{17}C_2H_4OH$) is the pivotal substance for telomer production. The most important difference between the two production processes is that ECF yields even and odd numbered, branched and straight perfluoroalkyl chains, whereas telomerisation only yields even, linear chains.

Both ECF-products and telomers have four major forms of appearance, namely monomeric, homo-polymeric, co-polymeric, and phosphate esters. Co-polymers, based on acrylates or methacrylates, are the most common form of appearance. Until the 3M company decided to phase out their PFAS production line, they were the major producer of PFAS. Other important suppliers of PFAS chemistry are DuPont, Asahiglass, Clariant, Daikin and Ciba.

For the present study 15 perfluoroalkylated substances have been selected. These substances are used in commercial products, monomers for polymers, important production intermediates or important degradation products. PFAS have special physical and chemical properties, including chemical inertness, high thermal stability, low surface energy, hydrophobicity and oleophobicity. These properties make PFAS valuable compounds for a wide variety of applications, including carpet, textile, leather and paper and board protection, fire-fighting foams, and specialty surfactants.

Sources and emissions

Several applications may lead to emissions of PFAS. The most important is the emission due to wear of PFAS treated tissue (carpet, textile, leather). These emissions are polymeric substances; whether this may lead to monomeric PFAS is not known. The use of fire-fighting foams for calamities or training leads to emissions of monomeric PFAS to the environment. Furthermore, emissions from fluorochemical production sites may be a route of introduction of PFAS into the environment.

Type of industry	Use of PFAS (tonnes/year)	Form	Emissions (tonnes/year)
Carpet	15	Polymers	10 (worst case)
Paper & Board	*60-105* (not in NL)	Phosphates	
Textile	N.A.	Polymers	100% of the applied polymers
Leather	10-20	Polymers	
Fire-fighting foams (mobile)	0.13-0.81	Monomers	0.13-0.81 (worst case)
Fire-fighting foams (stationary)	1.0-3.0	Monomers	1.0-3.0 (worst case)
Specialty surfactants	N.A.	Monomers	-
Polymerisation aid	> 1	Monomers	> 0.77 (77%)

Table S.1 Use and emissions of PFAS in the Netherlands. N.A. = not available.

The use and associated emissions from these applications were assessed in the current report. The most important application of PFAS in the Netherlands is in

paper and paper board treatment, but all this paper is imported. The carpet, leather and presumably the textile industry are the biggest users of PFAS based products in the Netherlands (see table S.1).

Behaviour in the aquatic environment

For a proper assessment of the behaviour of PFAS in the environment many data are lacking. The available data show that the standard concepts of environmental modelling are not applicable. PFAS distribution is not solely based on hydrophobic and hydrophilic interactions, but most likely also on electrostatic interactions. The most important accumulation positions in (aqiatic) biota are expected to be blood and liver.

n-EtFOSE, n-MeFOSE and n-EtFOSA (ECF-products) and 6:2 FTOH, 8:2 FTOH and 10:2 FTOH can readily escape from the water phase to air, considering their relatively high Henry's Law constants (HLC). Some of these chemicals have been detected in air recently. This may be an important factor in the global distribution of the PFAS. Other fluorinated chemicals have lower HLC and are expected to remain in the water phase.
PFOS and 8:2 FTOH exhibit a high sorption potential and desorption is difficult.

Test results show that the perfluoroalkyl chain of ECF-products is not affected by biodegradation, hydrolysis or photolysis. The non-fluorinated part of ECF-products is expected to degrade to sulfonate or carboxylate. The degradation products of telomers are not known, but it is expected that the perfluorinated chain is not affected by degradation, hydrolysis or direct photolysis. Indirect photolysis by OH radicals in air may lead to the decomposition of fluorinated chemicals. 8:2 FTOH was shown to be transformed to some extent in rats to PFOA. For fluorinated organic polymers no degradation data are available.

PFOS is highly bioaccumulative, considering its bioaccumulation factor of 6300-125000. PFOA hardly bioconcentrates (BCF = 1.8) and 8:2 FTOH has a bioconcentration factor of 87-1100.

Occurrence

PFOS and to a much lesser extent PFOA have been detected in the environment on a global scale. No validated sampling or analytical method for PFAS exist as yet. Point sources may lead to elevated levels of PFAS in biota and the abiotic environment. Concentrations of PFAS are higher in more urbanised or industrialised areas, in biota and in the abiotic environment.
Concentrations in biota from North America were highest, followed by biota from Europe. Concentrations in biota from remote locations such as the Arctic were much lower. All PFAS that have been detected in biota were present in blood, liver, kidney, muscle or brain. PFOS concentrations ranged from below limited of quantification to 907 ng/g wet weight. No data are available for the occurrence of telomers in the environment.
In humans, PFOS and PFOA has been detected in occupationally exposed workers and in the general public. Levels in fluorochemical production workers were 0.135-2.44 mg/L (PFOS) and 0.106-6.8 mg/L (PFOA); concentrations in the general public were 17-53 µg/L (PFOS) and 3-17 µg/L (PFOA).

Toxicity
Toxicity tests for PFOS and PFOA have been performed, although many of them with limited reliability. Therefore the assessment of toxicity of PFAS should be considered as a first estimation. The results show that PFOS has moderate acute toxicity to freshwater fish and slight acute toxicicity to invertebrates. Toxicity to algae is practically nihil. The chronic toxicity of PFOS to freshwater fish is low and practically nihil to invertebrates. PFOS has moderate acute and slight chronic toxicity to marine invertebrates. Due to the relative data richness an assessment factor of 50 can be applied to the lowest chronic toxicity data to derive the proposed value for the Dutch quality objectives (iMPC) for PFOS of 5 μg/L. PFOS concentrations in fresh water were shown to exceed the iMPC, in case of point sources. In other freshwaters, the iMPC was approached.
PFOA has slight acute toxicity to freshwater invertebrates and algae, while being practically non-toxic to freshwater fish. Due to the limited number of studies currently available, an assessment factor of 1000 has to be applied to the lowest acute toxicity data to derive the iMPC for PFOA of 3.8 μg/L. This iMPC may be approached close to point sources.
For telomers no conclusions regarding their toxicity can be drawn.

Both PFOS and PFOA have long half-lives (8.67 and 1-3.5 years, respectively) in the human body. Both chemicals are distributed to liver, plasma and kidney. To rodents PFOS and PFOA exhibit low acute toxicity, but they are eye irritating.

In chronic feeding tests with rodents and primates the primary target was the liver for PFOS and PFOA. PFOA was found to be weakly carcinogenic. Mutagenicity testing of PFOS did not show any mutagenic effects. PFOA did induce chromosomal aberrations and polyploidy in Chinese hamster ovary cells, but did not show mutagenic effects in most mutagenicity test, including an in vivo micronucleus test.

In a developmental effect study with PFOS the no observed adverse effect level (NOAEL) and the lowest observed adverse effect level (LOAEL) for the second generation of rodents were determined to be 0.1 mg/kg/day and 0.4 mg/kg/day, respectively.

Policy
In the Netherlands, no specific policy concerning PFAS exists. In the USA the production and import of some ECF-products is regulated and a hazard assessment on PFOA has been performed. The governments from Canada, the United Kingdom and Denmark have programmed studies on the potential risks of PFAS. Furthermore, the OECD has performed a hazard assessment on PFOS.

The 3M corporation has performed various studies on the toxicology, pharmaco-kinetics and environmental fate and effects of ECF-products, notably PFOS. The Association of Plastic Manufacturers in Europe, APME, has set up a research program on the toxicology, pharmaco-kinetics and environmental fate and effects of PFOA. The manufacturers of telomers, gathered in the Telomer Research Program (TRP), have set up a research program on the toxicology, pharmaco-kinetics and environmental fate and effects of 8:2 FTOH.

1 Introduction

1.1 Background

The presence of fluorine in human blood has been reported as early as in 1968 (Taves 1968). After some initial debate (Belisle 1981), in the mid 1990s the occurrence of perfluorooctanoic acid (PFOA) in humans was confirmed (Gilliland & Mandel, 1993; Gilliland & Mandel, 1996). A few years later several publications in the environmental literature started to draw attention to perfluorolkylated substances (PFAS) (Key et al., 1997; Moody & Field, 1999). This attention was made possible by improved analytical techniques, resulting in the characterisation of this group of chemicals in environmental samples. Nowadays, perfluorooctane sulfonate (PFOS) has been detected all around the globe, both in animals and in humans (Olsen et al., 1999; Giesy & Kannan, 2001). These findings did have consequences for the chemical industry. On May 16, 2000, 3M announced that it was phasing out the perfluorooctanyl chemistry production. The decision was based on '*[..] principles of responsible environmental management*.' (3M, 2000). USEPA and the OECD have classified PFOS as a PBT chemical (USEPA, 2000b, OECD, 2002b).

Although no adverse effects had been observed at the concentrations detected, this decision and its rationale resulted in international attention and awareness in scientific and non-scientific media (Atofina, 2000; Browne, 2000; USEPA, 2000a; Wood, 2000; Clarke, 2001, Renner, 2001).
Furthermore international research projects were started on the environmental behaviour of fluorinated chemicals. In June 2002, draft hazard assessments are available for PFOS (OECD, 2002a) and PFOA (USEPA, 2002). Furthermore, international research programs are executing studies on the environmental and toxicological properties of PFOA (APME, 2002) and 1H,1H,2H,2H-Perfluorodecanol (8:2 FTOH, TRP, 2002).

1.2 Objectives

The objectives of this study with regard to perfluoroalkylated substances are:
To provide an analysis of the potential issues in the aquatic environment: a description of the loads, occurrence, behaviour and effects and an analysis of the issues which indicate how the presence of perfluoroalkylated substances may disturb the functioning of the different aquatic systems by effects on sensitive organisms. Furthermore to give an overview of the national and international policies with regard to PFAS.

In this study the most recent information on perfluoroalkylated substances has been used. PFAS are under much international scientific attention. This results in continuous publications on this matter. This document tries to reflect the state of knowledge in June 2002.

The study has a broad set-up. The following aspects will be handled. In chapter 2 the chemical characteristics of perfluoroalkylated substances are described. In chapter 3 the production process is clarified and the use and associated emissions of these chemicals to the environment are described. In chapter 4 the behaviour in the environment is described, followed by chapter 5, dealing with the occurrence in the environment. In chapter 6 and 7 an overview is given of toxicity data and governmental policies, respectively.

1.3 Terminology

Fluorochemical:	A term used to describe broadly all chemicals containing the element fluorine; Specifically, the term is used most commonly to describe small (1-8 carbon length) fluorinated molecules which are most used for refrigeration, fire suppression and as specialty solvents
Fluorinated chemical:	a term used synonymously with "fluorochemical
Fluorotelomer:	a term used to describe an oligomer created by reaction of tetrafluoroethylene (TFE) with perfluoroethyl iodide CF_3CF_2I to produce $F(CF_2CF_2)_n$-I [n = 3-6, avg. 4], the term "*telomer*" is often used synonymously with *fluorotelomer*.
Fluoropolymer:	a term used to describe a polymer which has fluorine attached to the majority of carbon atoms which comprise the polymer chain backbone. Common fluoropolymers are: polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), fluorinated ethylene-propylene (FEP), etc.
Fluorinated organic polymer:	a term used to describe a polymer which has a hydrocarbon backbone (polyamide, polyester, polyurethane, etc.) to which is appended a fluorinate carbon chain.
Perfluoro- /Perfluorinated:	describes a substance where *all* hydrogen atoms attached to carbon atoms are replaced with fluorine atoms – CF_n- where n = 1 - 4.
Perfluoroalkylated substance:	a substance which bears a perfluorocarbon, also known as a perfluroroalkyl, functional group. $F(CF_2)_n$-R where n is an integer and R is not a halogen, or hydrogen.
Fluorinated organic surfactant:	a term to describe a surface active, low molecular weight, substance which contains fluorinated carbons; the term fluorosurfactant is used synonymously.
Perfluorinated surfactant:	a term used to describe a surface active, low molecular weight, substance where all carbons bear fluorine in place of hydrogen; the term fluorosurfactant is used synonymously.

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2 Physical-chemical properties

2.1 Identification

Perfluoroalkylated substances (PFAS) is the collective name for a group of fluorinated chemicals, including oligomers and polymers. This group of chemicals comprises several hundreds of compounds (NCEHS, 2001), and can be divided into 23 categories (NCEHS, 2001).
Important subsets are the (per)fluorinated organic surfactants and the fluorinated organic polymers.

Category	Substance type	Number listed
1	Perfluoroalkyl sulfonates	18
2	Perfluoroalkyl sulfonyl derivatives	10
3	Perfluoroalkyl sulfonamides	60
4	Perfluoroalkyl sulfonamide alcohol derivatives	12
5	Perfluoroalkyl sulfonamide phosphate derivatives	6
6	Perfluoroalkyl sulfonamide glycine derivatives	6
7	Perfluoroalkyl sulfonamide polyethoxylate derivatives	7
8	Perfluoroalkyl sulfonamide aminopropyl derivatives	28
9	Perfluoroalkyl sulfonamide chromium complex derivatives	6
10	Perfluorocarboxylic acids	29
11	Fluorosulfonamides	1
12	Fluoroesters	5
13	Fluorothioethers	9
14	Fluorocarboxylates	3
15	Fluorourethanes	2
16	Fluoroalcohols	14
17	Fluoroacrylates	84
18	Fluorophosphates	8
19	Fluoroalcohol derivatives	5
20	Perfluorosulfonamide acrylate polymers	13
21	Fluoroacrylate polymers	10
22	Perfluoroalkyl and -alkoxy silanes	6
23	Perfluorophosphonics	4

Table 2.1. Categories of perfluoroalkylated chemicals (NCEHS, 2001)

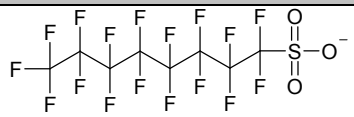
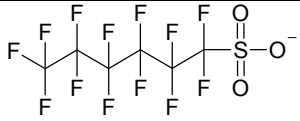
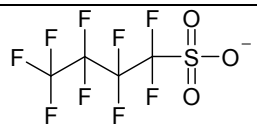
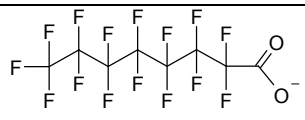
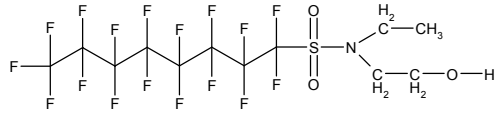
For many of these substances very few physical-chemical data are available. This study will focus on the most important commercial products, the primary production intermediates, and the major degradation products.

PFAS can be produced via two distinct routes of synthesis:
- Simons Cell Electrochemical Fluorination (ECF), as used by 3M and Miteni,
- Telomerisation, as used by among others Asahiglass, Atofina, Clariant, Daikin and DuPont.

The production processes will be discussed in the next chapter. The ECF process yields branched and straight chain perfluorinated products with a sulfonyl group (see table 2.1, categories 1-9, 20). The products from telomerisation are not perfluorinated, but have a linear perfluoroalkyl chain with an ethylene group followed by a functionalised group (see table 2.1, categories 12-19, 21; see section 3.2).

The products that are produced via the two routes of synthesis have four major forms of appearance, being monomeric, homo-polymeric, co-polymeric and phosphates esters. The form of appearance is dependent on the application, with co-polymers as the one used most often. The majority of the fluorinated organic polymers are co-polymers of fluorinated acrylates. Table 2.1 shows that many different (per)fluoroacrylates exist. The various applications and chemicals involved are described in more detail in chapter 3.

The co-polymers of fluorinated acrylates possess surface modifying properties. Polymers exhibit an environmental behaviour totally different from low molecular weight compounds. Furthermore, very few properties are known of fluorinated organic polymers, including fluorophosphates. Therefore the polymers will be treated in a different way in this study. They will not be included in the table of primary study substances, but their production intermediates will be. Since the degradation products or production impurities from fluorinated organic polymers can be low molecular weight fluorosurfactants, these will be incorporated in this study.
In commercial products the fluoroalkyl chain lengths can vary from four up to twenty carbon atoms. In general, most products have chain lengths of between six and ten. Most data are available on the chemicals with eight carbons. Therefore, this study will focus on the following products (see table 2.2):

Abbrevation	Full name	Selection Criterium*	CAS-number	Structure
PFOS	Perfluorooctyl sulfonate	1	Various salts	
PFHxS	Perfluorohexyl sulfonate	1	Various salts	
PFBS	Perfluorobutyl sulfonate	1	29420-49-3	
PFOA	Perfluorooctanoic acid	1,3	Various salts	
n-EtFOSE	n-Ethylperfluoro-octanesulfonamidoethanol	2	1691-99-2	

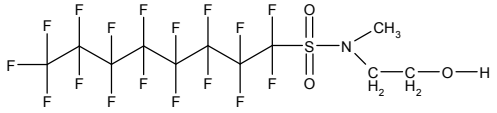
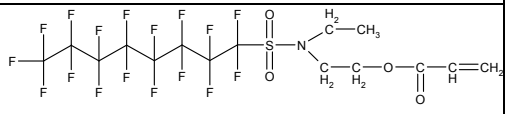
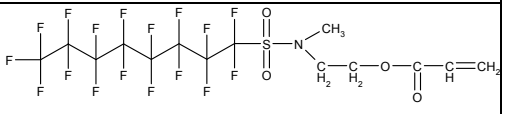
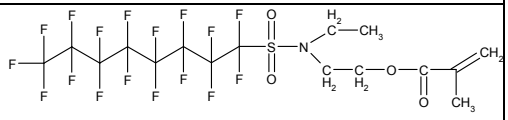
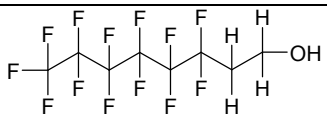
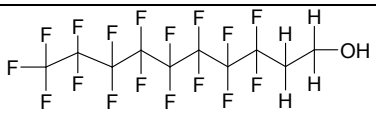
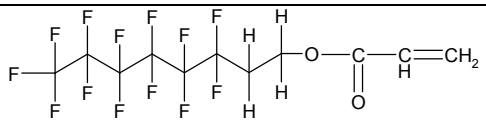
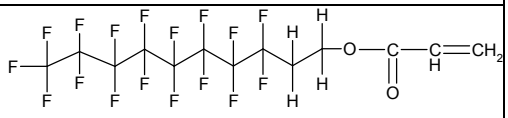
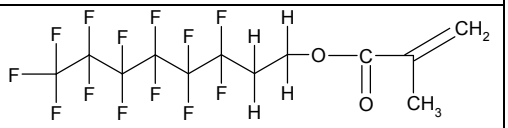
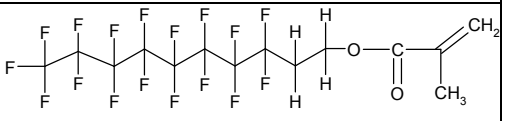
Abbrevation	Full name	Selection Criterium*	CAS-number	Structure
n-MeFOSE	n-Methylperfluorooctane-sulfonamidoethanol	2	24448-09-7	
n-EtFOSEA	n-Ethylperfluorooctane-sulfonamidoethyl acrylate	4	423-82-5	
n-MeFOSEA	n-Methylperfluorooctane sulfonamidoethyl acrylate	3, 4	25268-77-3	
n-EtFOSEMA	n-Ethylperfluorooctane sulfonamidoethyl methacrylate	3, 4	376-14-7	
6:2 FTOH	1H,1H,2H,2H-perfluorooctanol	2	647-42-7	
8:2 FTOH	1H,1H,2H,2H-perfluorodecanol	2	865-86-1	
6:2 FTA	1H,1H,2H,2H-perfluoro-octyl acrylate	4	17527-29-6	
8:2 FTA	1H,1H,2H,2H-perfluoro-decyl acrylate	4	27905-45-9	
6:2 FTMA	1H,1H,2H,2H-perfluorooctyl methacrylate	4	2144-53-8	
8:2 FTMA	1H,1H,2H,2H-perfluorodecyl methacrylate	4	1996-88-9	

Table 2.2. Primary study substances. * The selection criteria are (1) Most likely degradation product (2), Important production intermediate (3) Important commercial product (4) Important monomer for polymers

The above-mentioned substances bear various names, but may generically be described as perfluoroalkylated substances (PFAS). Specific subclasses can be referred to as fluorinated organic surfactants, (per)fluorosurfactants, (per)fluorinated surfactants, perfluorinated chemicals or fluorochemicals. The terminology is explained in section 1.3. ECF-based products are sometimes referred to as 'POSF-based' or 'POSF-related' substances, in contrast to fluorinated telomer-products. The products that are synthesised via telomerisation are also referred to as telomers. The commercial names for perfluoroalkylated substances can be found in table 3.9.

Fluorinated organic polymers are not to be confused with fluoropolymers (see section 1.3).

