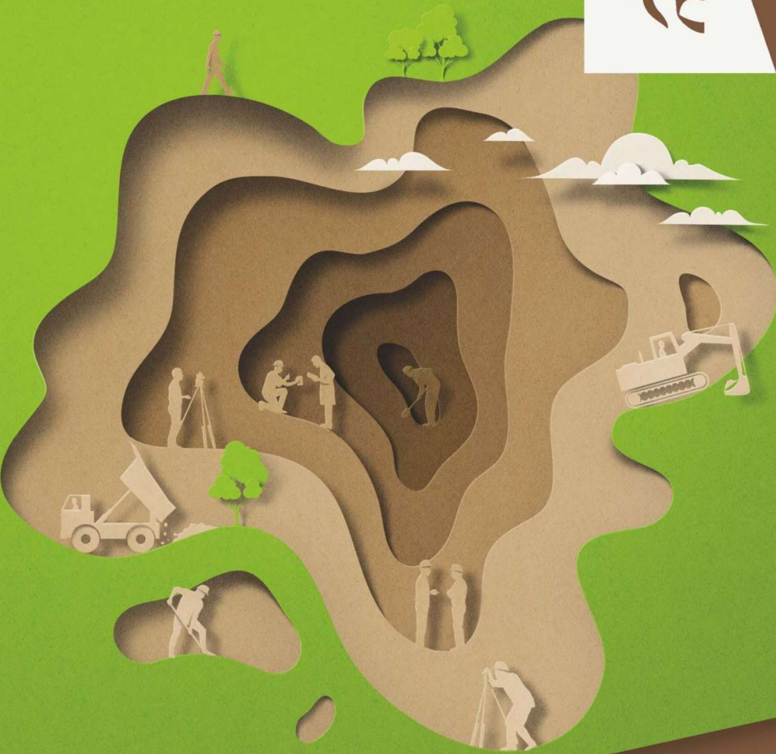

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STUDY OF THE PRESENCE OF PFAS IN GROUNDWATER, SOIL AND SEDIMENT NEAR RISK ACTIVITIES IN FLANDERS

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publication date / 26.06.2018

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DOCUMENT DESCRIPTION

1 *Publication title:*
Study of the presence of PFAS in groundwater, soil and sediment near risk activities in Flanders

2 *Responsible publisher:*
OVAM

3 *Official deposit number:*

4 *Keywords:*
Soil contamination, per- and polyfluoroalkyl substances, PFAS, PFOS, PFOA, measurement campaign

5 *Summary:*
See page 6

6 *Number of pages: 79*

7 *Number of tables and figures: 39 /19*

8 *Date of publication: June 2018*

9 *Price*: /*

10 *Supervisory group and/or author:*
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* Price changes reserved.

CONTENTS

LIST OF ABBREVIATIONS

AA-EQS	Annual Average Environmental Quality Standard for prolonged exposure (=JG-MKN)
AFFF	Aqueous Film Forming Foam
AR-AFFF	Alcohol Resistant Film Forming Foam
AR-FFFP	Alcohol Resistant Film Forming Fluoroprotein
ECF	Electrochemical fluorination
EFSA	European Food Safety Authority
SR	Serious Risk. Concentration at which a negative effect from direct exposure cannot be excluded for 50% of the organisms
EU	European Union
FEP	Fluorinated ethylene propylene
FFFP	Film Forming Fluoroprotein Foam
FP	Fluoroprotein Foam
FTOH	Fluortelomere alcohol
FTS	Fluortelomere sulfonate
FOSA	Fluorooctane sulfonamide
FOSE	Fluorooctane sulfonamide ethanol
FTAC	Fluortelomer acrylate
HFA	Hexafluoracetone
JG-MKN	Annual Average Environmental Quality Standard for prolonged exposure (=AA-EQS)
MAC-EQS	Maximum tolerable concentration for short-term exposure, environmental quality standard (=MAC-MKN)
MAC-MKN	Maximum tolerable concentration for short-term exposure, environmental quality standard (=MAC-EQS)
MSDS	Material Safety Sata Sheet
MTR	Maximum tolerable risk. Concentration below which no negative effect can be expected. Chronic exposure
PAP	Polyfluoroalkyl phosphate ester
PFAAs	Perfluoro Alkyl Acids
PFAS	Per- and polyfluoro alkyl substances
PFC	Perfluorinated compound
PFCAs	Perfluoroalkyl carboxylates
PFDA	Perfluorodecanoic acid
PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorhexanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFNA	Perfluornonanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluoroctaansulfonic acid
PFPeA	Perfluoroheptanoic acid
PFSAs	Perfluorosulfonic acids
PTFE	Polytetrafluoroethylene
POSF	Perfluorooctanesulfonyl fluoride
RIVM	Rijksinstituut voor volksgezondheid en milieu (Netherlands National Institute for Public Health and the Environment)
ADI	Acceptable Daily Intake
TM	Telomerization
US-EPA	United States Environmental Protection Agency
NR	Negligible risk

SUMMARY

Flanders has decades of experience in dealing with soil and groundwater pollution. The approach developed via the soil remediation policy has proved very successful in recent years. This mainly concerns heavy metals and the most common organic contaminants associated with activities from the past. It is becoming increasingly clear that all kinds of new contaminants (also known as Emerging Contaminants) are present in the environment. For several of these substances, there is insufficient knowledge of the size and risks in soil, groundwater and sediment.

From this perspective, OVAM commissioned an exploratory study into the presence of PFAS in soil, groundwater and sediments near risk locations in Flanders.

An initial part of the study includes a literature study concerning types of PFAS and their production as well as their behaviour and toxicity. The PFAS family includes 42 subfamilies and several thousand substances. This report focuses on the most important families and subfamilies, in particular the perfluorinated compounds and perfluorinated sulphonic acids and carboxylic acids subfamilies; the polyfluorinated compounds and fluoropolymer subfamilies and precursors; and the fluoropolymers. PFAS are used in various products and production processes. Among other things, in chrome-plating, the production of inks, varnishes, waxes, fire-extinguishing foam, cleaning agents, coatings, lubricants, water- and oil-repellent agents for leather, paper and textiles. From 1966 to 1990, the production and use grew due to their unique chemical stability and their water and dirt-repellent properties.

The toxicity data for PFAS are dominated by PFOS and PFOA due to the widespread occurrence of these components in the environment. Much less information is available for the other PFAS.

In this study, the selection and prioritization of relevant risk locations was mainly carried out on the basis of the nature of the risk activities as they determine the presence of PFAS in soil and groundwater. The study is too limited in scope to do a very extensive screening. From this perspective, emphasis was placed on the activities with a reasonable chance of PFAS being present, for example producers of PFAS, producers of fire-extinguishing foam, fire service training sites and fire incidents.

Within the context of this study, a total of 35 drillings were carried out at 24 selected sites in Flanders and 40 soil samples and 1 sediment sample were selected for analyses for PFAS. At the selected risk locations, for 66% of the measurement points, a concentration of $PFAS_{sum}$ (the total of all PFAS components measured in the laboratory) in the soil was 10x higher than the reporting limit (> 10 µg/kg ds). For 24% of the measurement points, the PFAS concentration is higher than 1000x the reporting limit (> 1,000 µg/kg ds).

Within the context of this study, 47 monitoring wells were also sampled and 47 groundwater samples and 1 effluent sample were analysed for PFAS.
It was established that at the selected risk locations at 71% of the measurement points a concentration of PFAS was measured in the groundwater higher than 100x the reporting limit (0.5 µg/l). At 42% of the measurement points, PFAS higher than 1000x the reporting limit (> 5 µg/l) was measured.

Based on the available dataset and the literature study, the following observations can be made:

- Based on the results of the limited sampling campaign, PFAS occur in elevated concentrations in soil and groundwater. In addition to PFOS and PFOA, other PFAS, such as 6:2-FTS, also occur in several of the samples analysed. 6:2-FTS is a precursor that can degrade into persistent perfluoro compounds.

- In this study, elevated levels are mainly measured in soil and groundwater at fire service training sites. However, not all types of risk activities were sampled within the context of this study. A number of locations do not show increased PFAS in soil or groundwater. However, this can also be the result of too limited sampling campaign at each location.
- Toxicological levels for soil, groundwater and sediment are not available for all common PFAS. Although the RIVM is working on ADIs for about 10 compounds, these are not available yet, and will only be applicable to human risks. They are not valid for toxicological levels for ecological risks or for risks resulting from leaching from soil into the groundwater.
- The assessment framework for PFAS is still evolving, generally more stringent toxicological levels are proposed in function of the time. For example, we expect that over time the ADI for PFOS will decrease.
- No data are yet available for possible background values for PFAS in Flanders.

INTRODUCTION

Flanders has decades of experience in dealing with soil and groundwater pollution. The approach developed via the soil remediation policy has proved very successful in recent years. This mainly concerns heavy metals and the most common organic contaminants that were associated with activities in the past. It is becoming increasingly clear that all kinds of new contaminants (also known as Emerging Contaminants) are present in the environment. The occurrence and risks of soil, groundwater and sediment are insufficiently known for several of these substances.

From this perspective, OVAM commissioned an exploratory study into the presence of PFAS in soil, groundwater and sediments near risk locations in Flanders.

The PFAS compounds have many applications in industry and in households. The expected presence in the environment is therefore great. Due to the complex and diverse properties and the low assessment criteria, proper sampling and analysis without disruptive influences (cross contamination) is also complicated. It requires thorough practical knowledge to carry out field work and analyses (field work, chemical analyses, research strategy, etc.) in a correct manner, partly because the toxicological levels for PFAS substances are often as factor of 1000 lower than we are used to in our (soil) field of work.

At present, an extensive measurement program is being implemented in the Netherlands via the PFAS Expertise Centre (set up by Witteveen + Bos, TTE and Arcadis) to gain clarity about the presence or absence of worrying situations. This study starts out from this expertise and insights.

The purpose of this project is to carry out a limited sampling campaign at risk locations in order to be able to estimate the presence of PFAS (including PFOS and PFOA) in the groundwater, soil and sediment in Flanders.

PART A – Technical knowledge document

The knowledge document has been drawn up in the context of the Dutch project "PFAS action framework", which is being carried out by Witteveen + Bos, Arcadis and TTE on behalf of the Municipality of Dordrecht and the Ministry of Infrastructure and Water Management.

This Technical Knowledge Document is a (comprehensive) summary of the Knowledge Document for the Netherlands and furthermore focused on the Flemish situation.

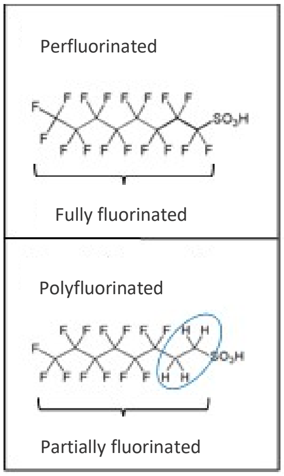
1 PFAS – EXPLANATION OF THE TYPES AND PRODUCTION

The group of poly- and perfluorinated alkyl compounds (PFAS) comprises a large group of more than 6,000 individual substances. PFAS have in common the fact that they contain a complete (per-) or partially (poly-) fluorinated carbon chain with a varying length, normally 2 to 16 carbon atoms.
The best known PFAS are PFOS (perfluorooctane sulfonic acid) and PFOA (perfluorooctanoic acid).

In Buck et al. (2011) PFAS are defined as substances containing the unit CnF2n+1-. More specifically, this means:

- Perfluorinated alkyl compounds: aliphatic substances of which all H atoms bound to C atoms in the carbon chain have been replaced by F atoms, except the H atoms whose replacement would change the nature of the functional groups (e.g. a hydroxyl group - OH).
- Polyfluorinated alkyl compounds: aliphatic substances of which H-atoms bound to at least one C atom (but not all) have been replaced by F atoms, so that they contain at least the perfluorinated unit CnF2n+1. Here too, the H atoms whose replacement would change the nature of the functional groups are still present.