2.2 Physical-chemical characterisation

Some of the substances in Table 2.2 are process intermediates, others are used themselves in formulations and some of these products only occur due to degradation processes. For the majority of these substances no physical-chemical properties are available. For the polymers no relevant data are available at all. Furthermore, the reliability of some of the available data is doubtful. To evaluate the reliability of the data a Data Reliability Indicator (DRI) is used, as developed by Klimisch et al. (1997). In Annex II the methodology of the DRI is explained.
In table 2.3 the available, reliable data are accumulated:

Substance	Molecular weight (g/mol)	Melting point (°C)	DRI[a)]	Boiling point (°C)	DRI	Wate (g/L)
PFOS (K^+)	538.23	> 400[1]	1	-	-	5.19 5.70
PFHxS	438.22	-	-	-	-	-
PFBS	338.21	-	-	-	-	5.1 E
PFOA (NH_4^+)	431.1	Sublimes at 130°C[6]	-	Sublimes at 130°C[6]	-	> 5.0 > 1.0
n-EtFOSE	571.26	55-60[7]	2	-	-	1.51
n-MeFOSE	557.23	-	-	-	-	-
n-EtFOSEA	625.30	27-42[10]	2	150 at 1mm[10]	2	8.9 E
n-MeFOSEA	611.28	-	-	-	-	-
n-EtFOSEMA	639.33	48-55[11]	-	-	-	-
6:2 FTOH	364.11	-	-	88-95 at 28mm[12]	-	1.2-1
8:2 FTOH	464.12	49-51[14]	-	113 at 10mm[14]	-	1.40
6:2 FTA	418.16	-	-	-	-	-
8:2 FTA	518.17	-	-	90 at 4mm[16]	-	-
6:2 FTMA	432.18	-	-	-	-	-
8:2 FTMA	532.20	-	-	120 at 4mm[17]	-	-

Table 2.3. Properties of selected fluorochemicals. a) DRI = Data Reliability Indicator (1) 3M, 1999a (2) 3M, 2000 (3) 3M Reports, 1999 (4) 3M, 1999b (5) Miteni, 2002 (6) APME, 2002 (7) 3M, 1999c (8) 3M, 2001 (9) 3M, 1998, (10) 3M, 1996 (11) Fischer Scientific, 2001(12) ABCR, a (13) DuPont, 2002 (14) ABCR, b (15) TRP, 2002 (16) ABCR, c (17) ABCR, d. Calc = calculated. N.D. = not determined.

2.3 References

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3 Production, Use & Emissions of PFAS in the Netherlands

3.1 Introduction

PFAS are used in numerous applications. Because fluorinated surfactants are relatively expensive, they are only used when other products do not possess the specific requirements (Kissa, 2001). Perfluorinated surfactants have special physical and chemical properties, including chemical inertness, high thermal stability, low surface energy, hydrophobicity and oleophobicity (Smart, 1994; Kannan et al., 2001). These characteristics make them valuable compounds in several fields of application.
The most important fields of application are (USEPA, 2002; NCEHS, 2001; DuPont, 2002):

- Carpet protection,
- Paper and board protection,
- Textile protection,
- Leather protection,
- Fire-fighting foams,
- Specialty surfactants,
- Polymerisation aid.

The distribution over use categories in the Netherlands is not precisely known. A recent inventory of the use of PFAS in the United Kingdom, shown in table 3.1, shows the relative importance of the several categories in the UK. Table 3.1 also presents the breakdown in global application categories of the perfluorinated products of the 3M company.

Application area	Use UK (NCEHS, 2001) (%)	Application area	Global 3M production (OECD, 2001) (%)
Carpet & Textile Treatment	48.8	Surface treatment	48
Paper & Board Treatment	15.0	Paper protection	33
Speciality Surfactants	17.5	Performance chemicals	15
Fire-Fighting Chemicals	16.3	Fire-fighting foams	3
Chemical Intermediates	2.5		

Table 3.1. Proportional breakdown of perfluorochemical use in the UK and global 3M production.

From these data it is obvious that carpet and textile treatment constitute the major use category, probably followed by paper treatment. Although this breakdown may be different for the Netherlands, because of the difference in relative importance of industry branches from country to country, it is expected that at least some of these use categories will be important users of PFAS in the Netherlands.

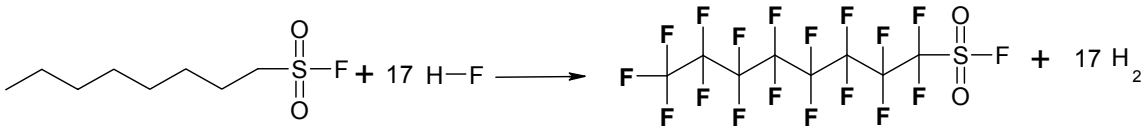
The applications and their corresponding emissions to the environment will be discussed in this chapter. Other applications such as herbicide, cosmetics, and electronics will not be discussed, because they are used in smaller quantities. Kissa (2001) reviewed most of the possible applications for fluorochemicals.

Another possible source of fluorinated chemicals in the environment are the emissions from fluorochemical production sites.

For all applications a few routes of emissions are possible. The emissions result from production, from use, from collected and uncollected waste after use (both monomeric and polymeric), as well as from waste treatments (incineration in a municipal waste incinerator, water purification in a waste water treatment plant (WWTP)).

3.2 Production

There are two major commercial production processes for PFAS: electrochemical fluorination (ECF) and telomerisation.
In the ECF process an organic compound is dissolved or dispersed in anhydrous hydrogen fluoride. A direct electric current is passed through the hydrogen fluoride, causing all the hydrogen atoms of the organic compound to be replaced by fluorine. The overall reaction is as shown in figure 3.2:



1-Octane sulfonyl fluoride — Perfluoro-1-Octane sulfonyl fluoride (POSF)

Figure 3.2. Example of the ECF process

In this process fragmentation of the alkyl chain can occur. Therefore, the products of this production process contain various impurities. The process, its products and its impurities are described more extensively in Annex III.

With the ECF process also PFOA can be produced from octanyol chloride. Hydrolysis of the obtained perfluorooctanyol fluoride yields PFOA (see figure 3.3).

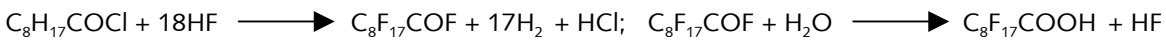
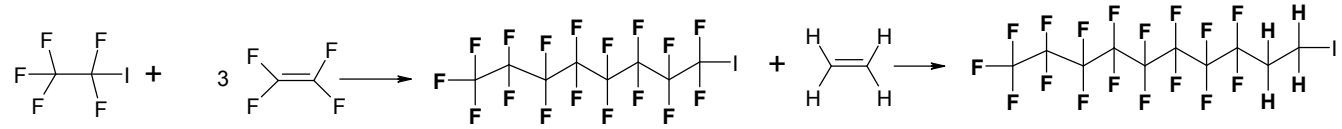


Figure 3.3 Production of PFOA with the ECF process (Kissa, 2001)

In the telomerisation process iodopentafluoroethane is reacted with *n* units of tetrafluoroethene (TFE); the reaction with 3 units is shown as an example in figure



Iodopentafluorethane — Tetrafluoroethylene — Perfluorooctyl iodide — Ethylene — 1H,1H,2H,2H-Perfluorodecyl Iodide

Figure 3.4. Example of the telomerisation process

3.4:
This production process yields straight chains, with hardly any impurities, but the products are not fully perfluorinated. The ethylene group is characteristic for this production process. The process and its products are described more extensively in Annex III.

3.3 Use and emissions

Many suppliers manufacture and market PFAS for a variety of applications. Until 3M decided to phase out their perfluorooctyl chemistry (3M, 2000a), they were the most important global producer of PFAS. Recently DuPont bought the

fluorinated telomer division of Atofina (Atofina, 2002). Other important PFAS suppliers are Asahiglass (Japan), Daikin (Japan), Clariant (Switzerland) and Bayer (Germany).

The different commercial names for the products based on perfluoroalkylated substances of these suppliers are reported in table 3.9 at the end of this chapter.

3.3.1 Carpet protection Introduction

Fluorinated surfactants are used to form a protective, soil repellent coating on carpets. The principle of soil repellence is based on the reduction of the surface energy of the fibre by the fluoroalkyl chains. These chains repel both water and oil. Therefore soil particles cannot enter the carpet. The mechanism is explained in figure 3.5:

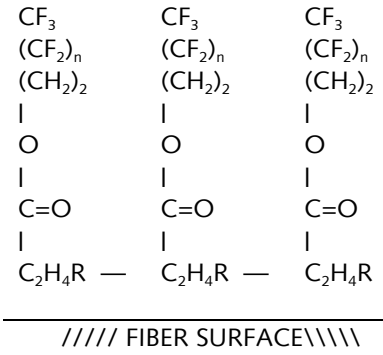


Figure 3.5. Mechanism of carpet protection with fluorinated polymers (Tomasino, 1992).

These soil repellent products for carpets are generally referred to as Scotchgard products, which is the brand name of the 3M product for this application. The commercial products for carpet protection contain approximately 15% fluoroalkyl acrylic polymers (Tomasino, 1992, 3M, 2000b, 3M, 2000c). Well-known products are Scotchgard (3M), Zonyl (DuPont), Baygard (Bayer) and Foraperle (Atofina). In general these products are used as foam-applied emulsions for the finishing of the carpets (VNTF, 2002).

Use figures

The estimated use of fluorinated organic polymers in the carpet industry in the Netherlands is approximately 100 tonnes of products annually (VNTF, 2002). With an average of 15% fluorinated organic polymers this corresponds to 15 tonnes of fluorinated polymers. The amounts used are not at all constant; the (temporary) withdrawal of the 3M products of the market has an important influence on the fluctuations (see Table 3.6).

Apart from carpet manufacturing in the Netherlands, also PFAS treated carpets are imported from foreign countries. For the total carpet industry 141 million m^2 is produced in the Netherlands, 125 million m^2 is exported and 75 million m^2 is imported (VNTF, 2001). Therefore in the Netherlands annually 91 million m^2 carpet is sold. For the production of these carpets approximately 65 tonnes PFAS-based products are used, with about 10 tonnes fluorosurfactants[1].

[1] 141-125 = 16 million m^2 produced for the Dutch market. 75 million m^2 imported makes 91 million m^2 used annually. It is assumed that production processes in foreign countries used approximately the same amount of PFAS for carpet protection. Therefore 91/141 * 100 tonnes makes 64.5 tonnes. 64.5 * 0.15 = 9.7 tonnes PFAS.

	1999	2000	2001
Amount fluorinated organic polymer based products used (tonnes)	102.4	136	80.9

Table 3.6. Annual consumption of fluorinated organic polymer based products in the carpet industry in the Netherlands in 1999-2001.

Emissions

There are several possible routes of emission of PFAS from the use and consumption in the carpet industry.

1. Losses during application in the factory,
2. Wear from the carpet,
3. Emission of monomers from polymers,
4. Emissions from reapplication on fixed carpets,
5. Emissions from the waste phase.

Ad 1) In the carpet factory the fluorosurfactant-based finishing is applied and the carpet is dried afterwards. From that application emissions may occur: these cannot be quantified in this study, because emission factors are not known (GuT, 2002).

Ad 2) The durability of the protective PFAS layer on carpets has been studied. ' [..] *it is expected that 50% of the FC [fluorochemical] treatment will be removed over the nine-year life of the carpet due to walking and vacuuming, while an additional 45% of the FC treatment will be removed in steam cleaning throughout the carpet life* (3M, 2000d). ' These percentages vary with products of different producers (DuPont, 2002). The wear of the protective layer with a corresponding emission of fluorinated organic polymers to the environment does not necessarily lead to the emission of PFAS. The degradation of fluorinated organic polymers is not known (see section 4.4.4).

In a worst case estimate it might be assumed that all the polymer degrades to form PFAS and that 95% of the polymer is removed. On carpets that are used in the Netherlands, 10 tonnes of fluorinated organic polymers are applied. Therefore 9.5 tonnes of PFAS may be released to the environment, due to wear of carpet protection polymers.

Ad 3) The use of fluorinated organic polymers may lead to the emission of PFAS to the environment via a direct or indirect route. The direct emission of PFAS is due to impurities in the products. During the various steps of the production process, used to form functionalised products, reaction impurities are formed. The impurities represent 1-2 percent of the total production volume and will be present in the finalised product (3M, 2000e). The impurities will also be present in the monomers used for manufacturing of the polymers. It is very likely that the impurities will not polymerise. Whether the impurities will be present in the polymer as monomer is not clear. If they are, it is possible that they will be released from the polymeric product after its application to the carpet.

Secondly, polymerisation is often not a fully efficient reaction. A small part of the monomer will not react and will be present in the final product as a low level residual (3M, 2000f). The monomers have a composition different from the impurities. They may also be released from the product, leading to the emission of fluorinated functionalised products.

The indirect route of emission of PFAS from polymers originates from PFAS that are not present in the polymer. Physical or chemical degradation may lead to the formation and subsequent emission of PFAS from the polymer. Fluorinated organic polymers are said to be stable (3M, 2002; Bayer, 2002), but the degradation to PFAS has not been studied.

A laboratory test with a polymeric PFAS treated tablecloth confirmed the release of monomers from a polymeric application. An extraction at moderate temperature

(60 °C) with an organic solvent showed the possible leakage of perfluorinated monomers from the treated tissue. The origin (direct or indirect) of the PFAS was not studied (Jonkers et al., 2002).
If a worst-case estimate is made, all the fluorinated polymers can be degraded or transformed to form PFS. As was calculated above, this may lead to the emission of 9.5 tonnes of perfluorinated surfactants. This is the worst-case estimate of ad 2 and 3 together.
Ad 4) Carpets that have been treated with fluorochemicals are sometimes re-treated. This can be done after cleaning by professional carpet cleaners, or by consumers, with spray applications. The consumer application does not appear to be an important application in the Netherlands. A short survey with carpet shops showed that fluorochemical protection sprays were not available (Alto, 2002; Carpetland, 2002; NTU, 2002; ITC, 2002). Carpet cleaners do use fluorochemical-based products for the application of a new protective layer (Chem-dry, 2002). This could lead to emissions. Neither the use, nor the emissions from this application could be quantified in this study.
Ad 5) Carpets that are disposed off after use will be added to the general waste stream. If the carpet cannot be recycled, it will be combusted or landfilled. In the Netherlands most of the non-recyclable waste is combusted (52%), and an important amount of the waste is landfilled (39%)(Milieuloket, 2001). Bond-energy calculations predict that combustion will lead to the destruction of PFAS (3M, 2001a; 3M, 2001b). In the leachate of landfill, PFOS and PFOA have been detected (3M, 2001c). The landfill of PFAS treated products may lead to the emission of PFAS to the environment.

The estimation of emissions of PFAS from the use and consumption in the carpet industry appears to be complicated. The worst-case estimate for emissions of PFAS from carpets that are used in the Netherlands is 9.5 tonnes. The treatment with sprays for re-application is not taken into account. These 9.5 tonnes have been applied in polymeric form and could be released by five different ways. Quantitative information about degradation and transformation of fluorinated organic polymers is the most important remaining question, with a possibly high influence on the worst –case estimate given.

3.3.2 Paper and board protection

Fluorinated chemicals are used in the paper industry to produce water and greaseproof paper. Among others, this paper is used for the wrapping of snacks, cookies and pet foods (Niermans, 2002; Pfleiderer, 2002; Proost & Brand, 2002). This type of material is generally referred to as *Ersatz* paper.
The products that are used for this application are generally based on fluoroalkyl phosphates (3M, 1999a; Kissa, 2001; NCEHS, 2001).

Proofing of paper does not take place in the Netherlands. The majority of this grade of paper that is present in the Netherlands is imported from Germany and Scandinavia (Niermans, 2002; Proost & Brand, 2002).
The main suppliers of fluorochemicals in the paper industry are 3M, Atofina, Bayer, Ciba, Clariant and DuPont with respectively the following products: Scotchban, Foraperle, Baysize-S / Baysynthol, Lodyne, Cartafluor and Zonyl (Pfleiderer, 2002).

Use figures

No production of this grade of paper or board is known in the Netherlands (VNP, 2002). A market survey in 2000 estimated that in the Netherlands between 6000 and 7000 tonnes of *Ersatz* paper is used annually (Niermans, 2002). It is estimated that for these types of paper 1.0-1.5% (based on the dry weight of the fibre) fluoroalkyl phosphate is needed (Kissa, 2001), corresponding to 60-105 tonnes of fluoroalkyl phosphate.

Emissions
Emissions of PFAS due to the use of Ersatz paper are from migration out of the paper to the wrapped product (DuPont, cited in NCEHS, 2001), and emissions from paper manufacturing plants in adjacent countries. The emissions from factories are believed to be very small (3M, 2000d).
Another source of emissions is the cutting waste in the paper converting industry, leading to solid waste of PFAS treated paper.
In the waste phase used paper may also lead to the emission of PFAS. During incineration all PFAS will be destroyed, but leachate from landfills may lead to emissions to the soil and water (see section 3.3.1, 3M, 2001c). Quantitative data are not available for these type of emissions.

3.3.3 Textile protection
Fluorinated chemicals are used extensively in the textile industry and by private consumers. The application is similar to that in the carpet industry. The products used are polymers, based on fluorinated acrylates and methacrylates, and are referred to as *fluorcarbon* (Lakatex, 2002).
The goal of the application of fluorinated chemicals is to provide water, oil, soil, and stain repellence (NCEHS, 2001). Textiles that are used for i.e. tablecloth, upholstery, rainproof clothing and bed linen are treated with these protective chemicals. There are two stages in the textile production process that use fluorcarbon, both intended to form a fluorinated coating.

Use figures
The textile industry in the Netherlands comprises many small and medium enterprises. Some of these companies use fluorosurfactants in their manufacturing process. Because the industry is scattered and public data are neither available from the Vereniging Textielindustrie Nederland (*Dutch Assocation for the Textile* Industry, VTN, 2002), nor from the European Apparel and Textile Organisation (Euratex, 2002), it is not possible to estimate the use of fluorochemicals in the Dutch textile industry.
For these applications approximately 2.0-3.0% (of the fibre weight) perfluorochemicals are necessary to obtain the water repellence (Kissa, 2001). However, the total amount of waterproof textile fabricated is not known. In the United Kingdom, textile and carpet applications together contribute for 48.8% of the fluorochemical active ingredients (NCEHS, 2001). It is likely that this industry branch in the Netherlands uses considerable amounts of fluorochemicals.
Textile chemicals are obtained from various manufacturers. Information from stakeholders indicates that Bayer, DuPont, 3M and Daikin are the most important suppliers and have all together a market share of approximately 90% (VTN, 2002; B.L.W. Visser, 2002). Unfortunately, sales figures are not available from the suppliers.

Emissions
There are five possible routes of emissions of PFAS from the use in the textile industry and consumption:

1. Losses during application in the factory,
2. Wear from the textile,
3. Emissions of monomers from polymers,
4. Emissions during reapplication to textiles,
5. Emissions from the waste phase.

Ad 1) The treatment of textiles with fluorinated chemicals in the factory leads to the emission of fluorinated polymers. There is an emission of fluorinated chemicals present in the cut-offs as solid waste. This is a very small percentage of the textile production (Lakatex, 2002). These two emissions together are estimated to form approximately 10 percent of the fluorinated chemicals used (3M, 2000d).

Ad 2) The fluorinated coating on textiles is vulnerable to wear. During the lifetime of the product a considerable part of the fluorinated polymer will be removed, analogous to the wear from carpets. For textiles the intensive washing may increase the amount of the coating that is lost to the environment. This emission has not been quantified. A worst-case approximation would estimate that 100 percent of the applied fluorochemicals are released to the environment.
Ad 3) The use of polymers may lead to the emission of monomers. Both product impurities and non-polymerised monomers may be a source of PFAS to the environment. This is extensively discussed for the application to carpets in section 3.3.1 and is analogously valid for the textile applications. Additionally the intensive washing of textiles may lead to the emission of monomers. In a worst-case estimation it is suggested that all the polymers degrade to form PFAS.
Ad 4) On the consumer market several products are available to improve water and grease proofing of textiles. These products are available as sprays and wash-ins. Some of these products contain fluorochemicals (Bever, 2002; Denig, 2002; Grangers, 1997; Grangers, 1998). Although sales of these products are said to be considerable, no estimation of the market can be made. Both types of (re-) application of fluorinated coatings may lead directly to emissions to the environment. 3M (2001) estimated that 34% of the product that is expelled from a spray is lost to air. Evidently, the part of the wash-in application that is not properly attached to the fibre will be emitted to the sewer. It might be assumed that all the fluorinated organic polymers that are used for the protection of textile on the consumer market are released to the environment. Possible emission routes are emissions during applications and wear of the protective layer. If this worst case estimation is continued it is assumed that all the emitted fluorinated organic polymers degrade to form PFAS.
Ad 5) Textiles that are not recycled will be combusted or landfilled. Presumably, combustion will lead to the destruction of monomeric and polymeric PFAS, whereas landfill may lead to the emissions of PFAS to the environment (see section 5.3).

3.3.4 Leather protection

Perfluoroalkylated substances are used for the treatment of leather. The main function is to provide waterproofing. For this application polymeric fluorochemicals are used (Kissa, 2001).
The water repellents are used in the finishing process. Water repellent consumer sprays are also available for leather products.

Use figures

The Dutch Federation of Tanneries (FNL, Federatie van Nederlandse Lederfabrikanten) is currently executing an inventory of the use of various products in the leather industry. Fluorinated chemicals are incorporated in this survey. Results are forthcoming (FNL, 2002). According to Kissa (2001), concentrations of fluorochemical in leather industry products are very low (0.025-0.05% on leather weight).
Furthermore, much of the leather used in the Netherlands is imported, and much of the produced leather is exported. In 1998 the production of leather in the Netherlands was approximately 7 million m^2, export was 5 million m^2, and import was 3.6 million m^2 (FNL, 2000). The average mass of leather is approximately 6 kilograms per m^2 (UNIDO, 2000). If we assume that all the leather has been treated with 0.025-0.05% PFAS (being a worst-case estimate), the total use in the Dutch leather production industry would be 10 – 20 tonnes of polymeric PFAS. The corresponding total consumption of PFAS for leather that is used in the Netherlands amounts to 8.4-16.8 tonnes[2].