This chapter provides an overview of the different types of PFAS, their production and uses.



1.1 TYPES OF PFAS

The PFAS family contains 42 subfamilies and several thousand substances (Buck et al., 2011). This report focuses on the most important families and subfamilies:

- Perfluorinated compounds
    - Perfluorinated sulfonic acids
    - Perfluorinated carboxylic acids
- Polyfluorinated compounds
    - Fluorotelomers
    - Precursors
- Fluoropolymers

Figure 1 shows a more extensive overview of (a part of) the different types of PFAS, in which other types of PFAS are mentioned. However, the emphasis in this report is on the compounds as shown above or in blue in Figure 1. The other groups of substances are discussed at a less detailed level because less information is available on these substances, or because these substances are used less and are less prevalent. Finally, in annex 11.1, a complete overview is given of various PFAS with the corresponding abbreviations and structural formulas of the separate PFAS compounds.

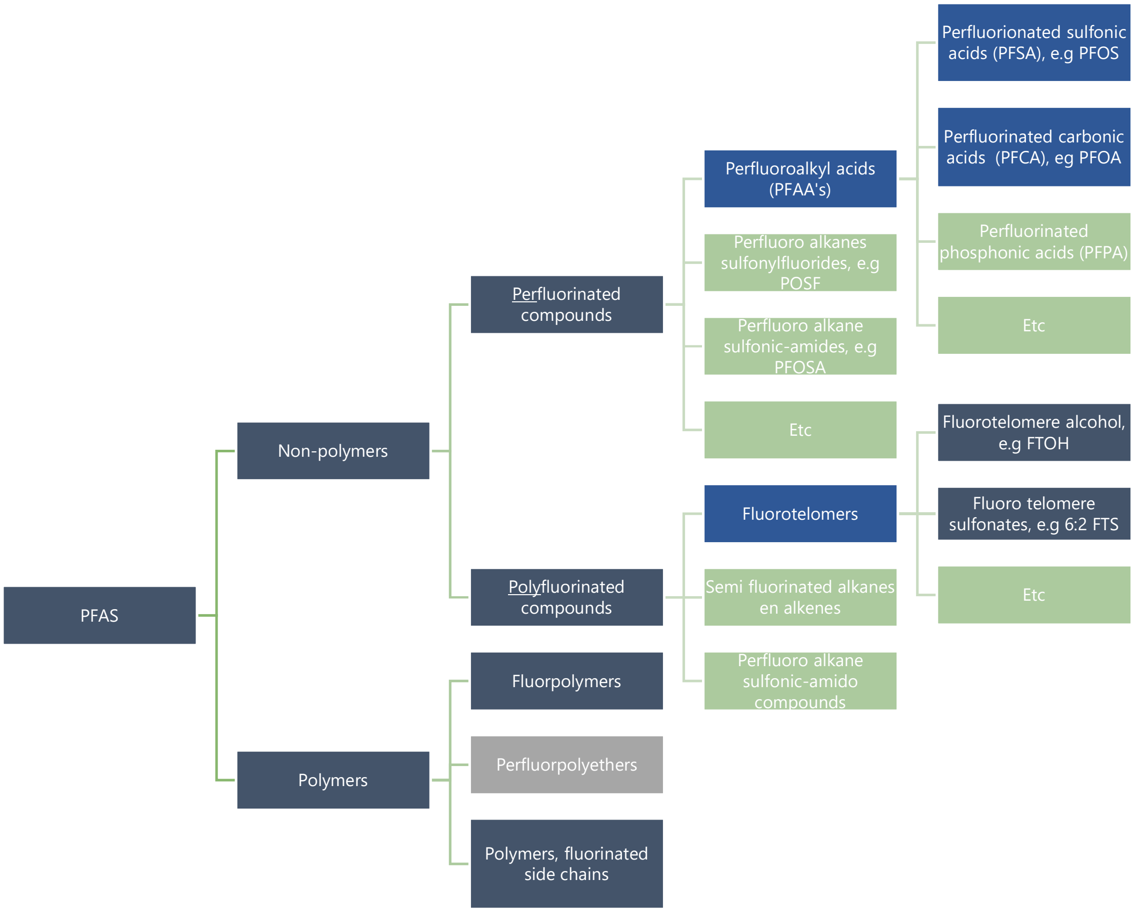


Figure 1: Overview of classes of PFAS compounds

1.1.1 Perfluorinated compounds

PFOS (perfluorooctane sulfonic acid) and PFOA (perfluorooctanoic acid) are the two most well-known PFAS. Both substances belong to the group of the perfluorinated alkyl acids (perfluoroalkyl acids, PFAAs). The group of perfluorinated alkyl acids can be subdivided into the different alkyl acids, such as the sulphonic acids (which include PFOS), the carboxylic acids (which include PFOA), but also other perfluorinated alkyl acids such as perfluorinated phosphonic acids. The PFAAs usually consist of a fully fluorinated carbon chain varying in length, generally from C2 to C16. The functional group varies, and is a sulfonic acid group in the perfluorinated sulfonic acids (PFSAs), and a carboxylic acid group in the perfluorinated carboxylic acids (PFCAs). In addition, there are perfluorinated alkyl acids with other functional groups (such as, among others, the phosphonic acids).

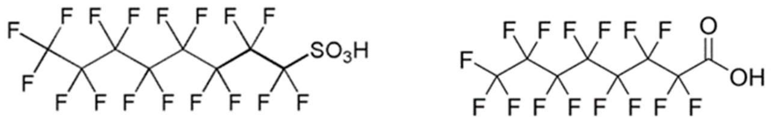


Figure 2: Chemical structure of PFOS (left) and PFOA (right)

In the production of PFAS, mixtures of substances often arise, including a mixture of linear and branched isomers. In addition, shorter and longer PFAS are also produced as by-products.

1.1.2 Polyfluorinated compounds

Polyfluorinated compounds are compounds whose carbon chain is not fully, but only partially fluorinated. Polyfluorinated compounds are often used as substitutes for PFOS and PFOA.

Fluorotelomers

Fluorotelomers fall under the polyfluorinated compounds; they contain an ethyl group (CH2CH2) between the fully fluorinated carbon chain and the functional group. They have been named fluorotelomers because of the fluoronomerization process, 1.2).

Fluorotelomers are produced with a wide variety of functional groups such as alcohols, sulfonamides, sulfonamidoethyl acrylates and methyl acrylates and sulfonamidoacetic acids. The majority of the fluorotelomers are used in production processes, such as, for example, as building blocks for polymers, surfactants and polymers with fluorinated side chains. Many of these products are so-called precursors (see below) and are converted into PFSAs and PFCAs in the environment, which are not further degraded (Lindstrom et al., 2011).

In

Figure 3 two examples are given with, left, 8:2 fluorotelomere alcohol (FTOH) and, right, 6:2 fluorotelomere sulphonate (6:2 FTS). 8:2 FTOH consists of 8 fully fluorinated carbon atoms, an ethyl group and an alcohol group and is an example of a PFCA precursor: a compound that can be converted in the environment into, among other things, PFOA (Parssons et al., 2008). 6: 2 FTS consists of 6 fully fluorinated carbon atoms, an ethyl group and a sulphonate group, and also an example of a PFCA precursor.

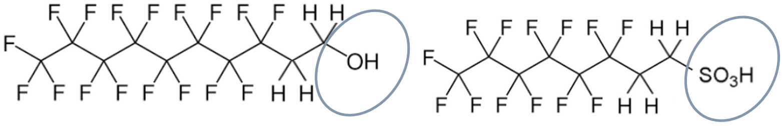


Figure 3: Examples of telomeres, with 8:2 FTOH (left) and 6:2 FTS (right)

6:2 FTS is used as a substitute for PFOS for various purposes, including in class B fire extinguishing foam and as surfactant in industrial applications. 8:2 FTOH is widely used for making textiles water-repellent.

1.1.2.1 PFAS precursors

PFAS precursors are substances that can break down in the environment into PFSAs and PFCAs such as PFOS and PFOA. This is a very large group of mostly unknown and difficult to analyse compounds.
The telomeres, as described above, are also included in this. Precursors are significant sources of PFAS to the environment. The worldwide production of polyfluoro chemicals, most of which are precursors, is many times greater than that of PFOS and PFOA combined (Liu et al., 2013). In commercially available analysis methods for PFAS, mainly PFCAs and PFSAs are measured, and some precursors. Studies of urban (rain) drainage water containing precursors in the San Francisco Bay have shown that PFSAs and PFCAs account for less than 25% of the total PFAS content (Houtz 2012). Insight into the presence of precursors is therefore important.

Fluoropolymers

Fluorinated polymers may or may not be covered by the PFAS, depending on whether or not they contain perfluoroalkyl groups. The fluoropolymer polytetrafluoroethylene (Teflon, PTFE), belongs to the PFAS and is used as a non-stick coating in pans. It is inert at normal temperatures, and breaks down at temperatures above 260 °C. Teflon resins contain small concentrations (in the order of ppm, parts per million) of hexafluoroacetone (HFA). PFOA was an essential recipient in the composition of these polymers. Since 2012 PFOA has been replaced in the Du Pont / Chemours PTFE production process by another PFAS; GenX. Part of the production process of non-stick coatings is a sintering process at high temperatures whereby, in theory, the remaining PFOA should evaporate (Herzke et al., 2007).

In textiles coated with PTFE (jackets, tablecloths, etc.) mainly fluorotelomere alcohols and fluorotelomere carboxylic acids are found in relatively large quantities (up to 11 mg/m^2 fluorotelomere alcohols and 0.4 mg/m^2 PFCA, Berger and Herzke 2006). In addition, there are also polymers with fluorinated side chains. These are mainly used in the textile industry. Upon degradation of the polymers, the fluorinated side chains are released and PFAAs can be formed. These polymers can therefore also be precursors.

1.2 PRODUCTION OF PFAS

In the past, two processes have been used for the production of PFAS: electrochemical fluorination (ECF) and telomerisation (TM).
PFAS production prior to 2001 was dominated mainly by the electrochemical fluorination process of 3M, the main product being 30-45% perfluorooctane sulfone fluoride (POSF), with a collection of other PFCAs and PFSAs. This process was also used at the 3M location in Zwijndrecht. Since 2001, the production of PFAS by electrochemical fluorination has been greatly reduced due to concerns about the environmental effects of PFOS and telomerisation became the main method of PFAS production. No PFOS or precursors of PFOS are consequently formed.
The two synthetic routes result in a different degree of purity of the product. Generally, even and uneven, branched and linear perfluorinated carbon chains are formed in the ECF process. In TM only linear chains are created. Today, telomerisation is the most used production process (Buck et al., 2011).

2 PFAS USE

PFAS are used in various products and production processes. Among other things, in chrome-plating, the production of inks, varnishes, waxes, fire-extinguishing foam, cleaning agents, coatings, lubricants, water- and oil-repellent agents for leather, paper and textile (Paul et al., 2009). From 1966 to 1990, production and use grew due to their unique chemical stability and their water and dirt-repellent properties. The annual production volume increased considerably from 500 tonnes per year in the 1970s to almost 5000 tonnes per year in 2000 (Carloni 2009).

In 2000, the main global producer of PFOS, 3M, began phasing out the production of PFOS. As a result of this initiative, global production decreased significantly between 2000 and 2003. During this period, production in China increased, but not to the same global production level as for the year 2000 (Paul et al., 2009, Carloni, 2009). The phasing out of PFOA began in 2005, through the PFOA Stewardship program. Under the leadership of the US-EPA, the 8 largest producers of PFOA participated. These parties (Arkema, Asahi, BASF, Clariant, Daikin, 3M/Dyneon, Du Pont and Solvay Solexis) had phased out the use of PFOA in 2015 according to plan.
In May 2009 PFOS was added to Annex B of the Stockholm Convention. Since then, the use of PFOS and related substances has been limited in countries that have signed the convention, although it is still used for applications where PFOS cannot be replaced by other chemicals. As of 13 June 2017, PFOA and its salts have been added to the list of substances of very high concern in REACH and Annex XVII of EC 1907/2016, as well as any related substance that has C7H15 as one of the structural elements. These substances may not be marketed as a substance themselves from 4 July 2020. In addition, it may no longer be used as a component of another substance, article or mixture in a concentration equal to or greater than 25 ppb (25 µg/kg) as PFOA itself or 1000 ppb (1 mg/kg) as an associated substance.
PFNA (17 December 2016), PFDA (12 January 2017) and PFHxS (June 2017) have also been put on the REACH candidate list (https://echa.europe.eu/candidate-list-table). The short-chain PFAS will also be further evaluated.

2.1 PFAS PRODUCTION LOCATIONS

The most well-known production sites of PFAS raw materials in Europe are the 3M location in Zwijndrecht (Belgium) and the Miteni location in Trissino (Italy). At both locations PFAS were manufactured by the electrochemical fluorination (ECF process).
Electrochemical fluorination was economically very interesting because of the low energy costs and the relatively inexpensive starting product. Many by-products and waste products were formed during the process.

The area surrounding the PFAS production sites is contaminated with PFAS due to years of (licensed) discharges of waste into the environment. In the area around Trissino (Italy) this has led to a polluted area of more than 200 km² (WHO, 2016). In the Antwerp port area, the area around the production site of 3M is contaminated. Higher concentrations of PFOS are thus found in birds and mammals in the Blokkersdijk nature reserve (Lopez Antia et al., 2017, Groffen et al., 2017, D'Hollander, 2014). The extent of the area affected in Flanders has not been determined.

2.2 POLYMER PRODUCTION

PFOA was used until around 2012 during the production process of fluoropolymers such as polytetrafluoroethylene (PFTE, Teflon). At Chemours (formerly Du Pont) in Dordrecht, the Netherlands, PFOA is used for the production of Teflon, FEP (perfluorinated ethylene-propylene resin) and Viton (a certain type of rubber). PFOA was also used in the production process of perfluoroalkoxy polymers (PFA polymers).
From 2013 PFOA in Dordrecht has been completely replaced by the GenX process. The GenX process is based on the perfluorinated compounds FRD-902/903 (ammonium or hydrogen) -2,3,3,3-tetrafluoro-2 (heptafluoropropoxy) propanoate) and the reaction product E1 (heptafluoropropyl-1,2,2,2 tetrafluoroethyl ether) (Beekman et al., 2016). There are also production locations in Mechelen and Zwijndrecht where PTFE is produced.
Studies have shown that if PFOA is used as an excipient in the production of polymers, the end product can contain a relatively high level of PFOA. The content can vary significantly, from 0.001-0.005 percent in dry matter to 0.1-0.5% in dispersed material. This also means that by importing PTFE from countries where PFOA is still used as an excipient, significant amounts of PFOA are imported (estimate of 3-16 tonnes of PFOA per year in the EU) (Kemi 7/15).
In 2006 the US-EPA, together with 8 PFAS producing companies, started the PFOA Stewardship program. The aim was to reduce the use and emission of PFOA before 2010 by 95%, and then to work towards complete phasing it out by 2015. All eight participating companies (Arkema, Asahi, BASF, Clariant, Daikin, 3M/Dyneon, Du Pont and Solvay Solexis) have met this.

2.3 USE IN FIRE-EXTINGUISHING FOAM

The use of fire-extinguishing foam is a source of PFAS to the environment because in the case of fire-extinguishing foam the PFAS end up directly in the environment. The foaming agent is added to the fire-extinguishing water during the extinguishing.
PFAS are used in fire extinguishers because of their ability to produce a barrier film very quickly (AFFF: aqueous film forming foam). The fluorine components are very stable chemically and thermally, even under extremely high temperatures and in extreme conditions the compounds remain intact and the foam continues to work (for example with very aggressive acidic or basic fuels and chemicals). Due to the unique property of rejecting both hydrophilic (water) and hydrophobic (fat, oil, fuel) compounds, the use of AFFF therefore has little risk of the fuel being absorbed into the foam.

PFAS-based class B fire-extinguishing foams (see the box) have therefore been used since the 1970s to extinguish fires at airports, refineries, bulk storage chemicals and other locations where large volumes of flammable liquid hydrocarbons are used. AFFF is also used in fire extinguishing training at these locations and can be released during the testing and use of automatic fire extinguishing systems in buildings.
Foam-forming agents consist of a large range of substances, which together ensure the effective spreading of the foam over the liquid, the storage life during storage and during fire. The foaming agent includes various surfactants (e.g. fluoro chemicals, proteins, hydrocarbons, silicones), stabilizers, solvents and special ingredients for anti-corrosion and biocides.

Depending on the specifications of the foaming agent, an admixture takes place in different concentrations. With a foaming agent with, for example, the indication of 3% (admixing percentage), an addition of 3 parts of foaming agent and 97 parts of water takes place. Double blending percentages are also indicated (for example 3x6). In that case, a different blending percentage is set for burning apolar and polar substances. Fluorine-containing foaming agents contain in the order of 5% PFAS. The amount of foaming agent that is put in depends on the size and the type of fire. This can involve tens to thousands of litres of foaming agent. With the use of foam-forming agents by the (company) fire service, tens of kilograms of PFAS can be released during large fires.

Types of fire extinguishing foams

A large range of fire extinguishing foams exist. Class B foams are used to extinguish flammable liquids. At present fluorotelomer containing foams and fluoro-free foams are used. Also protein foams, FluoroProtein foams (FP), Film Forming Flouroprotein Foams (FFFP), Alcohol Resistant Film Forming Fluoroprotein Foams (AR-FFFP), Aqueous Film Forming Foam (AFFF), Alcohol Resistant AFFF (AR-AFFF), foams from synthetic soaps and class A exist.

PFOS and its derivatives were used in fire-extinguishing foams until 2001. After that, the production of PFOS was phased out due to environmental considerations. Since 2001, fire-extinguishing foams have been produced using fluorine surfactants based on fluorotelomers such as 6:2 FTS and 8:2 FTS (fluorotelomere sulphonates) (Seow, 2013). These fluoropolymer sulfonates come under the so-called precursors and can degrade into PFAAs.

Due to the long lifespan of foam concentrates, it is likely that PFOS-containing foam was still used after 2001: the use of foams containing PFOS as the primary component (> 0.001 wt%) was only definitively banned 10 years later (27 June 2011) (Stockholm Convention). In countries that do not comply with the Stockholm Convention (including China), PFOS is still being used and produced.

PFOA is used to a lesser extent in AFFF, but is often present in AFFF, usually as a by-product of the production of the PFAS used in AFFF.

A wide spectrum of fluorine-containing precursors is present in AFFF. The composition of the AFFF varies per producer and is often a trade secret. The information given on an MSDS (material safety data sheet) for the fire-extinguishing foam is often not sufficient to determine which PFAS are present in the relevant AFFF (applied substances are trade secrets or the concentrations are too low to have to be specified in the MSDS). The terms PFOS-free and PFOA-free often indicate that there are other PFAS present in the fire-extinguishing foam. When the term PFAS-free is used (or free of PFC), it can be expected that no other PFAS are present in the foam.

PFAS terminology fire extinguishing foam
The extinguishing foam industry uses C6 and C8 as terminology. This represents fluorinated compounds with a C6 or C8 fully fluorinated chain, such as 6:2 FTS and 8:2 FTS.
This terminology is different compared to the general chemical terminology. The compounds have respectively 8 and 10 carbon atoms, hence C8 and C10 compounds (6:2 FTS; 6+2 and 8:2 FT; 8+2)

Backe et al. (2013) have developed a new method to quantify an extensive series of PFAS in groundwater and fire-extinguishing foam. The authors concluded that the PFAS profiles in groundwater differ from the PFAS profiles found in AFFF compounds. This indicates that PFAS are converted in the environment.

AFFF usually contains several types of PFAS compounds, in the meantime 240 individual PFAS have been detected in AFFF (Barzen-Hanson et al., 2017).

2.4 USE IN GALVANISATION

In galvanization, PFOS is mainly used in chromium plating. It was (and still is) used to reduce the exposure of employees to chromium VI. During the chrome plating an electric current is passed through a bath of chromic acid. This creates oxygen and hydrogen gas bubbles that burst at the surface.
PFOS is used to reduce the surface tension of the bath with chromic acid, reducing the size of the bubbles and causing fewer bubbles to burst at the interface, resulting in less carcinogenic chromium VI being released into the air (Brumm Poulsen et al., 2011).

Figure 4: Chromium plating bath (with orange foam) with rinsing baths (EPA, 2009)

After the chroming bath, the chrome-plated metal is rinsed with water in several rinsing baths. These rinsing baths therefore become contaminated with PFOS.

As an alternative to PFOS, mainly 6:2 FTS is currently used. This substance is comparable to PFOS, however the two carbon atoms next to the sulphate atom are not fluorinated. 6:2 is a precursor of PFHxA.

The search for alternatives is going on, but it is not easy. The functionality of alternatives to PFOS is significantly less, and increased release of chromium VI during the process is undesirable. PFOS is therefore still used in the chrome-plating industry, in closed systems to minimise the release of PFOS (UNEP-POPS, 2014).

2.5 USE FOR MAKING WATER AND DIRT REPELLENT

PFAS are used to make, amongst other things, clothing, shoes, tents, umbrellas, carpets and furniture water and dirt repellent. The amount of PFAS in these materials ranges from 2-3 percent of the fibre weight to 15 percent in synthetic carpets (KEMI Swedish Chemicals Agency, 2015). Polymers from PFAS are often used. These polymers may contain residues of PFAS from the production process or they may be degraded to fluorotelomers, such as FTOHs, but also to perfluorinated carboxylic acids such as PFOA and PFHxA.

Mainly two types (polymers of) PFAS are used to make water and dirt repellent:

- Polytetrafluoroethylene (PTFE/Teflon) is used to make (outdoor sports) clothing and tents waterproof. PTFE is a **fluoro polymer** with a high molecular weight and is therefore used in the manufacture of porous substances such as Gore-Tex®. A thin layer of PTFE is added to the material to strengthen the material and make it breathable. The thin layer of PTFE has 1.4 billion pores per cm^2. The pores are smaller than raindrops but larger than water vapour molecules, making the fabric waterproof but it can still breathe.
- Polymers with **fluorinated side chains**, such as, for example, fluorotelomere acrylate polymers. The method is used, for example, in textiles, carpets and leather because of its water and dirt repellent properties. The fluorinated side chains are released upon degradation of the polymer.

There are a number of PFAS-based coatings for textile products in the Netherlands on the market for consumer use. The products usually consist of a mixture of, among others, PFAS and solvents. The impregnation agents are applied with a spray can as a thin layer to the fabric, a thin polymer structure of both polyfluoroalkylated and non-fluorinated side chains being formed on the surface. These side chains provide dirt and water repellent properties. In these impregnation agents mainly FTOH are found, which eventually can break down to PFCAs. Median concentrations can be up to 146 mg/kg for 8:2 FTOH (a precursor of PFOA), with a maximum of 719 mg/kg (Kotthoff et al 2015).

2.6 OTHER USES

PFAS are used in the production process of many different materials. Below is a brief summary of other products in which PFAS may be present.

Paper industry

PFAS are used in the production of grease and water repellent paper used, for example, for packaging food. Polyfluoroalkyl phosphoric acids (PAPs and diPAPs) are mainly used during production. Other PFAS have also been used in the paper industry. A study in US showed that in 90% of the tested food packaging FTOH was present, the median level of FTOH was 0.4 mg/kg. (Liu et al. 2013). Research by Kotthoff (2015) indicated that many PFCAs were present in paper from before 2010 (muffin bakeware, PFNA + PFDA = 1 mg/kg), but that much lower values were measured in the 2015 samples (14 and 18 µg/kg for PFOA and PFPeA, respectively). In 2015, negligible concentrations of PFAAs were found in baking paper and paper to pack bread.