[2] 7 E6 m^2 – 5 E6 m^2 + 3.6 E6 m^2 = 5.6 E6 m^2. 5.6 E6 m^2 * 6 kg/m^2 = 33.6 E6 kg. 33.6 E6 kg *0.025% = 8.4 tonnes. 33.6 E6 kg *0.05% = 16.8 tonnes.

Emissions
No emission estimates have been made for this branch of industry. Emissions are possible from the application in the tannery, from fluorinated chemicals on leather waste and wear from leather during use. Land filling of leather waste may lead to the emission of PFAS to the environment.
Furthermore, the spraying of leather might lead to direct emissions of PFAS to the environment.

3.3.5 Fire-fighting foams

Introduction
Flammable liquid fuel fires form a serious threat to life. Aqueous film forming foams (AFFF) were developed in the 1960s as fire-extinguishing agent for this type of fires (Moody and Field, 2000). The AFFF, when mixed with water and air, provides a fire-extinguishing film consisting of a foam.
PFAS contribute to the performance of AFFF, but comprise only a relatively small fraction of the formulation (0.5-1.5%, Moody & Field, 2000; 3M, 1999b; Solberg Scandinavian, 2001). For this application monomeric perfluorinated salts are used (Moody & Field, 2000). A detailed description of the mechanism of fire-fighting foam can be found in annex IV.

In the Netherlands no foam-forming agents are produced; these are imported (Luttmer, 1998; Ajax, 2002). The use of foam-forming fire extinguishers can be divided in two groups:

1. Mobile fire extinguishers,
2. Stationary fire-fighting systems.

The first group comprises the mobile hand-held extinguishing equipment; the second group comprises stationary fire-fighting systems. The latter may contain large stocks of foam-forming concentrate.

Mobile fire extinguishers
Three types of mobile fire extinguishers exist, of which foam-forming extinguishers are becoming more and more important (Ajax, 2002):

- Powder,
- Carbon dioxide,
- Foam.

The last few years more environmentally friendly mobile foam fire extinguishers have been introduced, and a Dutch certification scheme 'Milieukeur' has been established. There are two suppliers that have products that comply with the scheme (Milieukeur, 2002). These extinguishers contain little or no PFAS and have a large market share with at least one supplier; this company sells approximately 95% so-called 'Eco-foam' (Ajax, 2002).

Use figures
It is estimated that in the Netherlands annually 150,000 mobile foam fire extinguishers are sold, with an average size of 6 litres (Ajax, 2002). For these extinguishers 54,000 litres foam forming concentrate is used annually, with 0.5-1.5% perfluorinated chemicals, corresponding to 270-810 kg PFAS. Due to the use of eco-foam this use has diminished with approximately 50% (135-405 kg PFAS). Apart for new extinguishers, an important part of the foam concentrate is used for the refilling of used extinguishers and for the standardised five-yearly revision. No data are available for the estimation of quantities of this application.

Emissions
There are two important emissions due to the use of fire-fighting foam in mobile equipment: the emission during use and the emission from the disposal of old filling when refilled. Both are non-controlled (Ajax, 2002).
The emission during use, for both training and real accidents is inevitable. Dependent on the place of fire, the fire-fighting foam, with the PFAS, is emitted to the environment.
Foam extinguishers have to be refilled every five year. Although presumably not all extinguisher owners do follow this standard, most of the equipment is refilled. On revision the entire filling has to be replaced with a new one. The old filling, with diluted foam-forming concentrate, is disposed to the sewer and treated in a sewage treatment plant. From an environmental monitoring study (3M, 2001c) it is known that PFOS is still present in the WWTP effluent. Moody & Field (2000) state that analytical methods are not accurate enough to estimate the removal efficiency for fluorinated surfactants. Furthermore, the use of AFFF may lead to problems at the WWTP. Excess foaming may occur from large discharges of AFFF. Other constituents of AFFF may lead to significant higher BODs and CODs (Moody & Field, 2000).

A worst-case approximation would estimate the release to the environment of all the AFFF purchased. This would lead to the emission of 135-810 kilograms PFAS annually, without the PFAS used for the refilling of fire-fighting equipment.

Stationary fire-fighting systems
Five types of fire-fighting agents are available for stationary systems (Ajax, 2002):
- Extinguishing powder
- Extinguishing gas (CO_2, Argon)
- Protein foam
- Fluoroprotein foam
- Synthetic foam

For these applications no eco-foam is available so far. Many standards have been set for these systems, including various tests; the eco-foam concentrate has not been subjected to these tests (Ajax, 2002).
In contrast with the mobile fire extinguishers, the emissions from stationary systems are much more controlled by regulation. Foam-forming concentrate, which has expired is not disposed to the sewer, but has to be collected and transported to a waste incineration plant. It was not possible to retrieve disposal data (LMA, 2002).

Use figures
At this moment no data for the total use are available. In the Royal Dutch Air Force approximately 3,200 litres AFFF concentrate are used for calamities or prevention annually. These are emitted to the environment. Until 2000 another 2,800 litres AFFF concentrate was used annually for fire-fighting training. Nowadays water is used for training (Koninklijke Luchtmacht, 2002). The fire brigade of Amsterdam International Airport Schiphol, used AFFF for training facilities until December 2001. Nowadays they train with water. The last use of AFFF in non-military aviation in the Netherlands for calamities was in 1998. The current annual use is estimated to be close to zero. The stock of AFFF at Schiphol Airport is about 1200 litres, the filling in the equipment excluded (Schiphol Airport Fire Brigade, 2002).
A large conglomerate of companies in the Rotterdam Harbour Area '*Rijnmond*' has an annual substitution of expired AFFF of 75,000 litres concentrate. For the protection of the newly constructed railroad route '*Betuwelijn*' 150,000 litres of AFFF concentrate was purchase by the Dutch government (Ajax, 2002). The latter is an incidental purchase and is not characteristic for the normal annual sales.

Calculated guesses estimate an order of magnitude of 200 tonnes of concentrate bought annually with 0.5-1.5% PFAS, equivalent to 1.0-3.0 tonnes of PFAS.

Emissions
The use of foam-forming concentrate for the extinction of fires obviously leads to the emission of PFAS to the environment, dependent on the location. The collection of emissions from stationary systems is regulated. Most indoor locations are obliged to have a collection system for used fire-fighting foam. For many applications this is not possible; fire extinction will then lead to PFAS emission (Ajax, 2002). Well-known examples are an accidental release at the International Airport of Toronto, Canada and use of AFFF on fire-fighting training sites (Moody & Field, 2000; Moody et al., 2002).
Since 2000, PFAS containing fire-extinguishing agents are no longer used in Dutch military air force training sites (Koninklijke Luchtmacht, 2002).
AFFF concentrate has a long lifetime. If this lifetime has expired, the AFFF can be disposed as chemical waste, and is incinerated (Ajax, 2002). Incineration will presumably lead to the destruction of PFAS.

A worst-case approximation would estimate the release to the environment of all the AFFF purchased. This would lead to the emission of 1-3 tonnes PFAS annually.

3.3.6 Specialty surfactants
PFAS are used as surfactants in various industrial applications. In total this group comprises a considerable amount of the PFAS used, but it consists of various low volume applications. In the United Kingdom these applications accounted for 17.5% of the use of fluorinated chemicals as active ingredient (NCEHS, 2001). No generally valid remarks can be made on the separate use figures and possible emissions.

3.3.7 Polymerisation aid
For the production of fluoropolymers, such as polytetrafluoroethylene (PTFE) a polymerisation aid is necessary. PFOA, or APFO (ammonium perfluoro-octanoate), improve physical properties of the polymer and increase the rate of polymerisation (Kissa, 2001).

Use figures
In the Netherlands only one production plant for fluoropolymers is present, where more than one ton PFOA is used annually (DuPont, 2002). In 1999 the worldwide use was 213 tonnes PFOA annually (APME, 2002).

Emissions
The emissions from this application have been studied by the Association of Plastic Manufacturers Europe (APME). The global mass balance for polymerisation aid for fluoropolymers is shown in table 3.7. This table shows that 77% of the PFOA may be emitted to the environment, via emissions from the plant or from products.

Emission route	Importance (%)
Emitted	61
Water	65
Air	23
Land	12
Reprocessed	14
In products	16
Destroyed	7

Table 3.7 Emission routes of PFOA in fluoropolymer production (APME, 2002)

3.3.8 Production sites

In the Netherlands no PFAS is produced. The nearest production plants are situated in Antwerp, Belgium (3M), and Villiers-St-Paul, France (presently Atofina, in the near future DuPont (Atofina, 2002)). It is possible that emissions occur from these sites, resulting in the presence of PFAS in the Netherlands, either by aerial or riverine transport.
Environmental monitoring has been executed upstream and downstream of a river to which the effluent of a fluorochemical production site is discharged in Decatur, Alabama, USA (3M). This study pointed out that '*effluent from a fluorochemical manufacturing faculty may be one route of introduction in the environment of some environmentally prevalent organic fluorochemicals* (Hansen et al., 2002).' Moreover, preliminary results of an environmental monitoring study revealed elevated concentrations of PFOS in aquatic organisms downstream of a manufacturing plant in Antwerp, Belgium (Van de Vijver et al., 2002).

3.3.9 Other sources

Apart from other uses with corresponding possible emissions, one study revealed the formation of perfluorinated chemicals by thermolysis of fluoropolymers, such as PTFE. Possible products were longer chain polyfluoro (C3-C14) carboxylic acids (Ellis et al., 2001).
A major producer of fluoropolymers questions the reliability of these results (DuPont, 2002).

3.4 Summary of use figures and emissions

In table 3.8 the use figures from the preceding sections are summarised. It becomes clear that the major application is in paper and paper board, followed by carpet, leather and presumably textile and specialty surfactants. For the latter two no reliable data are available. Data from the UK suggest that these two applications take an important share of the PFAS use.
To estimate the emissions from use in the carpet, textile and leather industry a worst case calculation was used. Hence, it was assumed that all the fluorinated organic polymer degrades to form PFAS. Also for fire-fighting foam a worst case estimate of 100% was made. From the use as polymerisation aid about three quarters of the used PFOA may be emitted.

Type of industry	Use of PFAS (tonnes/year)	Form	Emissions (tonnes/year)
Carpet	15	Polymers	10 (worst case)
Paper & Board	*60-105* (not in NL)	Phosphates	?
Textile	N.A.	Polymers	100% of the applied polymers
Leather	10-20	Polymers	?
Fire-fighting foams (mobile)	0.13-0.81	Monomers	0.13-0.81 (worst case)
Fire-fighting foams (stationary)	1.0-3.0	Monomers	1.0-3.0 (worst case)
Specialty surfactants	N.A.	Monomers	?
Polymerisation aid	> 1	Monomers	> 0.77

Table 3.8. Use and emissions of PFAS in the Netherlands. N.A. = not available

3.5 Overview of commercial names

All suppliers use different names for the same type of products. Not all suppliers offer products for all applications. This overview is not complete, but contains all major suppliers for the Dutch market.

Application	Supplier						
	3M	Atofina	Bayer	Ciba	Clariant	DuPont	Asah
Carpet	Scotchgard	Foraperle	Baygard	-		Zonyl	Asah
Paper & board	Scotchban		Baysize-S, Baysynthol	Lodyne	Cartafluor		
Textile	FC brand textile		Baygard-K	Oleophobol	Pekophob		
AFFF	AFFF		-	-	-		
Leather	Scotchgard		Xeroderm	-	-		
Specialty surfactants	Various commercial names per supplier						
Polymerisation aid	No commercial names						

Table 3.9. Commercial names of PFAS products

3.6 References

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4 Behaviour in the aquatic environment

4.1 Introduction

The behaviour of organic micropollutants in the aquatic environment is determined by the properties of the compound (solubility, hydrophobicity, volatility) and by the characteristics of the water system of concern (residence time of the water, sedimentation area, organic matter content, etcetera). These compound and system properties also determine to what extent a compound will accumulate in organisms.

4.2 Solubility and volatilisation

The water solubility of a compound is a good indication of the extent to which the compound will be transported with water. In general, poorly soluble compounds have a high affinity for the organic matrix of silt particles in a water system. Solubility and vapour pressure determine together whether a compound will evaporate out of the water. The volatility of a compound is characterised by its Henry constant (H). Since no Henry constants were available for PFAS, they have been calculated from the values for solubility and vapour pressure (Van Leeuwen & Hermens, 1995).

For PFAS there is a large variation in solubilities, vapour pressures and Henry constants (see table 4.1). Substances for which no data were available are excluded from table 4.1.

Substance	Solubility (g/L)	P_{vapour} (Pa)	H (atm*m3*mol-1) (calc)
PFOS (K+)	5.19 E-1	3.31 E-4	3.4 E-9
PFBS	5.1 E1	N.A.	-
PFOA (H+)	9.5	7.0 E1	4.6 E-6
PFOA (NH4+)	> 5.00 E2	< 1.3 E-3/ 9.2 E-3	<1.1 E-11/ 7.8 E-11
n-EtFOSE	1.51 E-4	5.04 E-1	1.9 E-2
n-EtFOSEA	8.9 E-4	N.A.	-
6:2 FTOH	1.2-1.7 E-2	N.A.	~ 1 E-2
8:2 FTOH	1.40 E-4	2.93	9.6 E-2

Table 4.1. Environmental relevant properties of selected fluorosurfactants

For PFOS the vapour pressure was determined to be 3.31 E-4 Pa. Although the vapour pressure determination study was rated with a Klimisch factor of 1 (see Annex II), there is discussion about the reliability of the result (Cahill, 2002). The hydrogen-salt of PFOA is relatively volatile (70 Pa); the ammonium-salt is not (<1.3 mPa) (Miteni, 2002). For PFOS and PFOA the combination of the good solubility, and their low vapour pressure, resulting in low Henry constants, makes it unlikely that they will be transported by air over large distances (Renner, 2001; Martin et al., 2002).

N-EtFOSE, 6:2 FTOH and 8:2 FTOH have low water solubilities. Combined with a moderately low vapour pressure, these chemicals could have the tendency to escape from the water phase to air. Martin and co-workers (2002) verified this suggestion in a preliminary study with only a few samples. They detected the

presence in air of six fluorinated chemicals, of which at least three can be degraded (after deposition) into PFOS (see section 4.4.2); these chemicals (n-EtFOSE, n-MeFOSE and n-EtFOSA) may thus play a role in the dissemination of perfluorinated chemicals in general and PFOS in particular (Martin et al., 2002). The other three chemicals were telomers; their degradation products are largely unknown hitherto (see, however, section 4.4.3).
The results of this initial investigation by Martin and co-workers, combined with the volatility of some perfluorinated chemicals and the presence of PFOS in remote locations (Kannan et al., 2001a; Kannan et al., 2001b) indicate the potential of some PFAS species to be transported over long distances.

4.3 Sorption

4.3.1 Octanol water partitioning

The distribution of a compound over n-octanol and water, commonly expressed by the partition coefficient K_{ow} is often used to predict or mimic the partitioning between hydrophobic phases and water. K_{ow} has been proposed as a model for the partitioning between the body fat of biota and water (bioaccumulation), between the sediment and water (sorption) and to estimate the soil sorption coefficient for organic compounds (Sabljic et al., 1995).

This derivation of properties is based on the assumption that the hydrophobic and hydrophilic interactions between compound and substrate are the main mechanisms for the partitioning. This assumption has been shown to hold for non-polar and slightly polar organic chemicals.
There are two reasons why this concept is not applicable for fluorosurfactants. First, fluorosurfactants do not behave like traditional organic chemicals, due to the perfluorination: *'[..] hydrocarbon chains are oleophilic and hydrophobic, perfluorinated chains are both oleophobic and hydrophobic'* (Key et al., 1997). Therefore, PFAS do not accumulate in fatty substances or adsorb to organic matter solely due to hydrophobic interactions. The oleophobic repellence prevents the accumulation of PFAS in fat (Kannnan et al., 2001a).
Second, fluorosurfactants are polar chemicals, intrinsically. PFOS is present in the environment as the dissociated salt (3M, 2001a) Therefore electrostatic interactions may play an important role in the distribution. Both biota and sediment have various polar parts with which interaction is plausible.

This 'theoretical' rejection of QSARs based on the octanol/ water partitioning is confirmed by the observation that PFAS accumulate in blood plasma and liver, rather than in adipose tissue (Ylinen & Auriola, 1990; Olsen et al., 1999). PFOA is shown to bind to macromolecules in the tissue (USEPA, 2002). This is different from several persistent neutral lipophilic compounds (Kannan et al., 2001a), which accumulate in fat.
The suggestion that hydrophobic interactions are not the primary sorption mechanism is supported by the assumption that PFOS binds to sediment via chemisorption (3M, 2001b). Therefore, the K_{ow} is not suitable for the prediction of sorption of surfactants.

Although the significance of the partitioning between octanol and water is limited for environmental behaviour on PFAS, there have been several studies that tried to determine the K_{ow} experimentally. Due to the surfactant properties of the substance it was not possible to obtain reliable results with the standard 'shake flask' method (3M, 2000a). Experiments with HPLC retention times made it possible to obtain more reliable K_{ow} results for n-EtFOSE and n-MeFOSEA (see table 4.2).

Substance	Log K_{ow}	References
n-EtFOSE	4.4	3M, 1994a
n-MeFOSEA	5.6	3M, 1994b

Table 4.2. Available values for partitioning n-octanol/water

4.3.2 Sorption

The partitioning between sediment and water is an important factor in the fate of chemicals. Often, the partitioning octanol/water is used to predict this factor. In the preceding section it was argued that this would not give correct predictions for perfluorinated compounds.

Direct measurements of the sorption to soil and sludge gave contradictory results for PFOS. Only two reliable studies are available (3M, 1978a; 3M, 2001b), with a Klimisch factor of respectively 2 and 1 (see annex II). The first study predicts a high mobility of PFOS in Brill sandy loam soil (3M, 1978a). In the second study a strong adsorption to all soils tested was observed, including sludge and river sediment. Once adsorbed, PFOS does not desorb readily (3M, 2001b). The latter study suggests that the primary sorption process is chemisorption. In chemisorption the substance forms a chemical bond with the phase it is adsorbed to.

For other perfluorinated surfactants only less reliable study results are available, having a Klimisch factor of 3. Two studies suggest that n-EtFOSE is very likely to adsorb to soil (3M, 1978a; 3M, 1978b). For PFOA two totally contradictory conclusions were drawn from one study (3M, 1978c).
The results of a monitoring study near a fluorochemical plant show that PFOS, PFOA, FOSA and PFHS do occur in the sediment (3M, 2001c). These findings are supported by the detection of PFOS in various sediments and sewage sludge in a multi-city environmental monitoring study (3M, 2001d). Therefore it is unlikely that these fluorinated chemicals have a high mobility in sediment.

There are no data available on telomers. However, laboratory experiments show that 8:2 FTOH is rapidly sorbed from aqueous solutions. Specific recovery methods have been developed to be able to make accurate measurement. Experts state that the sorption of telomers onto various types of surfaces is very high and that desorption is very difficult (TRP, 2002).

4.4 Transformation

4.4.1 Introduction

The fluorine-carbon bond is the strongest single bond with carbon, but its strength is very much dependent on the actual molecular structure. Given the high-energy content of the C-F bond, it is expected that many fluorinated organic compounds will be resistant to hydrolysis, photolysis and biodegradation (Smart, 1994). Indeed transformation rates (see table 4.3) suggest that the perfluorinated part of PFAS are relatively persistent in the environment.
The available data on transfrmation of PFAS are presented in table 4.3.

Substance	Biodegradation	Biotransformation	Photolysis	Hydrolysis
PFOS (K+)	0%[1,2,3,4,5,6,]		0%[7,8]	T1/2[a] > 41 years[9]
PFOA (NH4+)	0%[2,10]		0%[11,12]	T1/2 > 92 years[13]
n-MeFOSE				T1/2 = 6.3 years[14]
n-EtFOSE	To PFOS/ PFOA[2,3,]		0%[15]	T1/2 = 7.3 years[16] 92% after 24 hours to PFOS (alkaline) [17]
n-MeFOSEA				T1/2 = 99 days @ pH 7, 25˚C (extrapolated) [18]
n-EtFOSEA				T1/2 35 days @ pH7, 25˚C[19]
8:2 FTOH		To PFOA[20]	No direct photolysis expected[21]	

Table 4.3 Available data on the transformation of PFS, a) T1/2 = degradation half-life, (1) 3M, 1976 (2) 3M, 2001e (3) 3M, 2000b (4) 3M, 2000c (5) 3M, 2000d (6) 3M, 2000e (7) 3M, 1979a (8) 3M, 2001f (9) 3M, 2001g (10) 3M, 1978d (11) 3M, 1979b (12) 3M, 2001h (13) 3M, 2001i (14) 3M, 2001j (15) 3M, 1981 (16) 3M, 2001k (17) 3M, 1977 (18) 3M, 1999a (19) 3M, 1996 (20) Hagen et al., 1981 (21) TRP, 2002

4.4.2 ECF-products

Biodegradation

Many of the substances under study undergo primary degradation[3]. In this degradation step the non-fluorinated part of the molecule is transformed. The degradation pathway for n-EtFOSE in wastewater sludge is suggested to be as shown in figure 4.4.

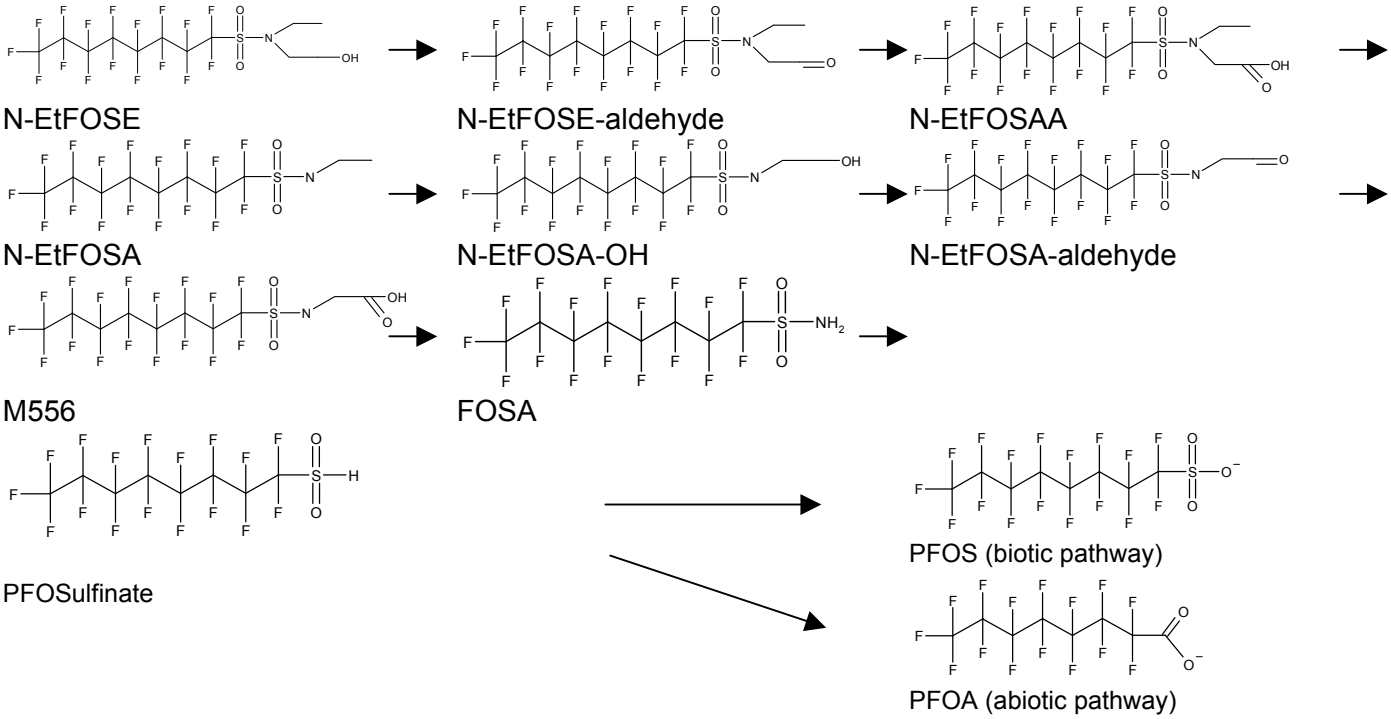

Figure 4.4. Degradation pathway of n-EtFOSE to PFOS and PFOA (3M, 2000b, 3M, 2001e).

[3] A compound is considered to be primary biodegradable if the original compound is altered, due to biodegradation processes. The degradation products can be persistent. With ultimate biodegradation, the original compound is completely transformed into CO_2 and H_2O and inorganic salts.

It is likely that the degradation of n-MeFOSE will follow an analogous pathway, because n-MeFOSE contains the same reactive structures that appear to be vulnerable to microbial (biodegradation) attacks. N-EtFOSE and n-MeFOSE are the two main building blocks of the ECF-based fluorochemistry (3M, 2000h). No research has been published on the transformation of other functional groups, but it is expected that they may also be transformed to n-EtFOSE or n-MeFOSE. The likely endpoints of aerobic degradation of ECF-products are PFOS and PFOA (3M, 2001e). In both compounds the perfluoroalkyl chain is not affected by biodegradation. PFOS is non-degradable under both aerobic (3M, 1976; 3M, 2001e; 3M, 2000b; 3M, 2000c; 3M, 2000e) and anaerobic circumstances (3M, 2000d). PFOA is non-degradable under aerobic circumstances (3M, 1978d; 3M, 2001e); no anaerobic degradation test results are available.

Hydrolysis and photolysis
The available studies on photolysis show that this transformation mechanism will be of no importance in the breakdown of perfluorinated chemicals. The tests with PFOS, PFOA, POSF and n-EtFOSE show no photodegradation at all (see table 4.3).

Experiments show stability toward hydrolysis for all chemicals tested, with exception of the acrylates (see table 4.3). Both n-EtFOSEA and n-MeFOSEA are vulnerable to hydrolytic attack under environmental conditions. The transformation products are not known, but n-EtFOSE and n-MeFOSE, respectively, and acrylic acid are the most logical products. This transformation does not affect the perfluoroalkyl chain. Therefore, hydrolytic products of both acrylates will presumably not be affected by further hydrolysis, photolysis or biodegradation.

4.4.3 Telomer-products
Only one source dealing with the degradation of telomer-products in the environment is available. This study (Key et al., 1998) showed the degradation of 1H,1H,2H,2H-perfluorooctane sulfonate under sulfur limiting conditions by Pseudomonas sp. Strain D2. Volatile degradation products were formed, containing carbon, oxygen, hydrogen and fluorine. Furthermore, the detection of fluoride indicated defluorination (Key et al., 1998).
The biotransformation in rodents of a telomer has been investigated and published. This study suggests that biotransformation of 8:2 FTOH to PFOA does occur in rats (Hagen et al., 1981). In this transformation two fluorine-carbon bonds are broken. Whether the same route of degradation is likely to occur in the environment is not known. If 8:2 FTOH is absorbed by biota in the environment, the same transformation might take place, leading to PFOA. Current research is dedicated to the biodegradation of telomer-products (Renner, 2001; TRP, 2002). Although few experimental supporting data are available, there are various suggestions that the perfluoroalkyl chain of telomerisation products cannot be biodegraded, which is supported by the high binding energy of the fluorine-carbon bond (Smart, 1994; Key et al., 1997; Renner, 2001). However, the research by Key et al. (1998) suggests that fluorinated alkyl chains are vulnerable to biodegradation, presumably yielding biodegradation products that are different than those originating from ECF-products (PFOS, PFOA).
Although direct photolysis is not expected to occur as an abiotic degradation route, there is evidence that decomposition of fluorinated chemicals may occur via indirect photolysis in air with OH radical reactions (Vésine et al., 2000; TRP, 2002).

4.4.4 Fluorinated organic polymers
The vast majority of the fluorochemicals are applied in polymeric form. Hence, most emissions will be in (co-)polymeric form. Until now, no research has been done on the degradation or transformation of fluorinated organic polymers. This is an important subject, since, in general, polymers cannot cross membranes, and

therefore will not have toxic effects. If monomeric PFAS may be formed from fluorinated organic polymers, these could cross biotic membranes.
In interviews with manufacturers, it was suggested that fluorinated organic polymers are very stable (3M, 2002; Bayer, 2002). 3M states that they '[..] *have data demonstrating the stability of high molecular weight fluorochemical polymers and phosphate esters to various mechanisms of degradation*.' (3M, 2000f). One study, predicting the hydrolytic stability, is available. Although the data of this study have to be treated with caution, due to limited reliability, they showed that fluorinated organic polymers are rather stable to hydrolysis, resulting in half-lives ranging from 1-5 years for acrylates and esters to 500 years for fluorinated urethanes (3M, 2000g).
From a chemical point of view it seems possible to hydrolyse the ester bond in polyacrylates and polymethacrylates, leading to the formation of PFAS. Also the ester bond in the fluoroalkyl phosphates might be vulnerable. These aspects have to be investigated in a reliable study.
An initial study with PFAS treated textile has been performed. The organic extraction of polymer treated textile lead to the release of monomeric perfluorinated compounds. The origin of these monomers can be different than from transformation of the polymers (see section 3.3.1) (Jonkers et al., 2002).

4.5 Bioconcentration

Bioaccumulation is a process in which a substance accumulates in an organism. There are two possible routes: biomagnification (uptake through food) and bioconcentration (uptake directly from the water).
Usually, for many organic compounds the bioaccumulation may be derived from the octanol/water partitioning coefficient, because most organic chemicals accumulate in lipids. Since perfluorinated surfactants likely elicit a different partitioning behaviour, the K_{ow} is not a suitable predictor for the bioaccumulation (see section 4.3.1).

Substance	Bioaccumulation	Bioconcentration	Biomagnification
PFOS (K+)	6300-125000[1]	484 (edible), 1124 (nonedible), 859 (whole) clearance >130d[2]	< 1[3]
PFOA (NH4+)		1.8[4] 2[3] <9.4[5] Clearance > 15d[6]	< 1[3]
8:2 FTOH		200-1100 (10 µg/L)[7] 87-310 (1µg/L)[7]	

Table 4.5. Available data on bioaccumulation, bioconcentration and biomagnification of PFAS (1) Moody et al., 2002 (2) 3M, 2001l (3) Martin et al., 2001 (4) 3M in APME, 2002 (5) APME, 2002 (6) 3M, 1995 (7) METI cited in TRP, 2002.

The available, reliable studies on bioaccumulation show that PFOS bioaccumulates, and is hardly excreted (see table 4.5). In an *in situ* bioaccumulation study in Canada a very high experimental bioaccumulation factors (BAF) for PFOS were observed: between 6300-125000 (Moody et al., 2002). This BAF is high in comparison with the BCF and BMF data available. Moody et al. (2002) suggest that accumulated perfluorinated derivatives are metabolised to form PFOS, thus overestimating the BAF of PFOS.
In a laboratory experiment the BCF for PFOA (NH_4^+) was determined to be 1.8 for fish (fathead minnows), 2 for fish (Rainbow trout) and < 9.4 (Carp). The fathead minnows experiment is believed to have limited reliability (USEPA, 2002).

For 8:2 FTOH a water concentration depedent bioconcentration factor was determined by METI. The Telomer Research Program is currently investigating the reliability of this study (TRP, 2002).

For other perfluorinated substances no bioaccumulation data are available.

4.6 Distribution

Research on the environmental fate of fluorinated chemicals is ongoing, including multi-species fate modelling (Cahill, 2002). Only one fate study using a fugacity model is available; this is qualified by the researcher as 'a small first step' (3M, 1999b). Although the preliminary fugacity modelling was tentative, and the Klimisch rating was 3, it is believed to give a rough approximation of PFOS behaviour (Cahill, 2002).
For this exercise the equilibrium criterion model (EQC) developed by Mackay et al. (1996) was used. In this model there are three different levels, with increasing complexity (see figure 4.6).

This ECQ modelling predicts an 80/20 % partitioning over water and soil in level I and level II calculations. In level II, advection is the main removal mechanism. In level III calculations discharges to air and soil are predicted to partition to soil, whereas discharges to water are predicted to stay in the water and are subject to removal by adjective flow (3M, 1999b).

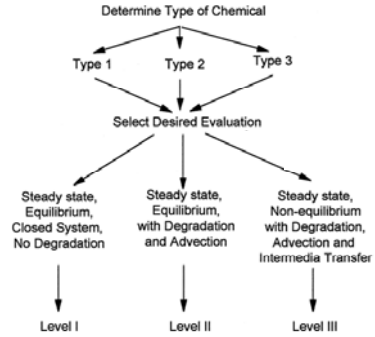

Figure 4.6 Schematic representation of the different levels in the EQC model (Mackay et al., 1996)

4.7 Conclusions and recommendations

From this chapter it is evident that many data on the behaviour of PFAS in the environment are not available. For telomers and fluorinated organic polymers, no data are available on sorption, degradation and distribution. It is recommended to fill these gaps of knowledge.

It was suggested that n-EtFOSE, n-MeFOSE and n-EtFOSA (ECF products) and 6:2 FTOH, 8:2FTOH and 10:2 FTOH (telomers) may escape from the water phase to air, as they have been detected in air. For n-EtFOSE, 6:2 FTOH and 8:2 FTOH this tendency to leave the water phase is supported by relatively high Henry constants. These products may be transported over long range. It is likely that the ECF products may degrade to form PFOS or PFOA. This mechanism may be an important factor in the global spreading of PFAS.

The sorption of PFAS cannot be modelled with Kow. Hydrophobic and hydrophilic interactions are not the primary partitioning mechanisms; electrostatic interactions may be important. It has been suggested that PFOS adsorbs via chemisorption. For PFOA no conclusions could be drawn considering the sorption potential. Laboratory experiment show that 8:2 FTOH is rapidly adsorbed from aqueous solutions and desorption is very difficult. These preliminary results are supported by expert judgements.

The perfluoroalkyl chain of ECF products is not affected by degradation, photolysis or hydrolysis. The most likely end products of degradation are PFOS and PFOA. PFOS is not degraded under aerobic or anaerobic circumstances, for PFOA only aerobic results are available, showing the persistence of this substance. None of

the tested chemicals could be transformed by light. Only the acrylates n-MeFOSEA and n-EtFOSEA can be transformed by hydrolysis, forming n-MeFOSE and n-EtFOSE, respectively, and acrylic acid.
The perfluoroalkyl chain of 6:2 perfluorooctane sulfonate was degraded in a study under sulfur limiting conditions, resulting in unidentified, volatile degradation products. In rats 8:2 FTOH is partially transformed to PFOA. 8:2 FTOH is not vulnerable to direct photolysis, but indirect photolysis in air via OH radicals might result in the complete breakdown. There are various suggestions that the perfluoroalkyl chain of telomers cannot be biodegraded.
No reliable data are available on the degradation or transformation of fluorinated organic polymers.

The bioaccumulation factor for PFOS is 6300-125000; its bioconcentration factor is 859 (whole fish). PFOA hardly bioconcentrates, with a BCF of 1.8 - <9.4. The telomer alcohol 8:2 FTOH a bioconcentration factor of between 87 and 1100 has been reported.

When discharged to water, PFOS will partially adsorb to soil and sediment; bioaccumulation of PFOS will take place. Therefore, water, sediment and organic matter are believed to be the most important environmental compartments.
PFOA will not evaporate from the water phase, and the sorption potential is not clear. PFOA does not bioaccumulate. Therefore, water is believed to be the primary compartment for PFOA.

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5 Occurrence in the environment

5.1 Introduction

The perfluoroalkyl chain of fluorinated chemicals is persistent (see section 4.4.1). Therefore they will be present in the environment. As was shown in chapter 4, their behaviour in the environment is not well known. It was shown that PFAS accumulate in blood plasma and liver of biota. Various publications on the occurrence in the environment have been published. Most of these publications concern the occurrence in Northern American biota.
Very few data on the Western European situation are available and with regards to the occurrence of PFAS in the Netherlands only the preliminary, non-reviewed results of one study are available.

5.2 Analytical techniques (based on Giesy & Kannan, 2002)

5.2.1 General remarks

General remarks
The interest in perfluoroalkylated substances has started relatively recently. The analytical methods for these chemicals are currently under development and their optimisation is the subject of many ongoing studies. In particular the validation and quality assurance of analytical methods for PFAS needs further work. Until now interlaboratory exercises on PFAS analysis have not been carried out. Currently there is no (certified/standard) reference material available on the market for any of the perfluoroalkylated substances. Below a short description is presented of analytical methods for PFAS described in the literature.

5.2.2 Qualitative methods

The fluorine content of organic molecules can be determined by destructive and nondestructive methods, such as neutron activation and X-ray fluorescence. These are low-sensitivity techniques that do not enable identification or quantification of individual organofluorine compounds. It is important to note that all biologically produced fluorinated organics contain only one fluorine atom (Key et al., 1997)

Fluorine in organic compounds can also be determined by combustion, converting it to an inorganic fluoride; however, rigorous conditions are required for quantitative mineralisation. These techniques have been used for determining total fluorine in environmental and biological samples (Sweetser, 1965; Kissa, 1986). In environmental matrices, tests that measure methylene-blue-active substances have been used to detect anionic PFAS, but the approach is non-specific (Levine et al., 1997).

5.2.3 GC-ECD/MS

Perfluorinated surfactants can be determined using derivatisation techniques coupled with gas chromatography followed by electron capture detection (Hagen et al., 1981) and mass spectrometric detection (Moody & Field, 1999; Moody & Field, 2000). PFOS has a low vapour pressure, and its derivatives are unstable.

5.2.4 HPLC-FD

Perfluorocarboxylic acid concentrations in biological samples have been measured using high-performance liquid chromatography (HPLC) and fluorescence detection (Ohya et al., 1998). The application of this method is limited to environmental samples.

5.2.5 NMR

Nuclear magnetic resonance (^{19}F NMR) can be used to determine the concentrations of fluorinated chemicals in biological samples. NMR techniques have been used to measure PFAS in contaminated water samples (Moody et al., 2001). The ^{19}F NMR-results were compared with LC/MS-data. It was suggested that the ^{19}F NMR technique overestimated the actual concentrations (see also section 5.3). In the 1970s, PFAS in human blood were analysed using non-quantitative NMR techniques (Hagen et al., 1981). Preconcentration is generally required with additional rigorous cleanup procedures.

5.2.6 HPLC/MS/MS

Compound-specific methods for analysing PFAS using HPLC-negative ion electrospray tandem mass spectrometry (HPLC/MS/MS) (Hansen et al., 2001) enable surveys of the environmental distribution of PFAS in wildlife at global scales (Giesy & Kannan, 2001; Kannan et al. 2001a; Kannan et al., 2001b). Further method improvements are needed to accommodate the range of PFAS concentrations in biological and environmental matrices and for monitoring PFAS in atmospheric media.

5.3 Freshwater environment

PFOS, PFOA and FOSA have been analysed in a variety of media in six cities in the United States of America including drinking water, surface water column, sediment, publicly-owned treatment works (POTW) sludge, POTW effluent and landfill leachate samples. Decatur, Mobile, Colombus and Pensacola are so-called supply chain cities. In these cities perfluorinated chemicals are either manufactured or industrially used. Cleveland and Port St. Lucie are control cities. Results are listed in table 5.1.

Sample	Decatur	Cleveland	Mobile	Columbus	Pensacola	Port St. Lucie
PFOS (μg/L or μg/kg)						
POTW effluent	4.98	0.436	0.048	0.427	0.896	0.069
POTW sludge (dry wt)	2980	123	58.9	158	125	61.6
Drinking water influent	N.D.	N.D	N.D.	0.057	N.D.	N.D.
Drinking water treated	N.D	N.D	N.D.	0.063	N.D.	N.D.
Drinking water tap	N.D	N.D	N.D.	0.058	0.045/N.D.	N.D.
Landfill leachate	52.7	N.C	N.D	N.D.	N.D.	0.382
Surface water	N.D/N.Q	N.D/N.Q	0.039	0.066	0.029/N.Q.	0.138/N.Q.
Sediment (dry wt)	0.452	N.D/N.Q	0.523	0.437	0.325/ N.D.	10.2
Quiet water	0.111	N.C	0.033	N.D.	N.Q.	2.19
Sample	Decatur	Cleveland	Mobile	Columbus	Pensacola	Port St. Lucie
PFOA (μg/L or μg/kg)						
POTW effluent	2.28	0.665	0.078	0.143	0.087	0.042
POTW sludge (dry wt)	173	0.297	N.Q.	16.4	2.46	N.D.
Drinking water influent	N.D.	N.D.	N.D.	0.026/N.Q.	N.D.	N.D.
Drinking water treated	N.D.	N.D.	N.D.	0.027	N.D.	N.D.
Drinking water tap	N.D	N.D.	N.D.	0.026/N.Q.	N.D.	N.D.
Landfill leachate	47.5	N.C.	N.D.	0.028/N.Q.	N.D.	0.946
Surface water	N.D./N.Q.	N.D.	0.056	0.026	N.D.	N.D
Sediment (dry wt)	N.D./N.Q.	N.D.	N.D./N.Q.	N.D.	N.D.	0.79
Quiet water	0.060	N.C.	0.027/N.Q	N.D.	N.D.	0.749
FOSA (μg/L or μg/kg)						
POTW effluent	0.056	N.Q.	N.Q.	0.085	N.Q.	N.Q.
POTW sludge (dry wt)	102.4	1.69	N.Q.	42.4	1.28	N.Q.
Drinking water influent	N.D.	N.D.	N.D.	N.Q.	N.D.	N.D.
Drinking water treated	N.D.	N.D.	N.D.	N.Q.	N.D.	N.D.
Drinking water tap	N.D.	N.D.	N.D.	N.Q.	N.D.	N.D.
Landfill leachate	0.254	N.C.	N.D.	N.D.	N.D.	N.Q.
Surface water	N.D.	N.D.	N.Q.	N.Q.	N.D.	N.D.
Sediment (dry wt)	N.Q.	N.D.	0.445	N.Q.	N.D.	N.Q./N.D.
Quiet water	N.Q.	N.C.	N.Q.	N.D.	N.D.	0.090

Table 5.1 PFOS, PFOA and FOSA in several media from six cities (average of duplicates; drinking water, surface water and sediment are averages of three different samples). N.D. = not detected, N.Q. = not quantifiable, N.C. = not collected (3M, 2001).

PFOS was detected most often, followed by PFOA and FOSA, all in relatively low concentrations. The highest concentrations were found in POTW sludge. The POTW effluent and landfill leachate were other important media (3M, 2001). The highest concentrations were observed in Decatur. There is a fluorochemical manufacturing plant in this city. PFAS was also present in the control cities, showing a general distribution of PFAS.

Sample	n	PFHxA	PFHpA	PFOA	Total
Site 1.1	3	372	149	6570	7090
Site 1.2	5	57	18	460	540
Site 1.3	3	N.D.	N.D.	N.D.	N.D.
Site 1.4	3	N.D.	N.D.	N.D.	N.D.
Site 2.1	2	144	38	116	298
Site 2.2	2	73	22	64	159
Site 2.3	5	64	19	42	124
Site 2.4	2	N.D.	N.D.	N.D.	N.D.