Cosmetics

In the cosmetics industry PFAS is used for various reasons. It can be used in sunscreen and body lotion to make the cream water repellent. PFAS are also used in cosmetics as anti-caking agents, solvents, emulsifiers, antistatics, stabilizers, emulsifiers, surfactants, film formers, viscosity regulators and solvents. Polyfluoroalkyl phosphoric acids (PAPs/diPAPs) are mainly used. But an analysis of various cosmetic products shows that PFCAs (including PFOA, PFHxA and PFHpA) can also be found in cosmetics (Fujii et al. 2013).

Household articles

PFAS can be present in hydraulic fluids, insecticides, cleaning agents, lubricants, paint and varnish and in wax for floors, cars, airplanes and snowboards. Non-stick pans can also contain PFAS (Teflon).

Other

PFAS are used as surfactants in drilling for the oil industry.

Alternative

After the phasing out of PFOS and PFOA, alternatives have been developed by the producers, the most well-known being GenX (Du Pont/Chemours), Adona (3M) and EEA (mainly in China). These are mostly compounds that are also fully or partly fluorinated, but have a different structure. GenX and Adona and EEA are perfluoroethers, and have one or more ether (-O-) groups in the molecular structure.
In addition, there are many other fluorinated alternatives.

The fluorinated alternatives are also currently in the spotlight. The compounds are less bioaccumulative, but certainly persistent due to the fully fluorinated chain. A preliminary (very conservative) estimate of the toxicity of GenX on the basis of permitted daily intake was only estimated twice as high for GenX than for PFOA (ADI = 21 ng/kg lg/day for GenX versus 12.5 for PFOA) (Smit, 2017).

2.7 OVERVIEW OF RISK LOCATIONS WITH A RISK OF CONTAMINATION IN SOIL, GROUNDWATER AND SEDIMENT

PFAS are produced and processed at various locations. The risk of dispersion into the environment depends on the quantities used and under which conditions the compounds have been handled or processed. In the case of firefighting activities, there was often a lack of soil protection facilities.

In addition to locations where PFAS was produced or applied, landfills and water purification plants have been added to this list. Landfills can be a source of PFAS due to the disintegration of PFAS-containing materials such as carpets, furniture, clothing, impregnating agents etc. In wastewater treatment plants the waste streams come together from the processing industries, or the remains of extinguishing activities.

Type of location	**Subcategory**	**Activity**	**Risk of release of PFAS into the environment (soil, groundwater, sediment, air)**
PFAS producing industry	Producers	Production of PFOS/PFOA, telomerea	Large
Processing industry	Teflon production	PFOA use during production	Large
	Galvanic industry	Mist suppressant (spray, chrome baths), especially in chrome-processing industry (but also other metals)	Large
	Textile industry	Treating textiles, leather, water-repellent, spray For example carpets, outdoor clothing, shoes	Limited
	Semiconductor industry	Use of PFAS in Printing plate production (suspect products/chemicals: photo acid, anti-reflective coating, photoresist and developing fluid).	Limited
	Photo industry	In the photo industry, products such as solvents, pigments, developing fluid were also used.	Limited
	Paper and packaging industry	PFAS was/is added to the composition of the paper to make it water and grease-repellent (as with food packaging, baking paper, etc.)	Limited
	Paint industry	Production of paints with PFAS as additive	Limited
	Hydraulic fluids	PFAS as an additive to hydraulic fluids used in filling and refilling of the liquid at least since 1970. Main use in aircraft construction and maintenance.	Limited
	Manufacture of cosmetics and cleaning products	Mainly used to reduce the surface tension or to extend the life of mainly cosmetic products	Limited
Use of fire extinguishing foam (AFFF) (1970-2011/present)	Fire extinguishing	Calamity	Large
	Fire service training sites	Regular, long-term use of, among other things, PFAS-containing foam	Large
	Fire service facilities (industry)	During calamities and/or testing. Chemical industry, storage and transhipment locations, automotive industry, plastics industry, waste and scrap processing companies, chemical wholesalers	Large
	Military training areas and airfields	During calamities and/or fire service training	Large
	Airfields (civil aviation)	During calamities and/or fire service training	Large
Landfill sites		Degradation material in landfill (e.g. treated textiles, paper), leaching from landfill	Limited
Water treatment plants		Mainly water treatment from industry	Limited
Waste incineration plants		PFAS are broken down but probably not completely excluded as a potential source	Limited

Table 1: Overview of suspected risk locations

Legend:

- Limited → limited, probable, present
- Large → certain, large

3 BEHAVIOUR OF PFAS IN THE ENVIRONMENT

PFAS are widespread in the environment due to their high solubility, low/moderate sorption to soil and sediment and resistance to biological and chemical degradation. Although many studies have been published on PFSAs and PFCAs in the environment, much less data is available on precursors, since standard analysis is not always performed and the importance of the precursors has only become better known in recent years.

PFSAs and PFCAs are not biodegradable. In addition, they are often end products of the biological conversion of precursors. These substances (including PFOS and PFOA) are therefore so-called dead-end daughter products, or the end products of natural degradation.

3.1 PHYSICOCHEMICAL PROPERTIES

The physicochemical properties for a number of PFAS, derived from scientific literature, are summarized in Appendix 11.2. Although PFOS and PFOA have been extensively investigated in comparison with other PFAS, the available data are still relatively scarce and the behaviour is still not completely understood. For example, physical and chemical properties are shown for the neutral form of the substances, but in water most PFAS dissociate into an anion and a cation (Wang et al., 2011). The anions have a strong tendency to the water phase, so that the substances are less volatile than is calculated on the basis of their physical and chemical properties (Prevedouros et al., 2006).

Fluorocarbon bonds are rarely found in naturally occurring organic substances. The carbon-fluorine bond is one of the strongest bonds in organic chemistry. PFAS usually consist of a hydrophobic tail (polyfluorinated or perfluorinated carbon chain) and a hydrophilic head (functional group consisting of, for example, sulfonate or carboxylate and/or the salts thereof). These amphiphilic (both hydrophobic and hydrophilic) properties of PFAS make them ideal for use as surfactants. However, in contrast to conventional surfactants, the tail of the PFAS also has lipophobic properties, as a result of which PFAS coatings are not only resistant to water, but also to oil, grease, other non-polar substances and dirt particles. PFAS surfactants have the ability to group together at interfaces and to form micelles on the other hand. This enables PFAS to accumulate in the environment in the interfaces between groundwater (hydrophilic) and soil air (hydrophobic). The physical and chemical properties are important for the behaviour of PFAS in the environment. This is explained in more detail below when discussing the transport routes.

3.2 DISPERSION, TRANSPORT AND DEGRADATION

Due to their persistent properties, PFAS can spread widely into the environment. They are resistant to hydrolysis, photolysis, biodegradation and metabolism. PFAS do not occur naturally, yet PFAS are found even in polar bears at the North Pole. The dispersion routes have been studied for several years, with two dispersion routes being accepted. The first route is through the transport of precursors through the air, followed by oxidative conversion of these precursors into PFAAs, which then precipitate via deposition. In addition, transport of PFAS via groundwater, surface water and seawater can take place. (Rigét et al., 2013).

In more detail, PFAS can spread from the discharge/release via the following dispersion and degradation routes into the environment:

- Leaching from soil to groundwater, and then spreading via groundwater.
- Dispersion via air (and deposition in soil or surface water).
- Dispersion by (contaminated) sludge, soil movement (excavation) or dredging.
- Degradation of precursors to PFAAs in the environment.

3.2.1 Dispersion via groundwater

Due to the relatively good solubility and the low adsorption of PFAS to the soil, PFAS can easily spread in the environment via groundwater. Because in addition there is no degradation of PFAAs and the assessment values are low, PFAS contaminants can form very large plumes, up to several kilometres long (Weber et al., 2017).

Within the usual pH range in soil, groundwater and surface water (pH 5-9), PFSAs and PFCAs are present as anions. Sorption to soil and sediment is limited because of the generally negative charge of the soil. Retardation during groundwater transport is greater as the perfluorinated carbon chain is longer and/or the amount of organic matter in the soil is higher. PFSAs have a stronger binding to organic matter than PFCAs with the same amount of carbon atoms (Higgins and Luthy, 2006).
The literature and experience in projects have shown that the heavier compounds and the PFSAs bind more strongly to the soil and that the PFAAs and the lighter compounds are more present in the water phase. PFOA is a more mobile compound than PFOS. The influence of any other contaminants on the mobility of PFAS differs, depending on the PFAS chain length, PFAS concentrations and the properties of the other contaminants. In general, the shorter PFAS have higher mobility than the longer PFAS. This is shown in Figure 5. The precursors show different behaviour in the environment. Because the precursors can be anionic, cationic or zwitterionic (both cationic and anionic), or neutral (not charged), the bond to the soil differs. The cationic and zwitterionic precursors generally bind the soil more strongly, these components are found closer to the source zone of the contamination. Precursors can also spread via the groundwater. When, at a greater distance from the source, the redox conditions change to aerobic, these PFAS precursors can be converted into PFAAs (see Figure 4).

Octanol-water partition coefficient
For most contaminants, the log Kow (octanol / water partition coefficient) can be used to predict the adsorption of contaminants to the soil. A high log Kow indicates that the substance would rather be in octanol (hydrophobic) than in water, indicating that the substance strongly adsorbs to the soil. However, this is not the case for PFAS. PFAS have a very low log Kow, which in many cases cannot even be measured by its water and fat-repellent properties. For the log Kow determination, PFAS will accumulate at the water-octanol interface instead of in the liquids. The log Kow is therefore for PFAS not a good indicator for soil adsorption.

PFAS behave like soaps and can accumulate on the water-air interface. They can also form micelles, and already coagulate at concentrations well below the critical micelle concentration (Vierke et al., 2013).

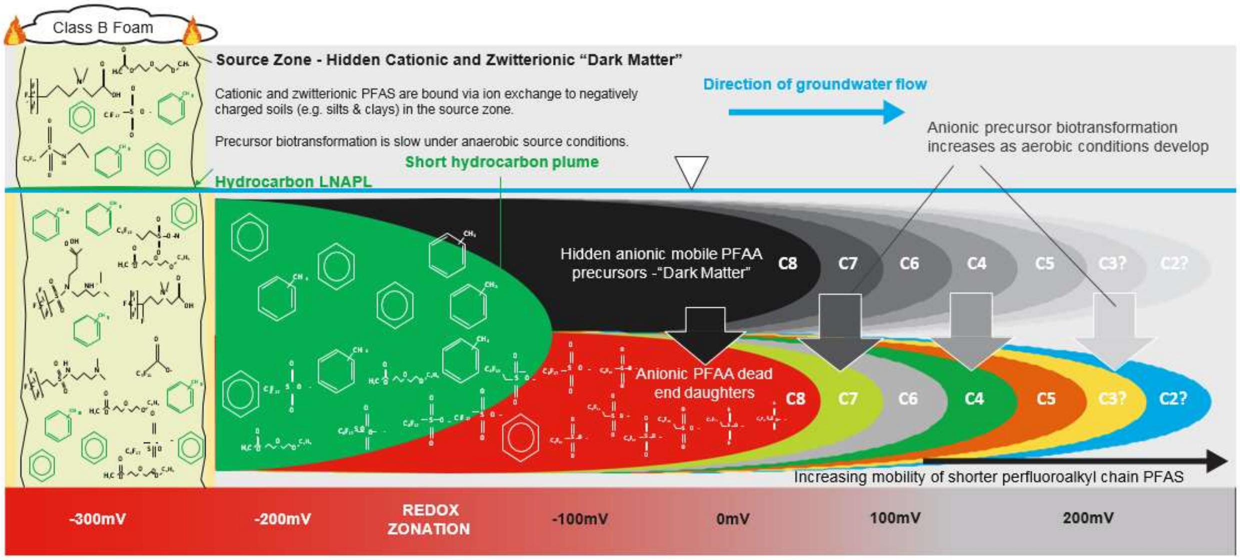


Figure 5: Conceptual model of PFAS dispersion (Arcadis, 2017)

3.2.2 Air dispersion

Due to the low equilibrium constant between air and water (Henry constant), PFAAs do not or hardly spread through the air. PFAS can be transported through the air when it is emitted into the air via a production process. PFOA, for example, coagulates and forms aerosols (small particles) (Zeilmaker et al., 2016). In the surroundings of both Dordrecht (NL) and Zwijndrecht (B), increased concentrations in the soil have been measured (tens of µg/kg), probably via atmospheric deposition (PFAS expertise centre, 2016, d'Hollander et al., 2011).