Table 5.2 Concentrations of perfluorocarboxylates in groundwater at two fire-fighting training sites (μg/L). N.D.= not detected above detection limit (Moody & Field, 1999).

The concentration of perfluorocarboxylates in groundwater near two airport fire-fighting training sites has been analysed (Moody & Field, 1999). The results listed in table 5.2 do not represent general groundwater concentrations.

Both sites showed contamination with PFAS. Sites that were closer to the training-site were more heavily contaminated. PFOA is the quantitatively most important fluorochemical present.

The surface water concentrations of perfluorinated surfactants after an AFFF spill have been analysed with two different analytical methods (Moody et al., 2001; Moody et al., 2002). Results are listed in table 5.3.

Sample	Distance downstream from airport (km)	Total concentration (^{19}F NMR)	Total concentration (LC/MS/MS)	PFHxS	PFOS	PFOA
1-1	-3.9	N.D.	0.022	N.A.	N.A.	N.A.
1-2	4.1	3820	815	N.A.	N.A.	N.A.
1-3	6.6	4900	1090	N.A.	N.A.	N.A.
1-4	8.2	6000	1130	N.A.	N.A.	N.A.
1-6	15	N.D.	0.20	N.A.	N.A.	N.A.
2-1	-3.9	N.D.	0.011	N.D.	N.D.	0.011
2-2	4.1	311	93.5	3.45	N.D.	0.81
2-3	6.6	417	114	N.D.	89.2	0.61
2-4	8.2	539	133	5.44 (n=3)	126 (n=3)	1.60 (n=3)
2-5	9.7	900	185	8.22	174	2.49
2-6	15	17000 (n=3)	2270	49.6	2210	11.3
3-1	-3.9	N.D.	0.028	N.D.	N.D.	0.028
3-2	4.1	N.D.	1.92	N.A.	N.A.	N.A.
3-3	6.6	931	205	3.44 (n=3)	201 (n=3)	0.513 (n=3)
3-4	8.2	267	69.3	1.47	66.7	1.14
3-5	9.7	709	64.2	N.A.	N.A.	N.A.
3-6	15	N.D.	N.D.	N.A.	N.A.	N.A.

Table 5.3 Concentrations of PFAS after an AFFF spill (μg/L). Sample 1-1 denotes the sample was collected 1 day after the spill at sampling site 1. N.D. = not detected, N.A. = not analysed. (Moody et al., 2001; Moody et al., 2002).

No PFAS was detected upstream of the airport. The contamination is spread downstream over time. PFOS was the quantitatively most important fluorochemical present.

The surface water of a river upstream and downstream of a fluorochemical manufacturing facility in the USA has been analysed for perfluorinated surfactants. Both PFOS and PFOA levels increased downstream from the plant as can be seen in figure 5.4 (Hansen et al., 2002).

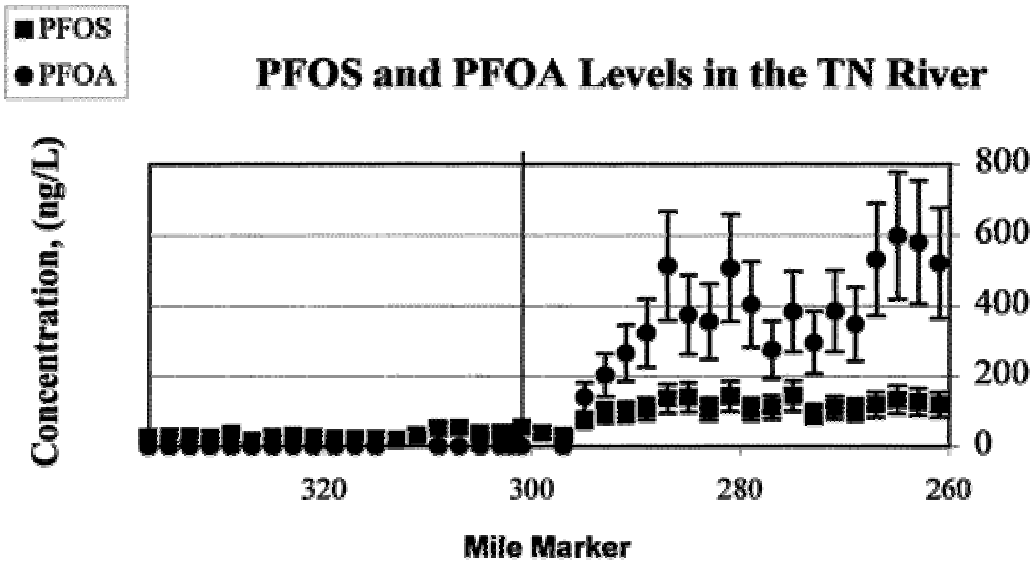

Figure 5.4 PFOS and PFOA Levels in the Tennessee River. The line at 301 mile indicates the location of the incoming effluent from the fluorochemical manufacturing plant (Hansen et al., 2002).

The occurrence of telomers in the freshwater environment has not been reported.

5.4 Marine environment

No data are available on the occurrence of perfluoroalkylated substances in the marine abiotic environment.

5.5 Biota

5.5.1 The Netherlands & Belgium

Until now only one study on the occurrence of PFAS in the Dutch environment has been performed (Van de Vijver et al., 2002). This study revealed the presence of PFOS in various marine and estuarine organisms in the Western Scheldt estuary and the Belgian North Sea.
All samples that were analysed contained detectable amounts of PFOS. The highest average concentrations (1.7 μg/g tissue) were observed in plaice (*Pleuronectus platessa*) from the estuary. Samples of shrimp and crab in the North Sea and the estuary showed concentrations between 40-320 ng/g tissue. Concentrations in *Trisopterus Luscus* (pouting) were the lowest: between 36 (North Sea) and 132 ng/g tissue (estuary) (Van de Vijver et al., 2002). Presumably, these results are not representative for the entire Netherlands. Upstream of the Western Scheldt estuary, along the river Scheldt, a factory producing fluorochemicals is operating. Sampling near a fluorochemical plant in the United States showed that the plant is a possible source of emissions of PFAS to the environment (see section 5.3) (Hansen et al., 2002). Therefore, concentrations downstream of the production site are expected to be higher than elsewhere. There are no data available for telomers in biota from the Netherlands.

5.5.2 Europe

Giesy & Kannan (2001) and Kannan and co-workers (2001a; ASAP) have published data on PFAS in European seals, dolphins, whales, cormorants, eagles, swordfish, tuna and salmon. Results are shown in table 5.5. PFOS concentrations were well above detection limits and PFOS was found in all samples analysed. Concentrations were higher in the more urbanised areas. Only few samples contained PFOA and PFHxS above LOQ. The highest PFOA concentrations were observed in Cormorant livers (29-450). None of the salmon samples and the muscle of a fin whale contained fluorochemicals above LOQ. PFOS concentrations in seal livers were high.
Concentrations in individual organisms varied within about an order of magnitude.

Livers of eagles from Eastern Germany and Poland have been analysed for PFOS from 1979 to 2000. PFOS was quantifiable in almost all samples. There was a statistically significant increase in the concentration of PFOS with time, but no clear temporal trend could be observed (Kannan et al., ASAP). Therefore two values are presented of samples from 1979-1989 and from 1990-1999.

At least one monitoring study is underway in Sweden. The preliminary results of that study showed low background concentrations in fish from unpolluted areas (1-2 ng/g fresh weight). Elevated PFOS levels were observed in fish from urbanised areas and a point source where fire-fighting foams had been used. Detailed results are not yet available (Järnberg, 2002).

No data for the occurrence of telomers in biota in Europe are available.

Species	Location	Tissue	n	PFOS	FOSA
Bottlenose dolphin	Riccione	Blood	4	143 (42-210)	223 (190-270)
Bottlenose dolphin		Liver	6	76 (<1.4-108)	63 (30-139)
Striped dolphin		Liver	4	26 (16.3-40)	<LOQ
Common Dolphin	Giglio island	Liver	1	940	878
Common Dolphin	Giglio island	Muscle	1	77	142
Fin whale	Livorno	Muscle	1	<LOQ	<LOQ
Long-finned pilot whale	Elba island	Liver	1	270	50
Long-finned pilot whale	Elba island	Muscle	1	52	48
Grey seal	Baltic sea	Liver	27	214 (140-360)	42
Grey seal	Baltic sea	Whole blood	26	38.3 (14-76)	-
Ringed seal	Baltic sea	Liver	25	454 (130-1100)	<LOQ
Ringed seal	Baltic sea	Whole blood	29	158	-
Cormorant	Cabras lagoon	Liver	12	61 (32-150)	89 (<LOQ-89)
White-tailed Sea eagle	1979-1989	Liver	7	22 (<LOQ-49.5)	-
White-tailed Sea eagle	1990-1999	Liver	36	40 (<LOQ-127)	-
Bluefin tuna	Palizzi	Blood	6	40 (27-52)	15 (13-19)
Tuna		Liver	8	47 (21-87)	<LOQ
Swordfish	Stretto Messina	Blood	7	7.2 (4-14)	15 (1.1-28)
Swordfish	Stretto Messina	Liver	5	6 (<1-13)	<LOQ
Atlantic salmon	Baltic sea	Liver	22	<LOQ	<LOQ

PFOS and FOSA in various animals from Europe. Mean concentrations are given in ng/g wet weight for liver, and ng/mL for blood . Values in parentheses indicate range. Values below LOQ are denoted by <. (Giesy & Kannan, 2001; Kannan et al., 2001a; Kannan et al., ASAP).

5.5.3 Global occurrence

Several publications are available on the global occurrence of PFAS in biota. Most information is available on concentrations of PFOS in wildlife from North America. In tables 5.6-5.12 levels observed in biota from North America and other parts of the world are presented.

As can be seen from table 5.6 large differences could be observed between individuals. Concentrations in eggs were higher than concentrations in liver and muscle.

Concentrations of PFOS in whole blood of birds were less than those in blood plasma (see table 5.7). Large differences between individual animals were observed. Concentrations of PFOS were much higher in species from more urbanised areas: PFOS concentrations are 10-100 fold less in species from the Midway Atoll than concentrations in species from the Mid Western USA.

In mustelids (table 5.8), invariably, PFOS was found above the LOQ. FOSA was the second most detected fluorinated chemical. Concentrations of PFOS in adults were higher than in juvenile mink. The suggested reason is a difference in feeding pattern (Kannan et al., 2002a). Another possible explanation is the bioaccumulation potential of PFOS. Concentrations of PFOS in mink and otter from more urbanised and industrialised areas were significantly higher than from more remote areas (Kannan et al., 2002a).

In marine mammals (table 5.9) several patterns in PFOS concentrations could be observed. The most plausible explanations for differences in concentrations are location of feeding (closer to shore gives higher concentrations) and habitat (more remote locations give lower exposure) (Kannan et al., 2001a).
Within species a high variability in PFOS concentrations between individual organisms was observed.

Few samples of amphibians and reptiles have been analysed. From the data in table 5.10 it can be concluded that for turtles and frogs large differences in PFOS concentrations between individuals are possible.

The data presented in table 5.11 show that PFOS concentrations in biota from remote locations were considerably lower than those observed from Europe and North America. Concentrations could not be quantified for many samples.
Large differences are observed between the same species from different locations: polar bear in the Beaufort Sea has tenfold lower concentrations on average than polar bear from several other locations (see table 5.11).

Many more data are available from the United States of America than from the rest of the world. However, a comparison of the available data (see Figure 5.12) shows that PFOS concentrations are highest in biota from North America, followed by biota from Europe. However, the PFOS concentration in liver from seals is higher in the European seals. PFOS concentrations in remote locations are much lower.

No data on the occurrence of telomers in biota are available.

Species	Location	Tissue	n	PFOS
Lake whitefish	Michigan waters	Eggs	2	260 (150-380)
Lake whitefish	Michigan waters	Liver	5	67 (33-81)
Lake whitefish	Michigan waters	Muscle	5	130 (97-170)
Brown trout	Michigan waters	Eggs	3	64 (49-75)
Brown trout	Michigan waters	Liver	10	<LOQ-26
Brown trout	Michigan waters	Muscle	10	<LOQ-46
Chinook salmon	Michigan waters	Liver	6	110 (33-170)
Chinook salmon	Michigan waters	Muscle	6	110 (7-190)
Carp	Saginaw Bay, Michigan	Muscle	10	120 (60-300)
Oysters	North America	Whole Oyster	77	312 (<LOQ-1225)

Table 5.6 PFOS in fish and invertebrates from Northern America. Mean concentrations are given in ng/g wet wt for egg yolk, liver and muscle and ng/g dry weight for oyster. Values in parentheses indicate range. Values below LOQ are denoted by <. Means are calculated only for the detectable observations (Giesy & Kannan, 2001, Kannan et al. 2002b).

Species	Location	Tissue	n	PFOS
Double Crested Cormorant		Whole blood	6	105 (34-188)
Cormorant	St. Martin Is., Great Lakes	Whole blood	2	184 (124-243)
Double Crested Cormorant		Blood plasma	2	185 (63-372)
Double Crested Cormorant	Lake Winnipegosis, Manitoba, Canada	Egg Yolk	4	157 (21-220)
Double Crested cormorant	St. Martinville, LA	Liver	2	169 (51-288)
Herring Gull	Little Charity Is., Lake Huron	Whole blood	2	63 (57-68)
Herring Gull	Little Charity Is., Lake Huron	Blood plasma	2	315 (239-391)
Herring gull		Liver	5	186 (16-353)
Ring-Billed Gull	Sulphur Is., Thunder Bay, Lake Huron	Egg Yolk	3	67 (30-126)
Bald eagle		Blood plasma	33	320 (<LOQ-2220)
Bald eagle		Liver	4	192 (24-467)
Black-crowned night heron	San Diego, CA	Liver	5	393 (32-648)
Brandt's cormorant	San Diego, CA	Liver	2	907 (46-1780)
Brown pelican		Liver	2	302 (118-533)
Common loon		Liver	14	129 (<12-595)
Franklin's gull	Red Rock Lakes, Beaverhead County, MT	Liver	4	40 (<12-61)
Great black-backed gull	Carteret County, NC	Liver	2	608 (187-841)
Great blue heron	St. Martinville, LA	Liver	2	539 (162-916)
Great egret		Liver	7	404 (27-1030)
Northern gannet	Carteret County, NC	Liver	1	85
Osprey		Liver	4	377 (42-959)
Red-throated loon		Liver	3	585 (34-1120)
Snowy egret		Liver	3	185 (43-413)

Species	Location	Tissue	n	PFOS
White pelican		Liver	6	270 (30-1120)
White-faced ibis	Sacramento Valley, CA	Liver	1	17
Wood stork	Charleston County, SC	Liver	1	158

Table 5.7 PFOS in piscivorous birds from North America. Mean concentrations are given in ng/mL for blood plasma and whole blood and in ng/g wet wt for egg yolk and livers. Values in parentheses indicate range. Values below LOQ are denoted by <. Means are calculated only for the detectable observations (Kannan et al., 2001b).

Species	Location	n	PFOS	FOSA	PFHxS	PFOA
Mink	Illinois	65	1177 (47-5140)	138	18	20
Mink	Massachusetts	31	298 (20-1100)	92	10	8
Mink	South Carolina	9	2081 (650-3110)	0	25	0
Mink	Louisiana	7	140 (40-320)	0	0	0
River Otter	Bremerton	1	288	22	<4	<7.5
River Otter	Eglon	2	297 (173-422)	60	<4	<7.5
River Otter	Fort Ward	3	156 (139-189)	55 (40-72)	<4-76	<7.5-19
River Otter	Silverdale	2	199 (151-248)	33 (27-39)	<4-52	<7.5-11
River Otter	Soleduck River	2	43 (25-62)	<4-4	<4	<7.5
River Otter	Willamette River	7	579 (97-994)	23 (4.4-44)	<4-68	<7.5-19
River Otter	Yaquina River	2	39 (34-45)	<4-7.4	<4	<7.5-9.9
River Otter	Nehalem River	1	82.8	13	<4	<7.5

Table 5.8 Concentrations of Perfluorochemicals in livers of Mink and otter in North America. Mean concentrations are given in ng/g wet wt. Values in parentheses indicate range. Values below LOQ are denoted by <. Means are calculated only for the detectable observations (Kannan et al., 2002a).

Species	Location	Tissue	n	PFOS
Pygmy sperm whale		Liver	2	14.8 (6.6-23.0)
Short-snouted spinner dolphin	Gulf of Mexico	Liver	3	123 (78.7-168)
Striped dolphin		Liver	2	212 (36.6-388)
Rough-toothed dolphin		Liver	2	54.2 (42.8-65.6)
Bottlenose dolphin		Liver	20	489 (48.2-1520)
California sea lion		Liver	6	26.6 (4.6-49.4)
Elephant seal		Liver	5	9.3 (<5-9.8)
Harbor seal		Liver	3	27.1 (10.3-57.1)
Northern fur seal		Liver	5	329
Sea otter		Liver	8	8.9 (<5-14.3)
Sea otter		Brain	2	<35
Sea otter		Kidney	3	<35

Table 5.9 Concentrations of PFOS in Livers, kidney and brain of marine mammals in North America. Mean concentrations are given in ng/g wet wt. Values below LOQ are denoted by <. Means are calculated only for the detectable observations (Kannan et al., 2001a).

Species	Location	Tissue	N	PFOS
Yellow-blotched map turtle	Mississippi	Liver	6	190 (39-700)
Green frogs	Southwest Michigan	Liver	4	<35-290
Snapping turtle	Lake St. Clair, Michigan	Plasma	5	72 (1-170)

Table 5.10 Concentrations of PFOS in Liver and plasma of turtles and frogs from North America. Mean concentrations are given in ng/mL for blood plasma and in ng/g wet wt for liver. Values in parentheses indicate range. Values below LOQ are denoted by <. Means are calculated only for the detectable observations. (Giesy & Kannan, 2001)

Species	Locations	Tissue	N	PFOS
Weddel seal	Terra Nova Bay	Liver	1	<35
Polar skua	Terra Nova Bay	Plasma	2	<1-1.4
Black-footed albatross	Midway Atol, North Pacific Ocean	Liver	5	< 30
Black-footed albatross	Midway Atol, North Pacific Ocean	Kidney	5	< 30
Black-footed albatross	Midway Atol, North Pacific Ocean	Serum	8	6.2 (3.0-17)
Laysan Albatross	Midway Atol, North Pacific Ocean	Liver	3	< 30
Laysan Albatross	Midway Atol, North Pacific Ocean	Kidney	3	<30
Laysan Albatross	Midway Atol, North Pacific Ocean	Serum	7	14 (5.7-34)
Yellow-fin tuna	Northern North Pacific ocean	Liver	12	<7
Northern fur seal	Pribilof Island	Liver	13	<10-122 [38][a]
Northern fur seal pup	Pribilof Island	Whole blood	19	<6-12 [5]
Northern fur seal adult	Pribilof Island	Whole blood	10	<6
Northern fur seal subadult	Pribilof Island	Whole blood	7	<6
Northern fur seal	Pribilof Island	Whole blood	8	<6
Polar bear	Beaufort Sea	Whole blood	14	34 (26-52)
Polar bear	Barrow; Nuiqsut; Point Lay; Gambell; Shishmaref; Little Diomede; Savoonga	Liver	17	350 (175-678)
Steller sea lion	Southeast Alaska	Whole blood	12	<6
Ringed seal	Spitsbergen	Whole blood	18	9.0
Ringed seal	Norwegian Arctic	Plasma	18	9 (5-14)
Gray seal	Sable Island	Whole blood	12	27.7 ± 11
Black-tailed gull	Korea	Liver	15	150 (70-500)
Black-tailed gull	Hokkaido, Japan	Plasma	24	6 (2-12)
Ganges river dolphin	Ganges River, India	Liver	2	<35-81

Table 5.11 Concentrations of PFOS in biota from locations outside North America and Europe. Mean concentrations are given in ng/mL for blood plasma and whole blood and in ng/g wet wt for liver and kidney. Values in parentheses indicate range. Values below LOQ are denoted by <. Means are calculated only for the detectable observations. Values in brackets [ ] indicate the percentage of detectable observations (Giesy & Kannan, 2001; Kannan et al., 2001a; Kannan et al., 2001b).

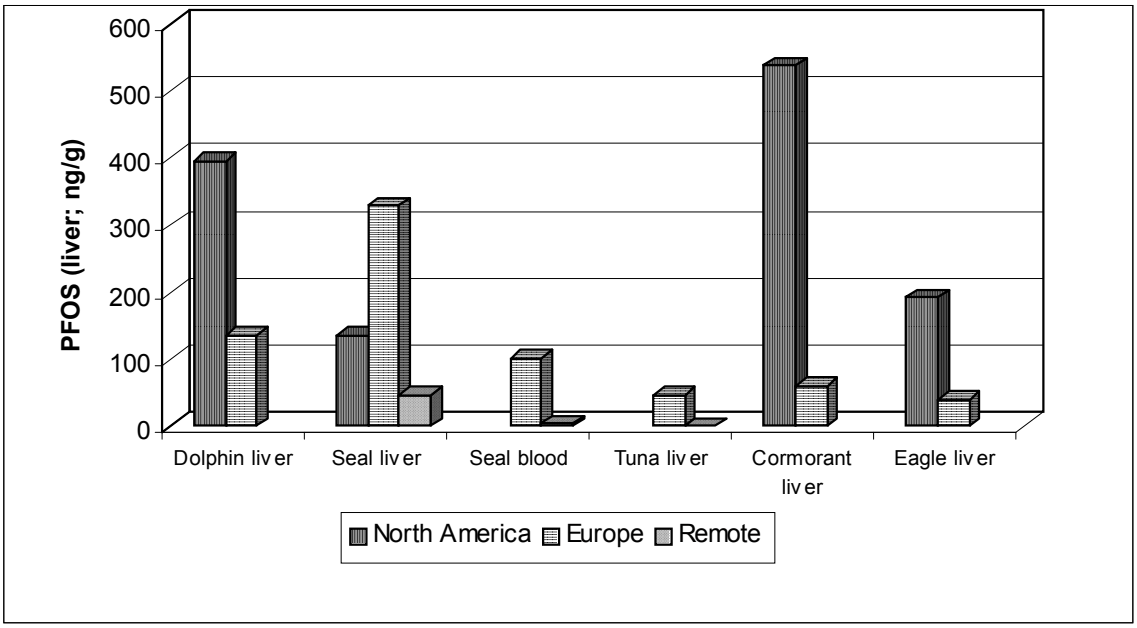

Figure 5.12 Comparison of PFOS concentrations between North America, Europe and remote concentrations. Mean concentrations are given in ng/mL for blood and in ng/g wet wt for liver. (Giesy & Kannan, 2001; Kannan et al., 2001a; Kannan et al., 2001b)

5.6 Air

Martin et al. (2002) have studied the occurrence of several perfluoroalkylated substances in air. These authors detected fluorinated substances in samples collected at a highly urbanised site (Toronto) and a rural site (Long Point).

Substance	Toronto (n=4)	Long point (n=2)
	($ng \cdot L^{-1}$)	
N-MeFOSE	101	35
N-EtFOSE	205	76
N-EtFOSA	14 (n=2)	Not measured
4:2 FTOH	< LOD	< LOD
6:2 FTOH	87	29
8:2 FTOH	55	32
10:2 FTOH	29	17

Table 5.13 Concentrations of PFAS in Canadian air samples (Martin et al., 2002). LOD = Limit of detection

Three ECF products and three telomers were detected and quantified in Toronto air. Samples from the rural site showed considerably lower concentrations, but still five out of six attempted measurements demonstrated the occurrence of fluorinated chemicals in air.

5.7 Human exposure

Human exposure to organic fluorine has been observed as early as 1968. Taves (1968) concluded that '[..] *if in fact there is a non-exchangeable fluoride in serum, it did not break down or diffuse under these conditions, implying a large stable molecule. These findings are consistent with the presence of a fluorocarbon molecule*.'
With the development of analytical methods in recent years, the identification of organic fluorine compounds has improved. Although there has been some debate on the origin of organic fluorine in humans (Belisle, 1981), nowadays it is generally accepted that there is an anthropogenic, non-functional origin.
Since 1993, several studies have been performed on the occurrence of PFAS in humans. Olsen and co-workers and Gilliland and Mandel published both two studies on levels of PFOS and PFOA in production workers with an occupational exposure (Gilliland & Mandel, 1993; Gilliland & Mandel, 1996; Olsen et al., 1999; Olsen et al., 2000). They reported that PFOS and PFOA accumulated in human serum and liver.

PFOS and PFOA serum concentrations in occupationally exposed workers are in the 1-2 mg/L range. Only the levels in workers from the Cottage Grove plant are higher.

In order to compare these data with the general population, also blood from people non occupationally exposed was analysed for PFOS and PFOA. Pooled serum samples from blood dated as far back as 1957 showed concentrations of several tens of μg/L (OECD, 2002). Samples from 1998-2000 showed average serum levels between 17-53 μg/L for PFOS and 3-17 μg/L for PFOA. No differences could be observed between children (37.5 μg/L) and elderly people (31 μg/L). Table 5.14 summarises the findings from these studies:

			PFOS		PFOA	
Origin	Year	n	Mean (mg/L)	Range (mg/L)	Mean (mg/L)	Range (mg/L)
			Occupationally exposed			
Cottage Grove Plant (USA)	1993	111	-	-	5.0	0.0-80.0
	1995	80	2.19	0.00-12.83	6.8	0.0-114.1
	1997	74	1.75	0.10-9.93	6.4	0.1-81.3
Decatur plant (USA)	1995	90	2.44	0.25-12.83	1.46	-
	1997	84	1.96	0.10-9.93	1.57	-
	1998	126	1.51	0.09-10.6	1.54	0.02-6.76
	2000	263	1.32	0.06-10.06	1.78	0.04-12.70
Antwerp plant (Belgium)	1995	93	1.93	0.10-9.93	1.13	0.00-13.2
	1997	65	1.48	0.1-4.8	-	-
	2000	258	0.80	0.04-6.24	0.84	0.01-7.04
Building 236 (USA)	2000	45	0.182	<0.037-1.036	0.106	0.008-0.668
Sagamihara (Japan)	1999	32	0.135	0.0475-0.628	-	-
	General population					
Origin	Year	n	Mean (μg/L)	Range (μg/L)	Mean (μg/L)	Range (μg/L)
Commercial sources (USA) (pooled)	1999	35	35	5-85	3	1-13
Blood banks (USA) (pooled)	1998	18	29.7	9-56	17[a)]	12-22
American Red Cross blood banks (USA)	2000	652	34.9	4.3-1656	5.6	4.27-52.3
Children (2-12y) (USA)	1999	599	37.5	6.7-515	5.6	4.27-56.1
3M Corporate managers (USA)	1998	31	47	28-96	12.5[b)]	Not reported
Plant management Sagamihara (Japan)	1999	32	40.3	31.9-56.6		
Plant management Tokyo (Japan)	1999	30	52.3	33-96.7		
Commercial sources, Intergen (USA)	1998	~ 500	44	43-44		
Commercial sources, Sigma (USA)	1998	~200	33	26-45		
Blood banks (the Netherlands) (pooled)	1999	5	53	39-61		
Blood banks (Belgium) (pooled)	1999	6	17	4.9-22.2		
Blood banks (Germany) (pooled)	1999	6	37	32-45.6		
Samples Seattle (65-96y) (USA)	1999	238	31	3.4-175		

Table 5.14 PFOS and PFOA serum concentration of production workers and general population (Olsen et al., 1999; Olsen et al., 2000; OECD, 2002; USEPA, 2002). A) PFOA detected in about 1/3 of the pooled samples but quantifiable in only two. B) Only 4 employees were above LOD of 10 μg/L.

5.8 Conclusions and recommendations

No validated sampling or analysis method yet exists for the measurement of PFAS. The data observed in the freshwater environment show that point sources of fluorochemicals lead to relatively higher levels of PFAS in the nearby environment. Investigated point sources are a manufacturing plant, AFFF spills and industrial use. However, freshwater samples from cities that served as control site also contained PFAS. The highest concentrations of PFAS were observed in sewage sludge and to a lesser extent in effluent and sediment.

PFOS was detected in liver, blood, muscle, kidney and brain of organisms around the globe, even in remote locations. Concentrations are higher in more urbanised or industrialised areas. Within species, sometimes, large differences are observed between individual organisms. Other perfluoroalkylated substances are less often detected.

A single study on the occurrence of PFAS in the Dutch environment showed the presence of PFOS in several marine and estuarine biota. All available data on occurrence of PFOS in European biota show concentrations far above LOQ.

PFOS concentrations in biota from North America exceed concentrations in biota from Europe. Concentrations in biota from remote regions were much lower.

No data are available for telomers in biota or water compartments.

Both ECF products and telomers have been detected in air in samples. Compared to an urban area, concentrations in samples from a more rural sampling site were considerably less.

PFOS and PFOA have been detected in human blood samples. Concentrations in professionally exposed persons were about 50 (PFOS) to 250 times higher than concentrations in the general public.

5.9 References

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6 Toxicity

6.1 Mechanism of toxicity

The mechanism of toxicity of individual perfluoroalkylated substances is not well understood. The perfluorocarboxylates (including PFOA) are peroxisome proliferators (Intrasuksri et al., 1998). Several other PFAS are hypothesised to exhibit the same mechanism of toxicity (Giesy & Kannan, 2002).

6.1.1 Metabolism

The scarcely available information on metabolism of PFAS shows that PFOS and PFOA are not transformed in biota (OECD, 2002; USEPA, 2002). 8:2 FTOH is transformed to some extend in rats into PFOA (Hagen et al., 1981).

6.2 Toxic effects in the aquatic environment

6.2.1 General

The toxicity to aquatic organisms of several PFAS has been investigated in several studies. For the telomer products few data are available. For the ECF products, many data are available. There are several reasons why the assessment of the aquatic toxicity of these products from these data is difficult (USEPA, 2002).

1) A variety of different lot numbers with different exact composition and impurities were tested. Impurities may affect toxicity. Moreover, the purity of the test material was not sufficiently tested. For some tests formulated products have been used, with varying concentrations of PFAS. Other tests have been executed with impure chemicals, with as low as 19% of the test chemical present.
2) Tests are performed during a long period of time. During this period the exact composition of the commercial substance may have changed, which makes the comparability of test results more difficult.
3) In many of the toxicity tests isopropanol is added, presumably as a carrier solvent. In tests where the test substance was not 100% pure, the toxicity values were corrected for the purity percentage.
4) In many of the tests only nominal test chemical concentrations were used. Measured test concentrations are always recommended, especially since it is known that PFAS have a high sorption potential. Actual concentrations have indeed been observed that were significantly below nominal (OECD, 2002). Some tests have been performed at levels above the aqueous solubility. Results from these tests have not been included in the present evaluation.
5) For PFOS, tests have been performed with various counterions. It was assumed that the test results with different salts are comparable, since PFOS dissociates immediately to its anion and the according counterion. It is unlikely that these counterions are toxicologically significant, except for the dodecyldimethylammonium salt (DDA) (OECD, 2002).

Following the methodology of Traas (2001), test chemical purity has to be over 80%. If the concentration is between 20-80%, the test protocols are called deviating. The methodology accepts test concentrations up to ten times the limit of solubility.
In the present evaluation only studies that had a Klimisch value of 1 or 2 are included. The algae species *Selenastrum capricornutum* has been renamed *Pseudokirchneriella subcapitata* (OECD, 2002). In this report the old name has been maintained. No tests results are available for sediment dwelling organisms. These organisms could be exposed to elevated concentrations in sediment.

For the classification of the toxicity data, the categorisation as developed by van Rijn and co-workers (1995) has been used. This categorisation is shown in table 6.1.

	Acute toxicity (LC_{50} in mg/L)	Chronic toxicity (LC_{50} in mg/L)
Extremely toxic	< 0.1	< 0.001
Highly toxic	< 1	< 0.01
Moderately toxic	1-10	0.01-0.1
Slightly toxic	10-100	0.1-1
Practically non-toxic	> 100	> 1

Table 6.1 Classification of toxicity data (Van Rijn et al., 1995)

6.2.2 Toxicity to freshwater organisms

Most of the reliable data that are available refer to PFOS and PFOA. Some reliable data are available for 8:2 FTOH, N-perfluorooctylsulfonyl-n-ethylglycinate (PFOSGE), N-EtFOSA, N-EtFOSE, N-EtFOSEA and POSF. Many of the data available are from test using protocols deviating from the standards and are reported separately.

PFOS

Acute toxicity

In table 6.2 the freshwater acute toxicity values for PFOS are summarised. The data in table 6.2a show that PFOS is practically non-toxic to freshwater algae and higher plants (Duckweed). Growth rate was used as end-point for the evaluation of toxicity to algae (USEPA, 2002). Towards invertebrates PFOS exhibits only slight toxicity. The lowest reliable toxicity value for fish is an LC_{50} of 7.8 mg/L (Rainbow trout).

The acute toxicity results from tests with deviating protocols are presented in table 6.2b.

Class	Substance	Concentration (mg/L)	Testing time	Effect type	Organism	Method	ref
Algae	PFOS-K	126 120	96h 72h	EC50 growth rate	Selenastrum capricornutum	OECD 201	11
Algae	PFOS-K	82	96h	EC50 cell density	Selenastrum capricornutum	OECD 201	12
Algae	PFOS-K	82	96h	EC50 cell-count	Selenastrum capricornutum	OECD 201	13
Algae	PFOS-K	176 94	96h	EC50 growth rate NOEC growth rate	Anabaena flosaqua	OPPTS 850.5400	12
Algae	PFOS-K	305 206	96h	EC50 growth rate NOEC growth rate	Navicula pelliculosa	OPPTS 850.5400	14
Higher plants	PFOS-K	108 15.1	7d	IC50 NOEC	Duckweed	OPPTS 850.4400	15
Invertebrates	PFOS-K	61 33	48h	EC50 NOEC	Daphnia magna	OECD 202	6
Invertebrates	PFOS-K	58	48h	EC50	Daphnia magna	ISO, 1982	5
Invertebrates	PFOS-K	59 20	96h	LC50 NOEC	Freshwater mussel	OECD 203	10
Fish	PFOS-K	9.5 3.3	96h	LC50 NOEC	Fathead minnow	OECD 203	1
Fish	PFOS-K	7.8	96h	LC50	Rainbow trout	Env. Canada	5
Fish	PFOS-K	22	96h	LC50	Rainbow trout	OECD 203	5

Table 6.2a Acute toxicity of PFOS to freshwater organisms (standardised protocols)

Class	Substance	Concentration (mg/L)	Testing time	Effect type	Organism	Method	Ref
Invertebrates	PFOS-Li	210 100	48h	EC50 NOEC	Daphnia magna	Not noted	8
Invertebrates	PFOS-DDA	4.0 2.2	48h	EL50 NOEC	Daphnia magna	OECD 202	9
Fish	PFOS-Li	4.7	96h	LC50	Fathead minnow	Not noted	2
Fish	PFOS-DDA	200 <170	96h	LL50 NOEL	Fathead minnow	OECD 203	3
Fish	PFOS-DEA	7.8 4.5	96h	LC50 NOEC	Bluegill sunfish	OECD 203	4

Table 6.2b Test results for acute toxicity of PFOS to freshwater organisms obtained from tests with deviating protocols

Sub-chronic/chronic toxicity

Fish appear to be much more sensitive than invertebrates and algae to sub-chronic/ chronic exposure to PFOS (see table 6.3). The same pattern was found with acute toxicity. The NOEC of 0.30 mg/L is consistent with results from a bioconcentration study. In that study no effects were measured at 0.086 mg/L during 62 days uptake, but 100% mortality occurred at an exposure concentration of 0.87 mg/L during 35 days.

The two available studies for daphnids show consistent results and practically no chronic toxicity.

Class	Substance	Concentration (mg/L)	Testing time	Effect type	Organism	Method	Ref
Invertebrates	PFOS-K	12	21d	NOEC reproduction, survival, growth	Daphnia magna	OECD 211	19
Invertebrates	PFOS-K	12 7 11	21d 28d 28d	EC50reproduction NOECreproduction EC50reproduction	Daphnia magna	ASTM/OECD, 1981	7
Fish	PFOS-K	0.30 0.30 >4.6	42d 42d 5d	NOECsurvival NOECgrowth NOEChatch	Fathead minnow	OECD 210	16
Fish	PFOS-K	1	30d	NOECearly-life stages	Fathead minnow	Not standard	17
Fish	PFOS-K	>0.086 <0.87	62d	NOECmortality	Bluegill sunfish	OECD 305	18

Table 6.3. Sub-chronic/chronic toxicity of PFOS to freshwater organisms

PFOA

Acute and sub-chronic/chronic toxicity

In table 6.4a the acute freshwater toxicity values for PFOA are summarised. Only studies that had a Klimisch value of 1 or 2 are reported. In the draft hazard assessment of the USEPA (2002) several other ecotoxicity data are reported. However, the reliability of some of these studies was limited. Only studies for which the reliability could be assessed were included in the present review.

The results of the reliable tests that are presented in table 6.4a indicate practically no acute toxicity of PFOA to all species tested. The results obtained from tests with deviating protocols, presented in table 6.4b, show that PFOA is moderately toxic to algae and slightly toxic to fish.

The few available sub-chronic/chronic values for PFOA indicate practically no sub-chronic/chronic toxicity of this compound to algae or fish.

Class	Substance	Concentration (mg/L)	Testing time	Effect type	Organism	Method	Ref
Bacteria	PFOA	722	30 min	EC50	Photobacterium phosporeum	Microbics microtoxs	35
Bacteria	PFOA	730	30 min	EC50	Photobacterium phosporeum	Microbics microtoxs	37
Algae	PFOA	310 >1000 62 500	96h	EC50cell density EC50growth rate NOECcell density NOECgrowth rate	Selenastrum capricornutum	EPA/TSCA 797.1050	34
Fish	PFOA	720 720 360	48h	EC50 LC50 NOEC	Fathead minnow	EPA/TSCA 797.1300	29
Fish	PFOA	843	96h	LC50	Fathead minnow	Not noted	24
Fish	PFOA	300	96h	LC50	Fathead minnow	Not noted	21
Fish	PFOA	766 400	96h	LC50 LC50	Fathead minnow	USEPA 660/3	20

Table 6.4a Toxicity of PFOA to freshwater organisms (standardised protocols)

Class	Substance	Concentration (mg/L)	Testing time	Effect type	Organism	Method	Ref
Sludge	PFOA	>450	3h	EC50	-	OECD 209	41
Sludge	PFOA	>664	3h	EC50	-	OECD 209	42
Sludge	PFOA	>450	3h	EC50	-	OECD 209	43
Bacteria	PFOA	>450	30 min	EC50	Photobacterium phosphoreum	Microbics microtox	36
Bacteria	PFOA	630	30 min	EC50	Photobacterium phosphoreum	Microbics microtox	38
Bacteria	PFOA	390	30 min	EC50	Photobacterium phosphoreum	Microbics microtox	39
Bacteria	PFOA	117	30 min	EC50	Photobacterium phosphoreum	Microbics microtox	40
Algae	PFOA	2.2 0.45	96h	EC50 NOEC	Selenastrum capricornutum	EPA/TSCA 979.1050	31
Algae	PFOA	1.3 3.8	96h	EC50cell density EC50growth rate	Selenastrum capricornutum	EPA/TSCA 979.1050	32
Algae	PFOA	396 666 42 86 86 166	96h	EC50 EC50growth rate NOECcell count NOECgrowth rate LOECcell count LOECgrowth rate	Selenastrum capricornutum	EPA/TSCA 979.1050	33
Fish	PFOA	>450	96h	LC50	Fathead minnow	OECD 203	22
Fish	PFOA	494	96h	LC50	Fathead minnow	EPA/TSCA 1993	23
Fish	PFOA	432 284	96h	LC50 NOEC	Fathead minnow	EPA/TSCA 797.1400	25
Fish	PFOA	400 270	96h	NOEC NOEC	Fathead minnow	EPA/TSCA 797.1050	26
Fish	PFOA	263	48h	EC50	Fathead minnow	OECD 202	27
Fish	PFOA	240 146	48h	EC50 NOEC	Fathead minnow	EPA/TSCA 797.1300	28
Fish	PFOA	15/35 6	48h	EC50/LC50 NOEC	Fathead minnow	EPA/TSCA 797.1300	30

Table 6.4b Results from deviating test protocols for the acute toxicity of PFOA to freshwater organisms

Class	Substance	Concentration (mg/L)	Testing time	Effect type	Organism	Method	Ref
Algae	PFOA	43	14d	EC50cell count	Selenastrum capricornutum	Modified EPA/ASTM/OECD	45
Fish	PFOA	>100	30d	NOEC	Fathead minnow	Adapted EPA, 1972	44

Table 6.5 Chronic toxicity of PFOA to freshwater organisms

8:2 FTOH

Acute and chronic toxicity

Acute no effects concentrations have been observed in toxicity tests with 8:2 FTOH (see table 6.6). Test results were based on nominal concentrations. It is not possible to appropriately judge the toxicity of this telomer from these data. Several chronic toxicity studies are underway (TRP, 2002).

Class	Substance	Concentration (mg/L)	Testing time	Effect type	Organism	Method	Ref
Algae	8:2 FTOH	0.20	72h	NOEC	Scenedesmus subspicatus	OECD 201	46
Invertebrates	8:2 FTOH	0.16	48h	NOEC	Daphnia magna	OECD 202	46
Fish	8:2 FTOH	0.18	96h	NOEC	Dario rerio	OECD 203	46

Table 6.6 Acute freshwater toxicity of 8:2 FTOH to freshwater organisms

Other PFAS

For the remaining PFAS discussed in the present study the toxicity data set is far from complete (see table 6.7). N-EtFOSA exhibits slight toxicity towards invertebrates, all other tests indicate practically no toxicity. The results of tests with deviating protocols show slight toxicity of PFOSGE to fish. PFDS is slightly toxic to invertebrates and moderately toxic to fish.