Air dispersion may be relevant for precursors. Precursors with high volatility such as FTOHs, fluorinated sulphonamides (FOSAs) and sulphonamidoethanols (FOSEs) can spread through the air. In the air they are subject to atmospheric oxidation, whereby PFAAs are formed, which then precipitate through atmospheric deposition on the soil and water (Rigét et al., 2013).

3.2.3 Dispersion by (contaminated) sludge, soil movement or dredging

Dispersion of PFAS into the environment may also have occurred physically without being noticed. Because PFAS are very widespread and are still being used, there are several routes known through which PFAS are unintentionally dispersed. Examples include spreading of contamination during dredging, but also moving of soil (excavation,…) without knowing that it is contaminated. The use of fire-extinguishing foam can also be seen as an example of physical dispersion.

One of the largest PFAS contamination cases in Germany is the use of contaminated sludge from the paper industry as a soil improver on agricultural plots. Paper sludge had been used on agricultural plots for several years until it was discovered in 2006 that these agricultural areas were the source of the increased PFAS concentrations in the surrounding rivers (Kröfges et al., 2007). The use of sludge from water treatment plants in Decatur, Alabama (near PTFE plant) has resulted in PFAS concentrations in the soil up to a few milligrams per kg (Washington et al., 2010).

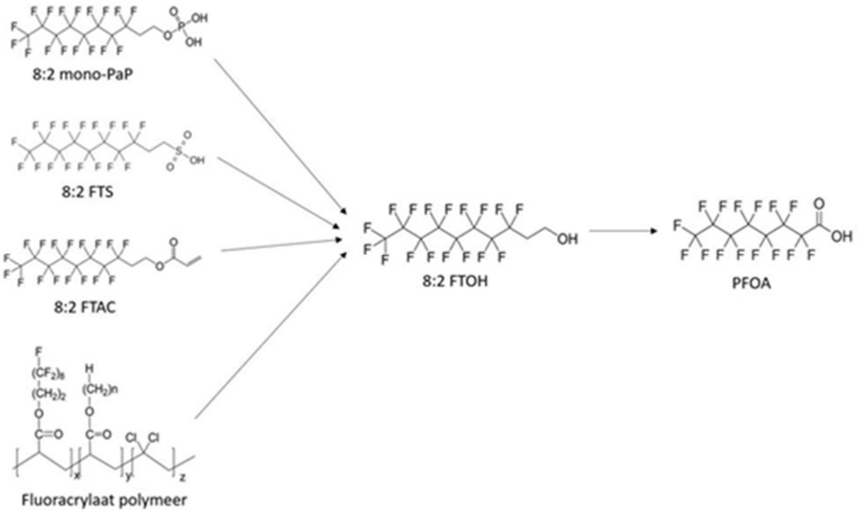
3.2.4 Degradation in the environment

As mentioned before, biological and chemical degradation in the environment is only relevant for the PFAS precursors. The non-fluorinated parts of the precursors can be degraded, leaving the perfluorinated PFSAs and PFCAs. PFSAs and PFCAs are not biodegradable. The biodegradation of precursors occurs mainly under aerobic conditions. In a single study, degradation of precursors under anaerobic conditions has also been demonstrated (Zhang et al., 2013). The degradation is much slower than under aerobic conditions, and not completely up to PFAAs. During the anaerobic degradation, other polyfluorinated intermediates are formed.

Most precursors degraded into PFCAs such as PFOA. Substances with a perfluorinated carbon chain of 8 carbon atoms degradede into PFOA via various intermediates, such as 8: 2 monoPaP, 8: 2 FTS, 8: 2 FTAC, 8: 2 FTOH.

Precursors that can degrade into PFSAs such as PFOS are, for example, EtFOSE and EtFOSA (Figure 6).

Not only PFOS and PFOA are formed during the degradation of precursors. A mixture of different PFAAs often occurs. For example, in the degradation of 8:2 FTOH, PFHxA, PFHpA and PFOA are formed (Wang et al., 2009).



(Liu et al., 2013)

Figure 6: Example of degradation routes of fluorotelomers into PFOA

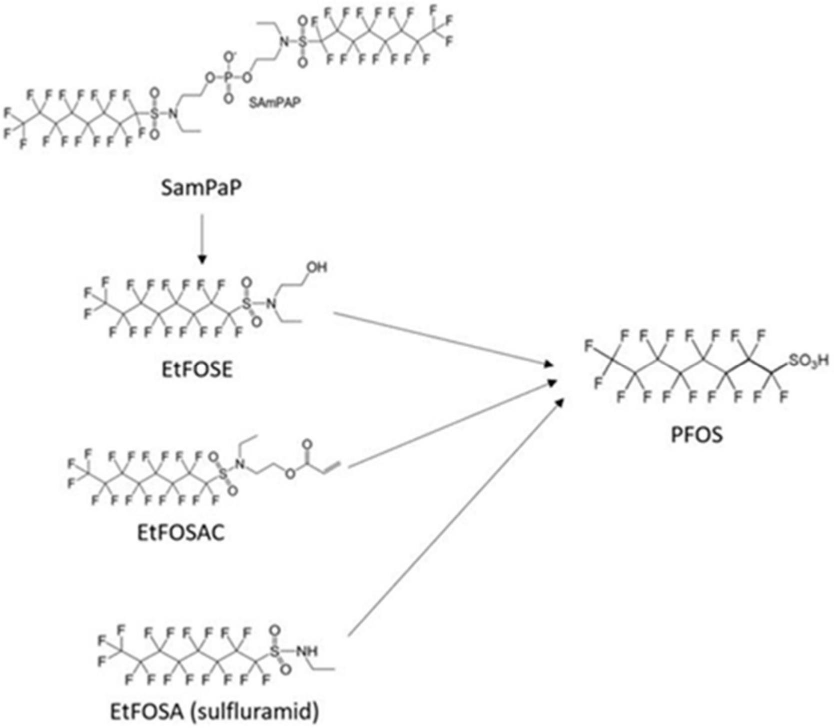


Figure 7: Example of degradation pathways from precursors to PFOS (Liu et al., 2013)

4 TOXICITY AND ASSESSMENT LEVELS

The toxicity data for PFAS are dominated by PFOS and PFOA due to the widespread occurrence of these components in the environment. Much less information is available from the other PFAS. An extensive overview of toxicity data is given in the Concawe report (Pancras et al., 2016) and in the RIVM reports on PFOS and PFOA (Moermond, 2010, Bodar, 2011, Zeilmaker, 2016, Verbruggen, 2017). Exposure to PFAS mainly takes place via drinking water or food (Noorlander et al., 2010). For children, household dust and contaminated soil intake can also be a major source of intake.

PFAS are not converted in the body and are not attached to fats as other contaminants, but are attached to proteins. The excretion of PFAS (mainly PFOS, PFOA and PFHxS) from the body is very slow, and can take years. The half-lives of PFOS, PFOA and PFHxS are approximately 3-4 years, 2-3 years and 5-7 years respectively (Olsen et al., 2007, Li et al., 2017). Smaller PFAS can be removed from the body in a few days. This is also reflected in the bioaccumulation of the PFAS. The long-chain PFAS (PFHxS and larger, and PFOA and larger) bioaccumulate, the short-chain accumulate not or hardly.

Chronic exposure to PFOS results in effects on liver, lungs, hormone levels, reproduction and on development in experimental animals. Chronic exposure to PFOA also results in effects on the liver and has an effect on the formation of antibodies during vaccination.

Whether PFOS and PFOA are carcinogenic has not been established with certainty. PFOS and PFOA are designated by multiple agencies (ATSDR, US-EPA and IARC) as being possible or likely to be carcinogenic (but not yet as a proven carcinogen). In the Netherlands PFOS and PFOA are included in the list of substances that have a negative effect on reproduction (SWZ, December 2016). Studies on large contamination cases have furthermore shown that there are strong links between exposure to PFAS and various types of cancer (e.g. renal, testicular, prostate, ovarian and breast cancer) (Vieira et al., 2013; Mastrantioni et al. , 2017).

PFOS and PFOA are not acutely toxic to humans (ATSDR, 2015). At high doses in animal studies effects on the liver and gastrointestinal tract occur. PFOS is more toxic than PFOA (CRC-Care, 2017).

4.1 ACCEPTABLE DAILY INTAKE (ADI)

Based on toxicity studies, an acceptable daily intake is derived (ADI).

The ADI is the starting point for the regulations that are derived in the different countries. In 2008, the EFSA derived ADIs for PFOS and PFOA, which until recently have been used as a basis for the deriving of assessment values (EFSA, 2008). The ADIs have been determined on the basis of calculating the results of animal testing to safe intakes for humans.

In recent years, a downward trend has been seen in the ADIs that have been derived (figure 8). The biggest change is that the very long half-lives have been passed on in the ADIs. Table 2 shows the ADIs derived for PFOS and PFOA by various institutes. At present the ADIs for PFOS and PFOA are being re-evaluated by EFSA (planned Spring 2018). It is expected that these will decrease at least to the same order of magnitude as the recently derived ADIs.

Source:	**ADI PFOS (ng/kg bw/day)**	**ADI PFOA (ng/kg bw/day)**
EFSA, 2008	150	1500
EPA, 2009	80	190
Denmark, 2015	30	100
EPA, 2016 (reference dose / RfD)	20	20
RIVM, 2016	-	12.5
Australia, 2017	20	160
EFSA, 2018	?	?

Table 2: Acceptable daily intake values (ADI) derived by various institutes

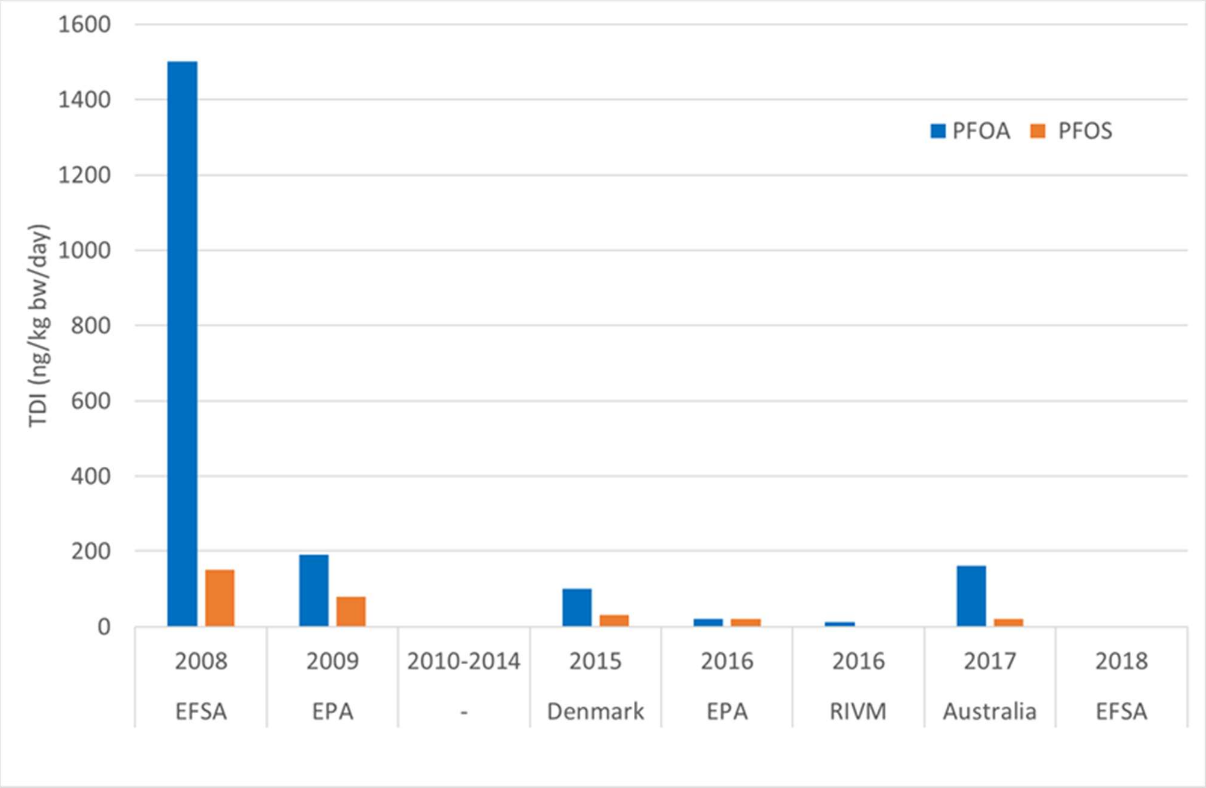


Figure 8: ADI developments over time

For GenX, a provisional (very conservative, on the basis of a worst-case scenario) ADI was derived from 21 ng/kg bw/day in 2017 (Smit, 2017).