Class	Substance	Concentration (mg/L)	Testing time	Effect type	Organism	Method	Ref
Fish	n-EtFOSE	> 20μg/L	Chronic	NOEC	Fathead minnow	USEPA, 1972	51
Fish	n-EtFOSEA	>1000	96h	LC50	Fathead minnow	Not noted	52
Fish	POSF	>1000	96h	LC50	Fathead minnow	Not noted	53
Sludge	n-EtFOSA	>1000	3h	EC50	-	OECD 209	56
Invertebrates	n-EtFOSA	14.5	48h	EL50	Daphnia magna	Adapted OECD 202	55
Fish	n-EtFOSA	206	96h	LL50	Fathead minnow	Adapted OECD 203	54

Table 6.7a Acute and chronic toxicity data of several PFAS to freshwater organisms (standardised test protocols)

Class	Substance	Concentration (mg/L)	Testing time	Effect type	Organism	Method	Ref
Bacteria	PFOSGE	115	30 min	EC50	Photobacterium phosphoreum	Microbics microtox	50
Algae	PFOSGE	125 254 91	96h	EC50cell count EC50growth rate NOEC	Selenastrum capricornutum	OECD 201	49
Fish	PFOSGE	41 23	96h	LC50 NOEC	Fathead minnow	OECD 201	47
Fish	PFOSGE	362	96h	LC50	Fathead minnow	EPA	48
Sludge	PFDS	327	30 min	EC50	-	Microbics microtoxs	61
Bacteria	PFDS	250	-	17.3% inhibition	Photobacterium phosphoreum	OECD 209	60
Invertebrates	PFDS	32	48h	EC50	Daphnia magna	EPA 660/3	59
Invertebrates	PFDS	11	48h	EC50	Daphnia magna	OECD 202	58
Fish	PFDS	4.8	96h	LC50	Fathead minnow	OECD 203	57

Table 6.7b Results for acute toxicity data of several PFAS to freshwater organisms from deviating test protocols

6.2.3 Summary of freshwater toxicity data

The lowest effect concentrations and NOECs that have been published in the literature have been summarised in table 6.8.

Substance	Acute/chronic	Trophic level	Species	Results (mg/L)
PFOS	Acute	Algae	Selenastrum capricornutum	72h EC_{50} = 120
		Invertebrates	Daphnia magna	48h EC_{50} = 58
		Fish	Rainbow trout	96h EC_{50} = 7.8
	Chronic	Invertebrates	Daphnids	28d NOEC = 7
		Fish	Fathead minnow	42d NOEC = 0.30
PFOA	Acute	Bacteria	Photobacterium phosphoreum	30 min EC_{50} = 722
		Algae	Selenastrum capricornutum	96h EC_{50} > 1000
		Fish	Fathead minnow	96h LC_{50} = 300
	Chronic	Algae	Selenastrum capricornutum	14d EC_{50} = 43
		Fish	Fathead minnows	30d NOEC > 100
8:2 FTOH	Acute	Algae	Scenedesmus subspicatus	72h NOEC = 0.20
		Invertebrates	Daphnids	48h NOEC = 0.16
		Fish	Danio rerio	96h NOEC = 0.18
N-EtFOSA	Acute	Invertebrates	Daphnids	48h EL_{50} = 14.5
		Fish	Fathead minnow	96h LL_{50} = 206

Table 6.8 Lowest observed L(E)C_{50} and NOECs of PFAS in freshwater organisms.

6.2.4 Toxic effects in the marine environment

For the marine environment toxicity data are only available for PFOS. Table 6.9 presents the published toxicity data for marine organisms.

The few data that are available for the toxicity of PFOS to marine organisms show moderate toxicity to invertebrates. For algae and fish no conclusions could be drawn in this present study, because no effects were observed at the highest concentration tested.
The chronic study with shrimps showed NOECs between 0.25-0.55 mg/L for reproduction, survival and growth.

Class	Substance	Concentration (mg/L)	Testing time	Effect type	Organism	Method	Ref
Algae	PFOS	>3.2 >3.2	96h	EC50growth rate NOECgrowth rate	Skeletonema costatum	OPPTS 850.5400	65
Invertebrates	PFOS	3.6 1.1	96h	LC50 NOEC	Mysid shrimp	OPPTS 850.1035	63
Invertebrates	PFOS	>3.0 1.9	96h	EC50 NOEC	Eastern oyster	OPPTS 850.1025	64
Invertebrates	PFOS	0.25 0.55 0.25	35d	NOECreproduction NOECsurvival NOECgrowth	Mysid shrimp	OPPTS 850.1350	66
Fish	PFOS	>15	96h	LC50	Sheepshead minnow	OECD 203	62

Table 6.9. Toxicity of PFOS to marine organisms.

6.3 Standards and derivation of iMPCs (Based on Groshart et al., 2001)

6.3.1 Introduction

In the Netherlands, harmonised standards for several environmental compartments are derived for a number of chemicals (MilBoWa, 1999). The purpose of MilBoWa (1999) is to create a system of limit- and target values for soil and surface water. A limit value is a quality level that minimally should be achieved or maintained. A target value is a quality level at which no adverse effects are expected. The limit value is based upon the 'maximal permissible concentration' (MPC), the target value on the 'negligible concentration' (NC). In 2001 the procedure for the derivation of MPCs for the setting of environmental risk limits was updated (Traas, 2001).
The MPC is defined as the concentration at which at least 95% of the species in the ecosystem will be protected (method of Aldenberg & Jaworska (2000)). The negligible risk level is defined as 1% of the MPC.

For PFAS there are no standards derived yet in the Netherlands.

6.3.2 Derivation method

For the derivation of MPCs directly from ecotoxicological endpoints two different methods are used: the refined effect assessment method and the preliminary effect assessment method. Long-term chronic data are preferred to short term acute data. The refined effect assessment method is preferable. However, application of this method is based on data availability: at least four NOEC values are needed for four different taxonomic groups. If these data are not available the preliminary effect assessment method is applied. In this case in principle the EU TGD (ECB, 1996) is applied (table 6.11). In figure 6.10 the direct method for MPC derivation is presented.

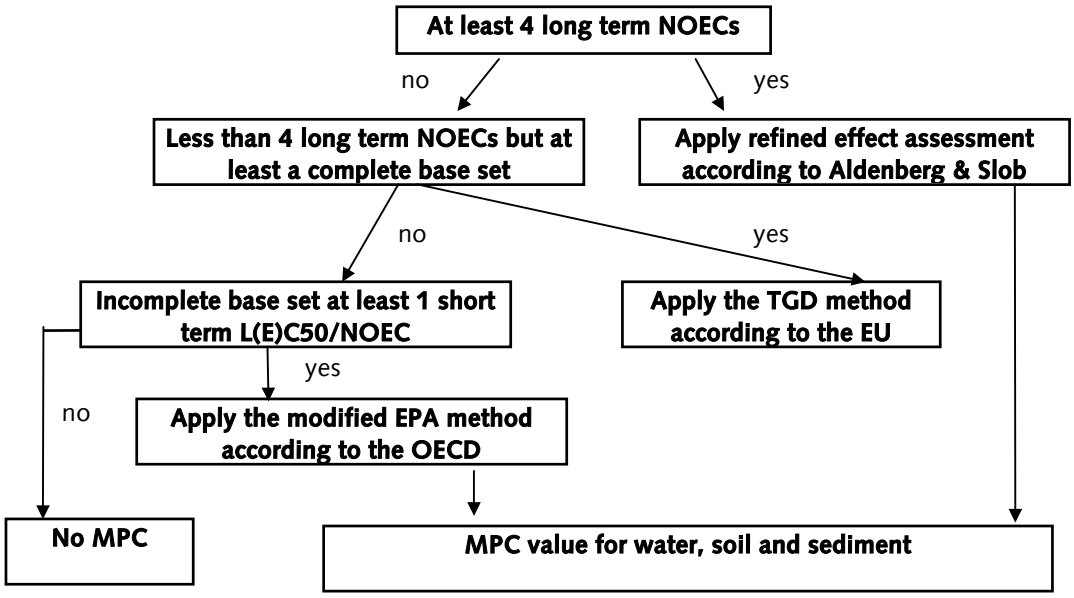

Figure 6.10 Scheme for the derivation of the MPC: direct method

There are two exceptions to the use of the TGD method:
1. Only when long term NOECs on three trophic levels are available, a comparison with data from the (complete) base set [4] is no longer demanded.

[4] The complete base set for toxicology data exists of acute $L(E)C_{50}$ for each of three trophic levels (fish, daphnia, algae).

2. It is inferred that for more hydrophobic compounds, short term toxicity data may not be representative, since the time span of an acute test may be too short to reach a toxic internal level. In those cases, base set completeness is not demanded and an assessment factor of 100 may be applied to a chronic test, which should not be an alga test if this is the only chronic test available.

If the base set is incomplete, the TGD method cannot be applied, and other arbitrary safety factors are used (the modified EPA-method (OECD, 1992)): a factor 10 and/or 1000 will be applied to the NOEC and/or L(E)C50, respectively, to derive the MPC. It should be stressed here that this exception may only be used if the TGD can not be applied. In table 6.11 the safety factors of the modified EPA method, dependent on the number of available toxicity data, are presented.

Available valid data	Assessment factor to be applied to the lowest L(E)C50 or long-term NOEC
At least one short-term L(E)C50 from each of 3 trophic levels of the base-set (fish, daphnia and algae)	1000
One long-term NOEC (either fish or daphnia)	100
Two long-term NOECs from species representing two trophic levels (fish and/or daphnia and/or algae)	100 50
Long-term NOECs from at least 3 species (normally fish, daphnia and algae) representing three trophic levels	50 10
Field data or model ecosystems	Reviewed on a case by case basis

Table 6.11 Assessment factors for aquatic toxicity data following EU/TDG (ECB, 1996) according to EUSES (EC, 1996)

The calculated MPC in the present report will be defined as 'indicative MPC' (iMPC).
Contrary to the limit and target values the derived iMPCs have only a technical status and no environmental policy value. They are not legally set and may change as soon as more toxicity data become available and/or an MPC is derived by the INS-project.

Available toxicity data	Safety factor
Lowest acute L(E)C_{50} or QSAR estimation for acute toxicity	1000
Lowest acute L(E)C_{50} or QSAR estimation for acute toxicity for at least algae, crustaceans and fish	100
Lowest NOEC or QSAR estimation for chronic toxicity	10*
Lowest NOEC or QSAR estimation for chronic toxicity for at least algae, crustaceans and fish	10

Table 6.12 Safety factors for the derivation of iMPCs in surface water (modified EPA method)
*this value will be compared with the value based on acute L(E)C_{50} values. The lowest value will be selected

Based on the toxicity data presented in this study, the iMPCs are derived using the procedure described by Traas (2001). The derivation is explained in annex V.
To derive the iMPC for sediment it is generally advised to use the equilibrium partition (EP) method, which relies on K_{ow} (see Slooff, 1992; Beek, 1993; Kalf,

1999; Traas, 2001). In this study this advice has not been followed, because K_{ow} is not a suitable predictor for the environmental behaviour (see section 4.3.1). Furthermore, the $iMPC_{sediment}$ could not be derived direct from effect concentrations, because no data were available on toxic effects in the soil or sediment.
In the present study iMPCs for PFOS, PFOA and PFOSGE were derived. For all other PFAS insufficient data were available. The results of this derivation are presented in table 6.13.

Only for PFOS many data were available, making it possible to use a relatively small assessment factor of 50. The other data have been derived using an assessment factor of 1000 (see annex V).

Substance	$iMPC_{freshwater}$ (µg/L)
PFOS	5
PFOA	300
n-EtFOSA	14.5

Table 6.13 iMPCs for PFOS, PFOA and n-EtFOSA.

6.3.3 Comparison of iMPCs to environmental concentrations

The PFAS concentrations that are observed in the environment can be compared to the indicative MPC. No occurrence data are available for n-EtFOSA, therefore this comparison will be limited to PFOS and PFOA.

PFOS

The highest freshwater concentrations that were observed in the multi-city environmental monitoring study (see section 5.3) were 4.98 µg/L for PFOS in POTW effluent from Decatur (3M, 2001). In quiet water from Decatur 0.111 µg/L PFOS was observed. The highest PFOS water concentration from control cities is 2.19 µg/L (Port St. Lucie). The highest PFOS water concentration after an AFFF spill (see section 5.3) was 2210 µg/L. These values indicate that the iMPC for PFOS may be approached close to point sources of PFAS. However, also PFOS concentrations in a non-point sourced city could approach the iMPC.

PFOA

The highest freshwater concentrations that were observed in the multi-city environmental monitoring study (see section 5.3) were 2.28 µg/L for PFOA in POTW effluent from Decatur. In quiet water from Decatur 0.060 µg/L PFOA was observed. The highest PFOA water concentration from control cities is 0.749 µg/L (Port St. Lucie). The highest PFOA water concentration in groundwater at a fire-fighting training site is 6570 µg/L; after an AFFF spill the highest observed PFOA concentration was 11.3 µg/L. These values indicate that the iMPC for PFOA might only be exceeded after spills.

6.4 Human toxicity

The human toxicity of PFOA and to a lesser extent PFOS have been and still are the subject of many studies (USEPA, 2002; OECD, 2002). For 8:2 FTOH few data are available, but many studies are underway. Results are expected by the end of 2002 (TRP, 2002).

6.4.1 Behaviour in humans

PFOS

PFOS was shown to be distributed in humans to serum and liver, where it is not metabolised. The excretion from the body is slow and occurs via urine and faeces

(OECD, 2002) PFOS has an estimated excretion half-life in humans of 8.67 years. This is high compared to adult rats (100 days) and Cynomolgus monkeys (200 days). PFOS is well absorbed orally.

PFOA

PFOA has an estimated half-life between 1 and 3.5 years in humans. PFOA is well absorbed following oral and inhalation exposure and to a lesser extent following dermal exposure. As was observed in other biota, PFOA does not partition to the body fat, but covalently binds to macromolecules. In liver, plasma and kidney PFOA is not metabolised in the human body.
Urine and faeces are the primary routes of excretion for PFOA; female rats possess an unidentified extra mechanism for the excretion of PFOA. Therefore this chemical is excreted much faster in female rats than in male rats. The difference between sexes has also been observed in dogs, but not in primates and humans (USEPA, 2002). For perfluorocarboxylic acids the length of the perfluoroalkyl chain is important for the excretion. Perfluorocarboxylic acids with longer chain length are less eliminated (Kudo et al., 2001).

6.4.2 Acute toxicity

PFOS

The available rodent toxicity data of PFOS have been summarised in table 6.14.

Application	Species	Result (mg/kg)
Oral	Rats	LD_{50} = 251
	Rats	1h LC_{50} = 5.2
Eye irritation	Rabbits	Mildly irritating
Skin irritation	Rabbits	Non-irritating

Table 6.14 Acute toxicity data of PFOS to rodents

PFOA

The available rodent toxicity data of PFOA have been summarised in table 6.15.

Application	Species	Result (mg/kg)
Oral	CD Rats	LD_{50} > 500 (male) LD_{50} 250-500 (female)
	Wistar rats	LD_{50} < 1000 (female)
Inhalation	Rats	1h NOEC > 18,6 mg/L
Dermal	Rabbits	LD_{50} > 2000 mg/kg
Eye irritation	Rabbits	Irritating
Skin irritation	Rabbits	Irreversible tissue damage
	Rabbits	Non-irritating

Table 6.15. Acute toxicity of PFOA to rodents

6.4.3 Chronic toxicity

PFOS

In repeat-dose oral toxicity studies with PFOS using rats and primates the exposure resulted in hepatotoxicity and mortality. At an exposure level of from 2mg/kg/day observed effects in rats are increases in liver enzymes, hepatic vacuolisation and hepatocellular hypertrophy, gastrointestinal effects, haematological abnormalities, weight loss, convulsions and death. These effects were confirmed by a 2-year test with rats. The lowest observed adverse effect level (LOAEL) in female rats was 5 mg/L; the associated no observed adverse effect level (NOAEL) was 2 mg/L. In male rats the LOAEL was 0.5 mg/L; no NOAEL could be determined. In a developmental effect study the NOAEL and the LOAEL for the second generation of rats were determined to be 0.1 mg/kg/day and 0.4 mg/kg/day, respectively (OECD, 2002).

In repeat-dose oral toxicity studies with PFOS using Rhesus monkeys the effects observed included anorexia, emesis, diarrhoea, hypoactivity, prostration, convulsions, atrophy of the salivary glands and the pancreas, marked decreases in serum cholesterol, and lipid depletion in the adrenals. These effects were observed at levels from 1.5 mg/kg/day and above. No survival was reported after three weeks treatment with 10 mg/kg/day and after seven weeks with 4.5 mg/kg/day. In a six-month study no effects were observed at doses of 0.15 or 0.03 mg/kg/day (OECD, 2002).

In mutagenicity test with bacteria (*S. typhimurium, E. coli*), human lymphocytes, rat hepatocytes and mouse micronucleus, PFOS was found to be non mutagenic (OECD, 2002).
In a 2-year carcinogenicity assay with Sprague-Dawley rats significant increase in the incidence of hepatocellular adenomas was observed at the highest dose of 20 mg/L of PFOS (OECD, 2002).

PFOA
In various studies with bacteria (*S. Typhimurium, E. Coli*) and human lymphocytes PFOA was found to be non-mutagenic. PFOA did induce chromosomal aberrations and polyploidy in Chinese hamster ovaries (USEPA, 2002). However, PFOA was negative in an essay with mouse embryo fibroblasts and in an in vivo mouse micronucleus assay.

Sub-chronic studies in rats and mice showed that the liver is the primary target organ. Observed effects are increased liver and kidney weight, hepatocellular hypertrophy, at 1000 mg/L for female rats (76.5 mg/kg/day) and 100 mg/L for male rats (5 mg/kg/day).
Studies with rhesus monkeys resulted in death, lipid depletion in the adrenals, hypoplasia of the bone marrow, and moderate atrophy of the lymphoid follicles in the spleen and lymph nodes at 30 mg/kg/day or higher (USEPA, 2002).

Rats fed with 300 mg/L PFOA showed increased liver and kidney weight, haematological effects and liver lesions in males and females. In addition, increases in testicular masses (males at 300 mg/L) and ovarian tubular hyperplasia (females at 30 mg/L) were observed (USEPA, 2002).

Carcinogenity studies with rats showed that PFOA is weakly carcinogenic, inducing Leydig cell adenomas in the males and mammary fibroadenomas in the females following 2-year exposure to 300 mg/L. At that level PFOA has also been reported to be carcinogenic to the liver and pancreas of male CD Rats (USEPA, 2002).

The results of several key studies on PFOA (90-day primate, two generation, kinetics) are ungoing (APME, 2002).

Telomers (based on DuPont, 2002)
For a mixture of 6:2 FTOH, 8:2 FTOH, 10:2 FTOH and 12:2 FTOH three NOELs have been determined. The repeated dose and the reproductive toxicity NOEL was 25 mg/kg/day. No developmental toxicity was observed at 200 mg/kg/day. Furthermore these substances reacted negative in the AMES, Chrom Ab geno-toxicity tests.

6.5 Conclusions and recommendations

Various data were available to evaluate the toxicity of PFOS and PFOA. The reliability of many of these tests must be considered as limited, because nominal concentrations were used. Due to the special, high sorptive behaviour, the actual concentration may have been significantly reduced. Furthermore, many of the test

were performed at low test chemical purity, and were therefore deviating from the standard methodology. Many of the results are therefore of limited reliability, but can very well serve as a first indication.

PFOS is moderately acute toxic to freshwater fish and slightly toxic to invertebrates. PFOS is practically non-toxic to algae. PFOS is slightly chronic toxic to freshwater fish and practically non-toxic to invertebrates. PFOS is moderately (acute) and slightly (chronic) toxic to marine invertebrates. For PFOS the derived iMPC is 5 μg/L. PFOS concentrations were shown to equal the iMPC in freshwater receiving wastewater effluents from a production site. In other freshwaters, the concentrations observed are usully far below, although the iMPC may be approached to within a factor of 4.
The acute toxicity of PFOA to freshwater algae, invertebrates and fish is practically nil. For PFOA an iMPC of 300 μg/L has been derived. It is unlikely that this iMPC will be exceeded for longer periods.
N-EtFOSA exhibits slight acute toxicity to invertebrates.
No effects have been observed for 8:2 FTOH. No conclusions regarding the toxicity of this substance can be drawn, since nominal concentrations have been used in tests.

Concerning humans, both PFOS and PFOA have long half-lives (8.67 and 1-3.5 years, respectively) in the human body. Both chemicals are distributed to liver, plasma and kidney. To rodents PFOS and PFOA exhibit low acute toxicity, but they are eye irritating.

In chronic feeding tests with rodents and primates the primary target was the liver for PFOS and PFOA. PFOA was found to be weakly carcinogenic. Mutagenicity testing of PFOS did not show any mutagenic effects. PFOA induced chromosomal aberrations and polyploidy in CHO cells, but did not show mutagenic effects in most mutagenicity tests, including an in vivo micronucleus test.

In a developmental effect study with PFOS the NOAEL and the LOAEL for the second generation of rodents were determined to be 0.1 mg/kg/day and 0.4 mg/kg/day, respectively.

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7 Policy and governmental awareness

7.1 National environmental policies

7.1.1 Netherlands

In the National Environmental Policy Plan (NMP, 1989) and the more recently published National Environmental Policy Plan-4 (NMP-4, 2001) the general environmental policy of the Netherlands is described.
By the year 2010 the environmental targets and target values must have been reached. Concerning the reduction of the risks caused by high concentrations of chemicals, specific policy targets have been set in the National Environmental Policy Plan of 1989. The targets imply the aim to not exceed the Maximum Permissible Concentrations (MPCs) and the Negligible Concentrations (NCs) in 2010, by means of prevention and reconstruction of production processes. While these values are guidelines they are not legally binding. When the environmental quality standards are set, other aspects, such as political and technical feasibility, are also taken into account. Target values are either set at the NC or at the background value.
In the report on integral standardisation on substances (INS, 1997) environmental quality standards have been derived. For PFAS no specific quality standards, MPCs or NCs have been set.
The current water policy is reflected in the Fourth Note on Watermanagement (4th NW 1997). In this note the targets and headlines of the policy for the national water management are given.