The ADI can be fairly easily converted into a drinking water toxicological level. This is based on an intake of 2 litres of water per day for a 70 kg person. The exposure route via drinking water may represent a maximum of 20% of the ADI. The 2016 PFOA ADI thus results in a drinking water toxicological level of 87.5 ng/l (12.5 x 70 kg x 20%/2 litres per day), and GenX at a value of 150 ng/l.

The drinking water assessment level for PFOS derived in Moermond et al., 2010 is based on the ADI of 150 ng/kg bw/day that was derived by the EFSA in 2008. In this case, drinking water could represent a maximum of 10% of the ADI (since 2011, 20% (WHO guideline) has been taken into account). This resulted in a drinking water assessment level of 530 ng/l (in practice the assessment level is assessed at a value of 100 ng/l). It is expected that the ADI for PFOS for the Netherlands will be revised. If the ADI is reduced, in line with the derivation of the TDIs for the other countries, the drinking water assessment level will be adjusted downwards.

4.2 ASSESSMENT LEVELS FOR SOIL AND GROUNDWATER

It is important to keep an eye on the change in the ADI since 2011 (see the previous section). The PFOS assessment levels are based on an ADI of 150 ng/kg bw/day from the EFSA in 2008. The PFOA assessment levels are based on the ADI of 12.5 ng/kg bw/day from the RIVM from 2016. Currently the ADIs for PFOS and PFOA are being re-evaluated by the EFSA. Adjustments of the ADIs will undoubtedly have an effect on already derived assessment levels.

4.2.1 Overview of soil and groundwater assessment levels for PFOS and PFOA (the Netherlands)

The RIVM derived lower and upper limits for PFOS in 2011 (Bodar et al., 2011) and for PFOA in 2017 (Lijzen et al., 2017). The lower and upper limits in soil, dredging, groundwater and surface water have been derived in accordance with methods that fit in with the European framework. This links up with REACH and the Water Framework Directive (Bodar et al., 2011).

The assessment levels for soil and groundwater have been derived by the RIVM on the basis of tolerable risk levels, in which three levels are of importance:

- Serious Risk level (SR): a concentration where serious effects can be expected for ecosystems or humans.
- **Maximum Tolerable Risk Level (MTR)**: a standard derived from scientific data for a substance that indicates at what concentration in an environmental compartment:
  - no adverse effect can be expected for ecosystems;
  - no adverse effect can be expected for humans (for non-carcinogenic substances);
  - for humans no more than a 10^{-6} per year chance of death can be calculated (for carcinogenic substances).
- **Negligible Risk Level (NR)**: a concentration where effects on human and the environment are negligible. The NR is set at 1/100 of the MTR.

Table 3 gives an overview of the most important assessment levels for PFOS and PFOA. To this end, various assessment levels derived by the RIVM were used. The values in the table are based on the standard soil as defined in the Netherlands (10% organic matter, 25% clay).

The assessment levels depend on the exposure route and/or are based on humantoxicological or ecotoxicological criteria. It is striking that the generic upper limit for PFOS (intervention level) is higher than the derived values on the basis of exposure routes (see for example the industry value compared to the upper limit). The opposite is often the case for the most common contaminants. In order to determine which assessment level can be used, it is particularly important to what extent soil and groundwater are in contact with the surface water and whether poisoning is important (for example in/near nature reserves). The ecological level of protection is also important (Wintersen et al., 2016). It should also be noted that the derived risk based levels for PFOS take into account a site specific (for Schiphol) dilution factor from soil and groundwater to surface water.

	PFOS	PFOA
SOIL		
Upper limit (intervention level)	6600 µg/kg dw[1] Lowest of MTR$_{human-soil}$ (6600 µg/kg) and SR$_{eco}$ (16000 µg/kg).	670 µg/kg dw Human risk limit according to standard scenario 'home with garden'
Lower limit	0.1 µg/kg dw Reporting limit (laboratory)	*0.1 µg/kg* *Reporting limit*
Home with garden	11 µg/kg dw Lowest of MTR$_{home, garden}$ (6600 µg/kg), ecological risks soil without secondary poisoning (400 µg/kg),	674 µg/kg dw
Home with vegetable garden	Not determined	390 µg/kg dw
Other green areas, buildings, infrastructure and industry	8 µg/kg[2]dw Lowest of MPR$_{industry}$ (16000 µg/kg), ecological risks soil with secondary poisoning (8 µg/kg), leaching from soil and drinking water (11 µg/kg).	1900 µg/kg dw
SLUDGE/SEDIMENT		
Upper limit	16000 µg/kg dw[3] ER$_{eco}$	*50000 µg/kg dw* *ER$_{eco}$*
Lower limit	0.1 µg/kg[4] Reporting limit	*0.1 µg/kg* *Reporting limit*
GROUNDWATER		
Upper limit (intervention level)	4.7 µg/l Direct use of groundwater as drinking water. Lowest of the values MTR$_{human, groundwater}$ (310 µg/l), MPR$_{dw}$ (4.7 µg/l) and ER$_{eco, groundwater}$ (930 µg/l)	0.39 µg/l Direct use of groundwater as drinking water. Lowest of the values MTR$_{human, groundwater}$ (98 µg/l), MTR$_{dw}$ (0.39 µg/l) and ER$_{eco, groundwater}$ (7000 µg/l)
Lower limit	0.23 x 10^{-3} µg/l *VR$_{eco}$ = 1/100 MTR$_{eco}$*	Not determined
Human risk limit 'home with garden' (Csoil)	310 µg/l	98 µg/l
Human risk limit 'home with vegetable garden' (Csoil)	Not determined	56 µg/l
SURFACE WATER		
Upper limit annual mean AA-EQS/JG-MKE	0.65 x 10^{-} µg/l Lowest of the values MTR$_{eco, water}$ (0.023 µg/l), MTR$_{sp, water}$ (0.0026 µg/l) and MTR$_{hh food, water}$ (0.00065 µg/l)	0.048 µg/l
Upper limit maximum (peak)MAC-EQS/MAC-MKE	36 µg/l[5]	2800 µg/l
DRINKING WATER		
Drinking water toxicity level	0.53 µg/l	0.0875 µg/l

Table 3: Overview of PFOS and PFOA assessment levels derived by RIVM (composed of data from Moermond et al., 2010, Wintersen et al., 2016, Lijzen et al., 2017)

Legend:

- *Italic* values are not mentioned in the RIVM reports but derived in a similar manner.
- Grey boxes are location-specific values.

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[1] This value is not protective for the groundwater when the criterion for groundwater is used as drinking water. In that case, a safe upper limit is 100 µg/kg (Lijzen et al. 2011).

[2] The RIVM has concluded that the data on which this value is determined may not be complete. A new inventory of the available data is necessary to determine whether this value of 8 µg/kg is correct. In this calculation, it is assumed that the areas with this function are large enough to serve as a habitat for birds and mammals, so that secondary poisoning to higher organisms can play a role. With 'home with a garden' this is not assumed (Wintersen et al., 2016).

[3] Effects of stacking in the food chain are not included. The SR$_{soil}$ is not considered a normative risk limit for PFOS because significant effects are expected.

[4] The lower limits in soil and sediment for PFOS are set at the reporting limit (0.1 µg/kg) because no background value is known (Wintersen et al., 2016). Establishing background values for PFOS in the Netherlands in relatively unencumbered areas gives more insight into the lower limit for PFOS. Because background values are not known for PFOA, PFOA has also assumed a lower limit at the reporting limit of 0.1 µg/kg. In a country-wide study by Kwadijk et al., 2010, sediment levels of 0.5-8.7 µg/kg were found (Wintersen et al., 2016).

[5] The value of this number is limited as it is only based on acute toxicity and non-chronic exposure. In addition, secondary poisoning to meat eaters and people is not included.

4.2.2 Assessment levels for other PFAS (the Netherlands)

For other PFAS, no assessment levels are known yet. A further evaluation by the National Institute for Public Health and the Environment (RIVM) of a method to also calculate the assessment levels of other PFAAs is expected in early 2018.

4.2.3 PFOS and PFOA assessment levels (Flanders)

The method to be used in Flanders differs from the Dutch one. This method is described in Part 1 of the Basic Information for risk assessments (method for the derivation of soil remediation standards and assessment levels, guideline values and background values, OVAM 2016). In Flanders, for example, in the approach with ADI the background exposure via food and air is also included. Furthermore, the standard soil in Flanders is defined differently than in the Netherlands. As the ADIs are still evolving strongly, in the context of the present study, no toxicological value was derived on the basis of the Flemish methodology. Currently the ADIs for PFOS and PFOA are being re-examined by the EFSA.
The levels for PFOS for surface water are set at European level in the Water Framework Directive. These levels are included in Vlarem II (Appendix 2.3.1 'Basic quality standards for surface water' dated 11/12/2015). The levels are derived by the RIVM (Moermond et al., 2010).

		Rivers and lakes		**Transition water**			
Parameter	Unit	MKN (JG-MKN)	MKN maximum (MAC-MKN)	MKN (JG MKN)	MKN maximum (MAC-MKN)	Biotanorm (mg/kg wet weight)	Classification criterion
PFOS	µg/l	0.00065	36	0.00013	7.2	9.1	Reporting limit (0.1)

Table 4: Overview of PFOS Vlarem II (surface water) environmental quality standard

4.2.4 Assessment levels for other countries

The assessment levels used for PFAS are still under development. For PFOS and PFOA, the assessment levels in different countries have been adjusted in the past few years. In Europe, the maximum tolerable doses are currently being revised by the EFSA, which means that the assessment levels are then expected to be adjusted again. In addition, assessment levels for other PFAS have already been included for some countries. An overview of the latest state of the assessment levels is given in Annex 11.3. These values are often included in guidelines (not in legislation).

PART B – Field campaign

5 INTRODUCTION

The plan of action for the field campaign includes the following phases:

- Inventory of risk locations and selection of sampling locations.
- Field campaign with sampling and analysis of groundwater, soil and sediment.
- Reporting the results.

6 INVENTORY OF RISK LOCATIONS AND SELECTION OF SAMPLING LOCATIONS

6.1 GENERAL APPROACH

The selection and prioritization of relevant risk locations mainly took place on the basis of the nature of the risk activities as they determine the presence of PFAS in the soil, groundwater and sediment. The study is too limited in scope to do a very extensive screening. From this perspective, it is important to focus strongly on the activities with a reasonable chance of PFAS being present, for example producers of PFAS, producers of fire-extinguishing foam, fire service training site and fire incidents (see also literature study Part A chapter 2).

6.2 METHOD FOR SELECTING RISK LOCATIONS

To arrive at a selection of sampling locations, the information from the overview table with potential risk activities (Table 1) was used as a starting point and these activities were combined with data obtained from the following sources:

- Information from the OVAM database (selection of relevant parcels, for example *Vlarebo* categories):
  - A targeted selection was not possible since the PFAS-suspicious activities cannot be unambiguously linked to Vlarebo categories. Therefore, a selection was made based on guide parameters (e.g. use chromium for galvanization). Subsequently, each dossier was checked to see whether it was eligible for this study, more specifically based on relevant increased concentrations of guide parameters.
- Information from the OVAM database (selection of relevant parcels, on the basis of already known contaminants):
  - In the OVAM database, two sites are already known with a PFAS contamination.
- Overarching organizations in which a number of potential risk activities are grouped:
  - These organisations include the Flanders Fire Service Association, industries with their own fire service (http://www.hulpdienstvoertuigen-database.be/bedrijfsbrandweer.htm), civil airports and military training sites and airports.
  - Based on these lists, a number of relevant locations were selected (see chapter 3).
- Tracing on the basis of data of the Flemish Environment Agency (VMM):
  - The Flemish Environment Agency has analysis results for PFOS concentrations in biota (measurement campaign September-October 2015) and sediment samples (measurement campaign March-May 2016) in Flanders. These data were requested from the VMM within the context of this investigation. Based on the location of the measuring points with increased concentrations, the OVAM Geoloket and OVAM database were subsequently checked as to whether there were activities upstream of these measuring points of production sites and sites with frequent use of PFAS products. This resulted in 6 sites, which were subsequently selected as risk locations.

7 FIELD CAMPAIGN: SOIL AND GROUNDWATER SAMPLING

7.1 INTRODUCTION

This chapter discusses the methodology of the field and analysis campaign.

7.2 OVERVIEW SAMPLING LOCATIONS

Based on the selection that was carried out for companies with potential PFAS risk activities, a number of the selected companies were contacted to obtain the available PFAS data or to obtain permission to carry out limited sampling of soil and groundwater at the potential risk locations.
Table 5 shows an overview of the type of risk locations from which data was received or access was obtained for carrying out field measurements in the context of this study. For confidentiality reasons, the risk locations/analysis results are not linked to specific companies in Table 5.

Type of location	**Subcategory**	**Activity**	**No. of sites**
PFAS processing industry	Galvanic industry	Use of PFAS as a spray suppressor	1
	Paint industry	Production of paint using PFAS	1
	Textile industry	Treating textiles with PFAS components	2
	Paper industry	Treatment (grease and water repellent) paper and cardboard	1
Use of fire extinguishing foam (AFFF)	Fire extinguishing	Calamity	2
	Fire service training site	Regular use of extinguishing foams	3
	Fire service facilities (industry)	Calamities and testing extinguishing foams	5
	Military training areas and airports	Calamities and testing extinguishing foams	3
	Civil airports	Use and testing extinguishing foams	3
Landfill sites		Demolition material + landfill material itself (carpets, textiles, paper, etc.)	2
Water treatment plant		Water treatment from industry	1

Table 5: Overview of risk locations included in this study

Some sites included in the field campaign fall under several subcategories if, for example, both extinguishing activities and a calamity have taken place. In this case, both risk locations were examined.
In addition, OVAM has some data from known PFAS contaminanted locations, based on the OVAM database. These files were not included in further evaluation. On these sites it also concerns a PFAS contamination at a former fire service training site.

7.3 SAMPLING PROTOCOL

Accurate and careful sampling is crucial when researching PFAS compounds in the environment. Because PFAS compounds have had many uses and need to be determined at very low concentrations, the chance of cross contamination by the sample material itself is real. The use of sample material (gloves, drilling material, pumps, recipients) with Teflon components absolutely must be avoided.

Glass sampling devices are also not suitable because PFAS compounds adsorb to glass, therefore completely plastic containers (polypropylene) were used. The annex includes the checklist that was used on the site to avoid PFAS containing materials or adsorbents.

The field campaign per location was carried out in accordance with the current CMA procedures for soil, groundwater and sediment sampling (CMA/1/A.2) supplemented with the PFAS protocol for sampling PFAS components (no CMA available yet). The samplings were carried out by Witteveen + Bos/Mava in-house fieldwork team during the period August - October 2017.

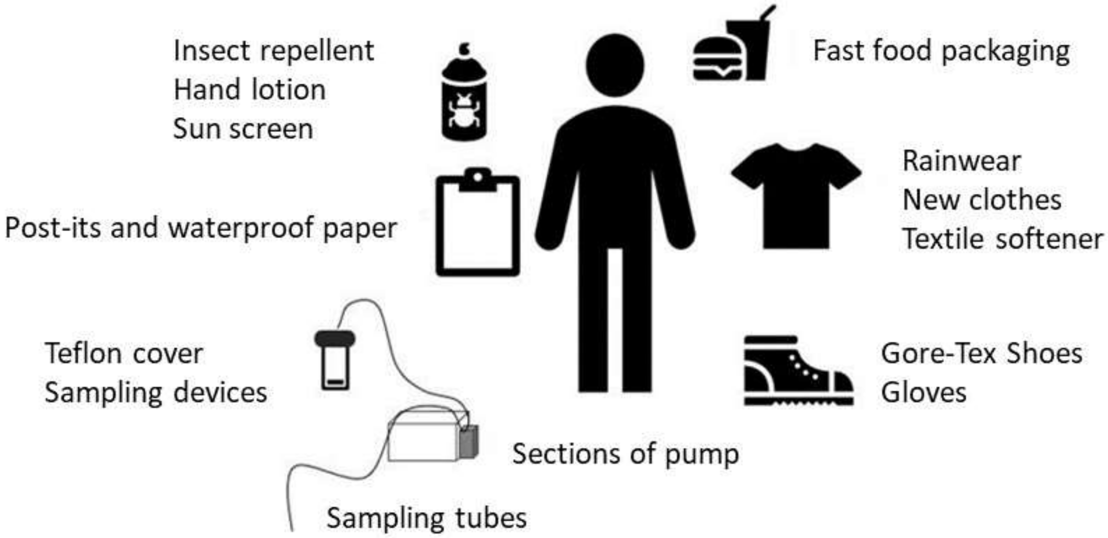

Figure 9: Schematic representation of points for attention in the avoidance of cross-contamination (source: PFAS Expertise Centre).

7.4 FIELDWORK STRATEGY AND SAMPLING

The tables below provide an overview of the risk locations with the samples taken at each site.

7.4.1 Site 1

This site is an industrial site with its own fire service training site. There is an old training site on the site. Nowadays infrastructure of the factory is present qt that location. There is also a new training location on another part of the site. Most samples were taken in the top soil. 1 soil sample was taken at groundwater level.

The groundwater samples with similar number as the drillings are samples taken at the same sample location. Drilling point 8010 and monitoring well MWB119 are in the immediate vicinity of each other.

Type	Risk location	Drilling number	Sample depth in m bgl	Comments
Industry	Fire service training site	7004	0.30-0.60	new training location (no pavement)
Industry	Fire service training site	7005	0.40-0.60	new training location (no pavement)
Industry	Fire service training site	8010	0.20-0.60	old training location (pavement probable)
Industry	Fire service training site	8010	1.6-2.0	old training location (pavement probable)

Table 6: Overview site 1 - soil: risk locations and drillings

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Industry	Fire service training site	MWB119 (existing)	2.28-3.28	1.79	monitoring well at old training site
Industry	Fire service training site	MWB120 (existing)	1.94-2.94	1.82	monitoring well at old training site
Industry	Fire service training site	P7004 (new)	1.9-2.6	1.6	new training area
Industry	Fire service training site	P7005 (new)	1.9-2.5	1.41	new training area

Table 7: Overview site 1 - groundwater: risk locations and monitoring wells

7.4.2 Site 2

This site is an industrial site with its own fire service training site. The site has not been used for performing exercises for the past 10 years. The current exercises are performed at an external company.

Type	Risk location	Drilling number	Sample depth in m bgl	Comments
Industry	Fire service training site	7014	0.0-0.50	sample next to pavement
Industry	Fire service training site	7015	0.0-0.50	sample next to pavement

Table 8: Overview site 2 - Soil: risk locations and drillings

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Industry	Fire service training site	P7014 (new)	1.8-2.8	1.24	Training site not used for more than 12 years
Industry	Fire service training site	P7015 (new)	1.8-2.8	1.39	Training site not used for more than 12 years

Table 9: Overview site 2 - groundwater: risk locations and monitoring wells

7.4.3 Site 3

This site is a training site on an unpaved area of a regional fire station. The drilling locations were chosen across the entire site.

Type	Risk location	Drilling number	Sample depth in m bgl	Comments
Fire service training site (regional)	Fire service training site	7011	0.0-0.30	no pavement
Fire service training site (regional)	Fire service training site	7012	0.0-0.3	no pavement
Fire service training site (regional)	Fire service training site	7013	0.0-0.50	no pavement

Table 10: Overview site 3 - soil: risk locations and drillings

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Fire service training site (regional)	Fire service training site	P7011 (new)	2.5-3.5	2.44	no pavement
Fire service training site (regional)	Fire service training site	P7012 (new)	2.45-3.45	2.2	no pavement
Fire service training site (regional)	Fire service training site	P7013 (new)	2.2-3.2	2.45	no pavement

Table 11: Overview site 3 - groundwater: risk locations and monitoring wells

7.4.4 Site 4

This site concerns a civil airport with various risk locations.

- At the fire service training site, at the wrong location was drilled because of wrong instructions. These samples/analyses are therefore not representative and are not included in further discussion. Therefore, no PFAS was present in these samples.
- For sludge sampling, sludge was collected from the water buffer basin at the airport, sample was taken from the bank side. It is a buffer basin with foil, so the amount of sludge was very limited.
- The incident zones concern 2 different incident zones, namely a crash zone of an aircraft and a fire at the hangar.

The groundwater is located at a greater depth at this location. Only an existing monitoring well was sampled at the crash site.

Type	Risk location	Drilling number	Sample depth in m bgl	Comments
Civil aviation	Fire incident	8012	0.10-0.60	no pavement
Civil aviation	Fire incident	8013	0.00-0.40	no pavement
Civil aviation	Fire incident	8014	0.00-0.50	no pavement
Civil aviation	Fire incident	8014	0.80-1.20	no pavement
Civil aviation	Fire service training site	8015	0.0-0.3	wrong location
Civil aviation	Fire service training site	8015	1.5-2.0	wrong location
Civil aviation	Fire service training site	8016	0.0-0.	wrong location
Civil aviation	Fire service training site	8017	0.0-0.5	wrong location
Civil aviation	Reservoirs	Discharge point	Sludge	Sludge sample from pond with foil
Civil aviation	Fire incident	7016	0.40-0.90	concrete pavement
Civil aviation	Fire incident	8018	0.5-1.0	concrete pavement

Table 12: Overview site 4 - Soil: risk locations and drillings

Type	Risk location	Monitoring well	Filter depth m bgl	GW depth In m bgl	Comments
Civil aviation	Fire incident	P7009 (existing)	unknown	10.82	Monitoring probably downstream of the incident area

Table 13: Overview site 4 - Groundwater: risk locations and monitoring wells

7.4.5 Site 5

This site is a provincial training site for the fire service and emergency services. On the site there is a very large fire plate, on which the exercises are performed. There is a water collection drain around the fire plate to direct the water towards the water treatment. Soil samples were taken at the top soil and 1 at groundwater level. Groundwater samples were taken at the location of the fire pit and the catch basin for the run-off from the fire site.

Type	Risk location	Drilling number	Sample depth m bgl	Comments
Fire service training site (provincial)	Fire service training site	7007	0.0-0.50	sample next to pavement
Fire service training site (provincial)	Fire service training site	7008	0.0-0.50	sample next to pavement (met afwatering naar zuivering)
Fire service training site (provincial)	Fire service training site	7008	3.50-4.00	sample next to pavement (met afwatering naar zuivering)

Table 14: Overview site 5 - Soil: risk locations and drillings

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Fire service training site (provincial)	Fire service training site	P1012 (existing)	2.5-4.5	3.72	exercises on fire plate with extinguishing water drain
Fire service training site (provincial)	Fire service training site	P7007 (new)	4.0-5.0	3.74	exercises on fire plate with extinguishing water drain
Fire service training site (provincial)	Fire service training site	P7008 (new)	3.9-4.9	3.76	exercises on fire plate with extinguishing water drain

Table 15: Overview site 5 - Groundwater: risk locations and monitoring wells

7.4.6 Site 6

This site is an industrial site with its own fire service training site. The zone is paved with a concrete pavement. Currently the site is still used for fire extinguishing exercises.