7.1.2 Other country specific policies/ governmental awareness

United States of America

Significant new use rule

The United States of America Environmental Protection Agency (USEPA) has initiated a significant new use rule (SNUR) for perfluoroalkyl sulfonates. It concerns 13 chemicals[5], including polymers that are derived from perfluorooctanesulfonic acid and its higher and lower homologues. The rule requires manufacturers and importers to notify the new use of these chemicals to USEPA, giving the USEPA the opportunity to evaluate the intended new use and associates activities (USEPA, 2002b).

Hazard Assessment PFOA

The USEPA has performed a hazard assessment on PFOA. The corrected draft version has been released on April 15, 2002 and is under discussion (USEPA, 2002a).

Canada

The Canadian government is performing a environmental screening assessment on perfluoroalkyl substances for possible priority chemicals. This assessment is to be completed in Autumn 2002 (Windle et al., 2002).

[5] The CAS-numbers of the concerning chemicals are: 2250-98-8, 30381-98-7, 57589-85-2, 61660-12-6, 67969-69-1, 68608-14-0, 70776-36-2, 127133-66-8, 148240-78-2, 14868-79-1, 178535-22-3, P-94-2205, P-96-1645 306974-63-0

United Kingdom
The National Centre for Ecotoxicology & Hazardous Substances of the United Kingdom has reviewed the occurrence and hazards of perfluoroalkylated substances in the UK in 2001. It has been initiated as a response to the decision of 3M to phase out the perfluorooctanyl chemistry. This study takes a broader perspective and tries to incorporate the telomers as well (NCEHS, 2001).

Denmark
The Danish EPA has performed a survey of perfluorooctyl substances in consumer products. In three out of 21 purchased consumer products fluorinated chemicals were detected (PFDS, FOSA and n-EtFOSE) (NERI, 2002).

7.2 International policy/ awareness

7.2.1 OECD
The Organisation for Economic Co-operation and Development (OECD) is carrying out a hazard assessment on PFOS and its salts. The draft version of May, 13, 2002 is being discussed in the OECD task force of existing chemicals (OECD, 2002). Once the information is available, this will be followed by a risk assessment. Accordingly decisions will be taken on the need for international risk management (NCEHS, 2001).

7.2.2 OSPAR
The OSPAR Convention for the Protection of the Marine Environment of the Northeast Atlantic has performed a selection process for possible bioaccumulative, persistent and ecotoxic substances. Candidates were selected from a Danish QSAR database (Tyle et al., 2001, Tyle et al., 2002). About 60 perfluorinated chemicals were selected, out of a total of 92 possible substances (NCEHS, 2001).

7.3 Actions of industry

7.3.1 3M studies
3M has performed many studies on toxicology, pharmaco-kinetics and environmental fate and effects of perfluorinated chemicals. They have submitted the results of these studies to the USEPA, and discussed the results with them (3M, 2000). These data are available from USEPA (USEPA, 2001).

7.3.2 Telomer Research Program
The united perfluorinated telomer manufacturers (Asahi Glass, Atofina, Clariant, Daikin and DuPont) have set up a research program on the principal raw material common amongst the TRP members: 8:2 FTOH. The program focuses on three parallel work streams: toxicology, pharmaco-kinetics and environmental date and effect studies. Publication in the open literature of study results is encouraged. Environmental fate and effect studies that are included in the research are hydrolysis, adsorption/desorption, aerobic and anaerobic degradation, photolysis and chronic toxicity to fish and daphnids. It is anticipated that the current research plan will take two more years to complete (TRP, 2002).

7.3.3 APME research program
Asahi Glass, Atofina, Ausimont, Daikin, DuPont, Dyneon, Miteni, 3M and Solvay have set up a research program on PFOA under the umbrella of the Association of Plastics Manufacturers in Europe (APME). The program focuses on two parallel work streams: pharmaco-kinetics and environmental date and effect studies. Environmental fate and effects studies that are included in the research program are adsorption/desorption, chronic toxicity to fish, daphnia and algae. It is anticipated that the current research plan will take another year to complete (APME, 2002).

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List of Annexes

Annex 1 List of abbreviations

6:2 FTA	1H,1H,2H,2H perfluorooctyl acrylate
6:2 FTMA	1H,1H,2H,2H perfluorooctyl methacrylate
6:2 FTOH	1H,1H,2H,2H perfluorooctanol
8:2 FTA	1H,1H,2H,2H perfluorodecyl acrylate
8:2 FTMA	1H,1H,2H,2H perfluorodecyl methacrylate
8:2 FTOH	1H,1H,2H,2H perfluorodecanol
10:2 FTOH	1H,1H,2H,2H perfluorododecanol
12:2 FTOH	1H,1H,2H,2H perfluorotetradecanol
AFFF	Aqueous Film Forming Foam
APME	Association of Plastic Manufacturers Europe
BAF	Bioaccumulation Factor
BCF	Bioconcentration Factor
BMF	Biomagnification Factor
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DDA	Dodecyldemethylammonium salt
DRI	Data Reliability Indicator
EC_{50}	Concentration that causes an effect for 50% of the tested organisms
ECD	Electron Capture Detection
ECF	Electrochemical Fluorination
EL_{50}	Level that causes an effect for 50% of the tested organisms
EP	Equilibrium partition
EQC	Equilibrium Criterion (Model)
FD	Fluorescence detection
FOSA	Perfluorooctane sulfonamid
GC	Gas Chromatography
HPLC	High-performance Liquid Chromatography
IC_{50}	Concentration that inhibits 50% of the tested organisms
iMPC	Indicative Maximal Permissible Concentration
LC	Liquid Chromatography
LC_{50}	Concentration that is lethal for 50% of the tested organisms
LL_{50}	Level that is lethal for 50% of the tested organisms
LOAEL	Lowest Observed Adverse Effect Level
LOD	Limit of Detection
LOQ	Limit of Quantification
MPC	Maximal Permissible Concentration
MS	Mass Spectrometry
n-EtFOSA	n-Ethyl perfluorooctane sulfonamid
n-EtFOSE	n-Ethyl perfluorooctane sulfonamidoethanol
n-EtFOSEA	n-Ethyl perfluorooctane sulfonamidethyl acrylate
n-EtFOSEMA	n-Ethyl perfluorooctane sulfonamidethyl methacrylate
n-MeFOSE	n-Methyl perfluorooctane sulfonamidethanol
n-MeFOSEA	n-Methyl perfluorooctane sulfonamidethyl acrylate
NMR	Nuclear Magnetic Resonance
NOAEL	No observed Adverse Effect Concentration
NOEC	No observed Effect Concentration
NOEL	No observed Effect Level
OECD	Organisation for Economic Co-operation and Development
PFAS	Perfluoroalkylated substances
PFBS	Perfluorobutyl sulfonate
PFDS	Perfluorodecyl sulfonate

PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfllluorohexyl sulfonate
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctyl sulfonate
PFOSGE	n-perfluorooctylsulfonyl-N-ethylglycinate
PFS	Perfluorinated surfactants
POSF	Perfluorooctane sulfonyl fluoride
POTW	Publicly owned treatment plant
ppb	Parts per billion
ppm	Parts per million
PTFE	Polytetrafluorethylene
QSAR	Quantitative Structure-Activity Relationship
RIKZ	Rijksinstituut voor Kust en Zee (Insititute for Coastal and Marine Management)
SNUR	Significant New Use Rule
TFE	Tetrafluoroethylene
TGD	Technical Guidance Document
TRP	Telomer Research Project
USEPA	United States Environmental Protection Agency
VNTF	Vereniging van Nederlandse Tapijt Fabrikanten (Association of Netherlands Carpet Manufacturers)
VTN	Vereniging Textielindustrie Nederland (Dutch Association for the Textile Industry)
WWTP	Wastewater Treatment Plant

Annex II Data reliability Indicator

Data Reliability Indicator

In the data that were gathered for this study large discrepancies were found in values for comparable properties. Although different test methods mostly result in different outcome, well-conducted experiments should give values in the similar range.
Several researchers have tried to develop indicators for data quality. For the present study two important publications on this subject have been used: Kollig (1988) and Klimisch et al. (1997). Both researchers describe indicators for evaluating data reliability.

Kollig (1998) divides the indicator in four categories:

1. Analytical information,
2. Experimental information,
3. Statistical information,
4. Corroborative information.

Ad 1. Was the analytical method appropriate and suitable for the particular compound? If no standard method has been used, is the method sufficiently described?
Ad 2. Are all experimental parameters (temperature, pH, purity, etc.) well stated? Is the chemical identified by testing?
Ad 3. Is the uncertainty and the reproducibility of the test mentioned?
Ad 4. Are the data in accordance with the results of another independently conducted study?

Each category contains subcriteria that are developed for various properties in order to enable the estimation of the reliability of the measurement within one category. The Data Reliability Indicator (DRI) consists of the relative reliability for all four categories.

Klimisch et al. (1997) use four reliability scores for experimental data-generating studies:

1. Reliable without restrictions,
2. Reliable with restrictions,
3. Not reliable,
4. Not assignable.

Ad 1. The tests are performed according to internationally accepted test guidelines and preferably in compliance with Good Laboratory Practice (GLP).
Ad 2. The tests are not entirely performed according to internationally accepted test guidelines. Nevertheless the conditions are acceptable. This category also includes investigations that have no official testing guideline, but that are scientifically acceptable.
Ad 3. The test designs that are assigned to this category may have interference between the test substance and the measuring system or the test system is not relevant in relation to the exposure or the test method is not acceptable.
Ad 4. No reliability can be assigned if insufficient experimental details are given.
For various tests subcriteria are supplied for the evaluation of tests that were executed not according to internationally accepted test guidelines to be assigned 'reliable with restrictions'. Nevertheless, data in category 3 or 4 can very well be

used as corroborative information, or as a 'first estimation' if no other data are available.

Both methods can be useful in the assessment of reliability. The Kollig method does not supply a final judgement of reliability; the Klimisch method does not give a detailed set of criteria. All data that are supplied by the 3M company have been evaluated with the Klimisch ranking system. Furthermore, most of the data-generating experiments in the present study have been performed (partially) according to ISO, OECD or EPA testing. Therefore it will more practical to use the Klimisch ranking system.

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ANNEX III Production processes

Introduction

Perfluoroalkylated substances can be produced by two routes of synthesis; fluorination of organic compounds, in which hydrogen atoms of non-fluorinated or partially fluorinated organic compounds are substituted by fluorine atoms (Moldavsky et al., 1999), or reactions with perfluorinated compounds to form PFAS. Two important routes of production are used commercially: 1) electrochemical fluorination and 2) telomerisation. Also methods of fluorination using high-valence metal fluorides (CoF_3, MnF_3, AgF_2) or elemental fluorine (F_2) are known (Field, 1994; Moilliet, 2001), but these techniques are not important for the commercial synthesis of surfactants. In the following sections the first two routes of synthesis of perfluoroalkylated substances will be discussed.

Electrochemical fluorination

The electrochemical fluorination is being used by the 3M company, and will be terminated for the largest part by 2003 (3M, 2000a). In this reaction an organic compound is introduced in liquid anhydrous hydrogen fluorine (aHF) at nickel anodes. An electric current is led over these electrodes, resulting in the substitution of the hydrogen atoms of the organic compound by fluorine atoms. This method was developed by Simons et al. in 1944 (3M, 2002). 3M bought the patent immediately, but did not have any commercial application until 1956 (Riecher, 2000). Since then it has been used as a commercial process by 3M for more than 40 years (Noel et al., 1996).
The overall reaction is the following:

$C_8H_{17}SO_2F + 17\ HF \rightarrow C_8F_{17}SO_2F + 17\ H_2$

1-Octanesulfonyl fluoride (POSF)

Perfluorooctanesulfonyl fluoride

and exists of two subreactions, at the anode and cathode (Alsmeyer et al., 1994):

anode: $C_mH_nX + n\mathrm{HF} \rightarrow C_mF_nX + 2n\mathrm{H}^+ + 2n\mathrm{e}^-$
cathode: $2n\mathrm{H}^+ + 2n\mathrm{e}^- \rightarrow n\mathrm{H}_2$

POSF is further reacted with methyl or ethyl amine, resulting in N-ethyl (and methyl) perfluorooctane sulfonamide (N-EtFOSA), and subsequently with ethylene carbonate to form either N-methyl or N-ethylperfluorooctanesulfonamidoethanol (N-EtFOSE). N-EtFOSE and N-MeFOSE are the principal building blocks of 3M's product lines (3M, 1999).

Various sources provide estimations of the yield of the fluorination of 1-octanesulfonyl fluoride (3M, 1999; 3M, 2000b; 3M, 2001).

Percentage	Substance
35-40%	n-POSF
20-25%	Perfluorinated alkanes and ethers
18-20%	Branched non-C8 perfluorinated sulfonyl fluorides
10-15%	Tars (high molecular weight fluorochemical byproducts) and molecular hydrogen
7%	Linear non C8-perfluorinated sulfonates

Table III.1 Impurities in POSF production

These percentages may vary from plant to plant, due to differences in raw materials, equipment and process conditions. The tars and non functional molecules are easily removed from the reaction mixture. The final product will contain approximately 70% n-POSF and 30% branched impurities with odd and even chain length (3M, 2000b).

The impurities can be due to impurities in the reactant or rearrangement during fluorination. Although n-octanesulfonyl fluoride is used, there are always traces of other C8 compounds, leading to non-linear POSF. However, their presence does not affect the application properties (Moldavsky & Furin, 1998). Similar impurities can be expected in PFOA production. The PFOA production process is as follows:

$$C_8H_{17}COCl + 18HF \longrightarrow C_8F_{17}COF + 17H_2 + HCl;\ C_8F_{17}COF + H_2O \longrightarrow C_8F_{17}COOH + HF$$

Figure III.2 Production of PFOA with the ECF process (Kissa, 2001)

Other impurities may be partially fluorinated. This is due to the production process itself: '*[..] Simons processes [is] a step by step fluorination process which leads to the formation of all possible partially fluorinated compounds [..]*' (Sartori & Ignatiev, 1998).

According to several sources (Moldavsky & Furin, 1998; Moldavsky et al., 1999; 3M, 1999, 3M, 2001) also non-C8 compounds can be found: '*[..] fragmentation and rearrangement of the carbon skeleton can also occur and significant amounts of cleaved, branched and cyclic structures may be formed.*' (3M, 1999). Fragmentation of the carbon framework is to be expected, because the energy of the C-F bond formation exceeds that of the C-C bond (Moldavsky et al., 1999). With electrochemical fluorination perfluorinated compounds with even and odd numbers of perfluorocarbon atoms are generated (Kauck & Diesslin, 1951 cited in Moody & Field, 2000; Kissa, 2001).
The commercially available POSF contains more than 90% of C8-molecules, of which approximately 25% is branched. The perfluorinated C6 compounds constitute 5-10% of the POSF product and the remainder is C7 (2-3%) and C5 (3M, 2001). The distribution of chain length is assumed to be comparable for the fluorination of octanoic acid to form PFOA.

Telomerisation

The second important route of synthesis of PFS is telomerisation. This process is used by Atofina, DuPont, Clariant, Daikan and Asahi Glass (Wakselman & Lantz, 1994; Atofina, 2001). Telomerisation is a process in which '[..] a polymeric product [is] formed from a monomer and an initiator, R, obtained by a chain-transfer reaction between a radical from a catalyst and some other compound, called a telogen.' (Kirk & Othmer, 1954). In the first stage of this production process perfluoroalkyl iodides are synthesised. In the second the iodide is substituted by a functional group, depending on the application.
The first stage of the process, the manufacturing process for the perfluoroalkyl iodide, involves two steps:

1) $5\ C_2F_4 + IF_5\ (\text{from } I_2 + F_2) + 2I_2 \xrightarrow{catalyst} 5\ C_2F_5I$

2) $C_2F_5I + n C_2F_4 \rightarrow C_2F_5(C_2F_4)_nI$

The second step uses a radical-initiated mechanism. This can be initiated using heat, UV light or radical sources (Wakselman & Lantz, 1994). This manufacturing process is developed by Haszeldine in 1949 and adapted by the DuPont company in the 1960s (Rao & Baker, 1994).
The price of compounds produced via this production route is high. The main reasons are the properties of the starting materials. The I_2 and IF_5 are highly aggressive and the tetrafluorethylene is expensive and potentially explosive (Wakselman & Lantz, 1994).

In the second stage of production the iodide has to be substituted with a functional group. Only two important commercial products can be produced *directly* from C_nF_mI, being perfluorocarboxylic acid (using oleum as reactant) and perfluoroalkanesulfonyl chloride (using SO_2/Zn and Cl_2). Indirectly products can be produced by ethylenation, followed by substitution of the iodide by a functional group of choice, thus forming $R_FC_2H_4X$ (Wakselman & Lantz, 1994), where R_F represents a perfluorinated alkyl group. The compounds that are produced via this indirect route are the most important intermediates for perfluorinated surfactant production, with 1*H*,1*H*,2*H*,2*H*–perfluorodecanol (8:2 FTOH, see figure III.2) as primary building block.

During the telomerisation also C4 and C6 iodide can be formed by the radical reaction. Two other important possible by-products can be formed with this production process, due to the following reactions (Rao & Baker, 1994):

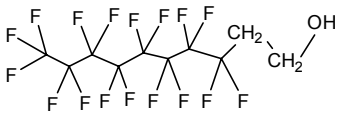

Figure III.2. 8:2 FTOH

1) $R_FI + IF_5 \rightarrow R_FF + (I_2F_4)$

2) $2\ R_FI \rightarrow R_FR_F$

All undesired products are removed by distillation. This is a simple process. Because of the radical mechanism, only linear perfluoro-*n*-alkyl compounds are to be expected.

Comparison of production processes

The most important difference between the two major production processes of PFS, is the final product. Electrochemical fluorination can produce all types of PFS and will be largely dependent on the starting organic material that is used, and its purity. ECF was used by 3M to produce POSF and PFOA. Almost all products that are synthesised using telomerisation have $R_FC_2H_4X$ as an intermediate, in which X represents any functional group.
When electrochemical fluorination and telomerisation are compared, also the purity of the final products is an important difference. The products from the telomerisation process are more pure than the products formed via electrochemical fluorination. The telomerisation process gives fewer by-products and furthermore it is easier to separate those from the desired product, so that relatively pure products are obtained. The perfluorinated products from the electrochemical process yield both even and odd numbered perfluorinated carbons, in contrast to the perfluorochemicals that are synthesised via telomerisation, which have only even numbers of perfluorinated carbon atoms. Approximately 30% of the ECF-product will be branched, whereas the telomers will have a straight alkyl chain (Kissa, 2001).

Last, there is a price difference between the two processes. Telomers are exceptionally expensive products (Wakselman & Lantz, 1994), whereas the electrochemical fluorination process is relatively cheap (Hudlicky & Pavlath, 1995; cited in Moody & Field, 2000). Exact figures are not available.

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ANNEX IV Mechanism of AFFF

AFFF is used by several types of fire fighters, including fire departments at airports, military, chemical plants and off-shore drilling platforms (3M, 1999a, Moody & Field, 2000). The products are also called *light water*, because they form a film on the burning fluid.

The fire fighting mechanism of foam is based on four principles (Luttmer, 1998):

1. The capability to seal the surface and isolate it from contact with atmospheric oxygen,
2. Thermal stability,
3. Low density,
4. Cooling by the water that percolates through the foam.

The first two principles are partially based on the properties of fluorochemicals. As stated earlier surfactants form micelles in water. Perfluorinated surfactants form lamellar micelles, thus perfectly covering the burning fluid with the foam (Pabon & Corpart, 1999; Moody & Field, 2000).

The foam provides better grip to the material in flames, producing a continuous cover (Figueredo et al., 1999). The combination of hydrocarbon and perfluorinated surfactants is responsible for the covering. '*The films formed by fluorocarbon and hydrocarbon solutions consist of two mixed monolayers of surfactants where the air-aqueous phase monolayer is dominated by the fluorocarbon surfactant and the aqueous-hydrocarbon phase is dominated by the hydrocarbon surfactant* (see figure IV.1) (Moody & Field, 2000).'

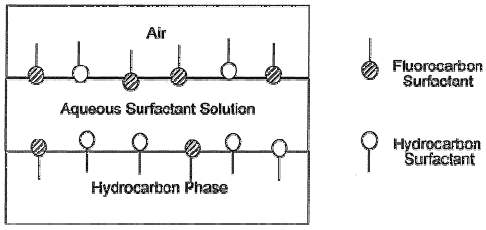

Figure IV.1. The mechanism of fire fighting foams (Moody & Field, 2000)

The film that is formed is less permeable for heptane vapours than the films formed by hydrocarbons surfactants, thus preventing re-ignition of the fuel (Pabon & Corpart, 1999; Moody & Field, 2000).

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Annex V Derivation of iMPC

PFOS

For PFOS for two trophic levels chronic NOECs are available, covering the trophic levels that showed the lowest acute $L(E)C_{50}$. Therefore, following the TGD method (ECB, 1996), an assessment factor of 50 is applied to the lowest NOEC, being 0.25 mg/L (marine mysid shrimp)
Therefore, the $iMPC_{freshwater}$ is 5 μg/L.

PFOA

For PFOA no reliable chronic NOECs for fish or daphnia are available. Therefore the iMPC has to be derived from the reported $L(E)C_{50}$. The lowest acute $L(E)C_{50}$ is 300 mg/L for fish. Applying an assessment factor of 1000, this results in an iMPC of 300 μg/L.

8:2 FTOH

For 8:2 FTOH insufficient data area available to derive an iMPC.

N-EtFOSA

For N-EtFOSA sufficient data are available to derive the iMPC, following the modified EPA method. Two acute $L(E)C_{50}$s are available; the lowest is 14.5 mg/L for Daphnia. Applying an assessment factor of 1000, the freshwater iMPC = 14.5 μg/L.

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