Type	Risk location	Drilling number	Sample depth in m bgl	Comments
Industry	Fire service training site	7002	1.6-2.0	sample next to pavement
Industry	Fire service training site	7003	0.0-0.3	sample next to pavement
Industry	Fire service training site	8009	0.0-0.3	sample next to pavement

Table 16: Overview site 6 - Soil: risk locations and drillings

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Industry	Fire service training site	P7002 (new)	2.0-3.0	1.67	pavement
Industry	Fire service training site	P7003 (new)	1.9-2.9	1.28	pavement

Table 17: Overview site 6 - Groundwater: risk locations and monitoring wells

7.4.7 Site 7

This site is a fire service training site for military purposes. The site is professionally equipped for carrying out fire exercises. The fire extinguishing water is collected and sent to a water treatment plant. The soil samples were taken in the top soil, 1 at the groundwater level, and one at the level of the discharge point of the water treatment plant. The drillings were not carried out in the immediate vicinity of the monitoring wells.

Due to the presence of a paving (permeable) in the ditch where the water was discharged after the water treatment it was not possible to take a sediment sample. For this reason, a soil sample was taken below the level of the ditch, right next to the ditch.

Type	Risk location	Drilling number	Sample depth in m bgl	Comments
Fire service training site (military)	Fire service training site	8000	0.00-0.30	sample next to pavement
Fire service training site (military)	Fire service training site	8001	0.00-0.30	sample next to pavement
Fire service training site (military)	Fire service training site	8001	1.10-1.60	sample next to pavement
Fire service training site (military)	Fire service training site	8002	0.00-0.30	sample next to pavement
Fire service training site (military)	Fire service training site	8003	1.70-2.00	sample at WWTP discharge point

Table 18: Overview site 7 - Soil: risk locations and drillings

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
military	Fire service training site	P16 (existing)	1.2-2.2	1.69	pavement at training areas
military	Fire service training site	P18 (existing)	1.0-2.0	1.6	pavement at training areas
military	Fire service training site	P40 (existing)	1.0-2.0	1.81	pavement at training areas
military	Fire service training site	P42 (existing)	1.0-2.0	1.63	pavement at training areas

Table 19: Overview site 7 - Groundwater: risk locations and monitoring wells

7.4.8 Site 8

This site concerns a former sludge basin of a textile treatment company for sludge originating from the water treatment plant. The drilling was carried out next to the sludge basin, drilling in the sludge basin was not possible.

Type	Risk location	Drill number	Sample depth in m bgl	Comments
Textile industry	textile industry	7001	1.50-2.00	former factory sludge basin

Table 20: Overview site 8 - Soil: risk locations and drillings

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Textile industry	textile treatment	P2003 (existing)	0.8-2.8	1.1	Monitoring well next to sludge basin
Textile industry	textile treatment	P4001 (existing)	1.36-1.86	1.01	Monitoring well next to sludge basin
Textile industry	textile treatment	P7001 (new)	2.2-3.2	2.61	Monitoring well next to sludge basin

Table 21: Overview site 8 - Groundwater: risk locations and monitoring wells

7.4.9 Site 9

This site concerns a military airport where a fire pit was present where possibly also small extinguishing exercises have taken place. There was no pavement. A sample was taken at the groundwater level and two top soil samples were taken.

Type	Risk location	Drilling number	Sample depth in m bgl	Comments
Military aviation	Fire service training site	8006	0.00-0.50	no pavement
Military aviation	Fire service training site	8006	1.0-1.50	no pavement
Military aviation	Fire service training site	8007	0.00-0.50	no pavement

Table 22: Overview site 9 - Soil: risk locations and drillings

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Military aviation	Fire service training site	P207 (existing)	?	0.97	fire pit without pavement
Military aviation	Fire service training site	P503 (existing)	2.2-3.2	2.39	fire pit without pavement

Table 23: Overview site 9 - Groundwater: risk locations and monitoring wells

7.4.10 Site 10

This site is a civil aviation site with its own fire service training site. The fire training site is paved.

Type	Risk location	Drilling number	Sample depth in m bgl	Comments
Civil aviation	Fire service training site	7006	0.0-0.40	sample next to pavement
Civil aviation	Fire service training site	8011	0.0-0.15	sample next to pavement

Table 24: Overview site 10 - Soil: risk locations and drillings

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Civil aviation	Fire service training site	P1037 (existing)	2.3-3.3	2.56	pavement at training area
Civil aviation	Fire service training site	P7006 (existing)	3.0-4.0	2.6	pavement at training area

Table 25: Overview site 10 - Groundwater: risk locations and monitoring wells

7.4.11 Site 11

This concerns a civil aviation site with its own fire service training site. The fire service training site is paved with a concrete pavement. There is also an area that was filled with landfill material (not related to aviation).

Type	Risk location	Drilling number	Sample depth in m bgl	Comments
Civil aviation	Fire service training site	7000	0.10-0.60	sample next to pavement
Civil aviation	Fire service training site	8004	0.00-0.30	sample next to pavement
Civil aviation	Fire service training site	8004	1.3-1.8	sample next to pavement
Civil aviation	Landfill site	8005	1.5-2.0	shallow area filled with landfill material (sample not in landfill material)

Table 26: Overview site 11 - Soil: risk locations and drillings

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Civil aviation	Fire service training site	P72 (existing)	?	1.38	probably downstream
Civil aviation	Fire service training site	P7000 (new)	2.0-3.0	0.55	probably downstream

Table 27: Overview site 11 - Groundwater: risk locations and monitoring wells

7.4.12 Site 12

This site is a former industrial landfill of the textile industry. The sampled monitoring wells are existing monitoring wells from the remediation work that took place on this site. No soil samples could be taken at the landfill as it has an upper seal.

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Industrial landfill site	Textile industry	MON OB 4 (existing)	Not known	3.15	monitoring well around landfill
Industrial landfill site	Textile industry	MPB3 (existing)	?	4.53	monitoring well around landfill
Industrial landfill site	Textile industry	MPB7 (existing)	?	3.05	monitoring well around landfill
Industrial landfill site	Textile industry	MPB9 (existing)	?	9.83	monitoring well around landfill
Industrial landfill site	Textile industry	PL20 (existing)	?	10.45	monitoring well around landfill

Table 28: Overview site 12 - Groundwater: risk locations and monitoring wells

7.4.13 Site 13

This site is an industrial location used by a galvanic company. No soil samples could be taken on this site at the request of the owner of the site.

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Galvanic industry	Galvanic industry	P17001 (existing)	?	4.12	
Galvanic industry	Galvanic industry	P17002 (existing)	?	4.16	most downstream
Galvanic industry	Galvanic industry	P308 (existing)	2.1-4.1	3.84	
Galvanic industry	Galvanic industry	PA8 (existing)	3.0-5.0	4.06	most downstream

Table 29: Overview site 13 - Groundwater: risk locations and monitoring wells

7.4.14 Site 14

This site is a provincial fire service training site. Due to a fire exercise being carried out it was not possible to take samples near the fire plate at the time of fieldwork. An existing monitoring well was sampled on the site. However, this was some distance away from the fire plate and probably not in a straight line downstream of the fire plate.

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Fire service training site (provincial)	Fire service training site	P7010 (existing)	5.5	4	Monitoring well is approx. 50 m from the training site, possibly downstream but not in a straight line with the fire plate

Table 30: Overview site 14 - Groundwater: risk locations and monitoring wells

7.4.15 Site 15

This concerns a WWTP installation for domestic waste water. The effluent purified water from the WWTP was sampled. There was no sludge at the point where the purified water was discharged, so that it was not possible to take a sludge sample.

Type	Risk location	Name sample	Comments
Domestic waste water treatment	waste water treatment	WWTP discharge point	water directly from treatment

Table 31: Overview site 15 – water from water treatent plant

7.4.16 Site 16

This concerns a former landfill for presumably mainly domestic landfill material. A container park and a WWTP installation are also located on top of the landfill. It was not possible to take soil samples at this site. Only existing monitoring wells were sampled around the landfill.

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Domestic landfill	Landfill site	P100 (existing)	9.3-11.3	6.15	monitoring well around landfill
Domestic landfill	Landfill site	P101 (existing)	9.5-11.5	6.7	monitoring well around landfill
Domestic landfill	Landfill site	P201 (existing)	6.0-8.0	6.76	monitoring well around landfill

Table 32: Overview site 16 - Groundwater: risk locations and monitoring wells

7.4.17 Site 17

This site is a company active in the coating industry (including Teflon coatings). Because of the large number of monitoring wells on this site, the company preferred not to have additional drillings to take soil samples. Therefore, only existing monitoring wells were sampled.

Type	Risk location	Monitoring well	Filter depth m bgl	GW level m bgl	Comments
Coating industry	Coating industry	P101a (existing)	0.97-2.97	DNAPL tar	Because of the presence of tar, interference with the PFAS analysis cannot be excluded
Coating industry	Coating industry	P105 (existing)	1.59-3.59	1.38	
Coating industry	Coating industry	P303 (existing)	0.94-2.94	1.58	

Table 33: Overview site 17 - Groundwater: risk locations and monitoring wells

7.4.18 Site 18

This site is a chemical company with extinguishing facilities with extinguishing foams and fire service training sites. Measurement data for PFAS from the soil were made available within the context of this study.

The samples were taken at various places at the site with a different risk of increased PFAS concentrations. Both samples in top soil (samples with entry 1) and samples at the groundwater level approx. 1 m bgl (samples with entry 2) were taken.

The samples were obtained through a manual drilling. The samples were analysed by the Eurofins laboratory in Hamburg using analysis method GLS OC 400, LC-MS/MS.

Type	Sample number	Comments
Fire service training site	H900-1.1	in top soil
Fire service training site	H900-1.2	at groundwater level
Fire service training site	E100-1.1	in top soil
Fire service training site	E100-1.2	at groundwater level
Fire service training site	F50-1.1	in top soil
Fire service training site	F50-1.2	at groundwater level
Fire service training site	E1	in top soil
Fire service training site	D1	in top soil
Fire service training site	E1500-1.1	in top soil
Fire service training site	E1500-2.1	in top soil
Fire service training site	E1500-3.1	in top soil
Fire service training site	E1400-1.1	in top soil
Fire service training site	E1400-1.2	at groundwater level
Fire service training site	E1400-2.1	in top soil
Fire service training site	E1400-2.2	at groundwater level
Fire service training site	D1200-1.1	in top soil
Fire service training site	D1200-1.2	at groundwater level
Industrial site	J800-1.1	in top soil
Industrial site	J800-1.2	at groundwater level
Industrial site	G1200-1.1	in top soil
Industrial site	G1200-1.2	at groundwater level

Table 34: Overview site 18 - Soil: risk locations and drillings

7.5 LABORATORY STUDY

The analyses for PFAS in soil, sediment and groundwater were carried out in accordance with CMA method CMA/3/D for the analysis of perfluorinated compounds. The analyses were carried out by the certified laboratory SGS Belgium, Polderdijkweg 16, 2030 Antwerp (IAC - Institute of Applied Chromatography).
The analytical technique used for soil samples involves high pressure liquid chromatography with electrospray ionisation tandem mass spectroscopy (LC-ESI-MS-MS). Applied analytical technique for groundwater samples concerns the LC-MS-MS technique after a solid phase extraction.

Table 35 summarises the PFAS components and reporting limits that were routinely analysed using a target type of technique.

Parameter	Reporting limit solid matrix	Reporting limit groundwater
Perfluorinated carboxylic acids		
Perfluorbutanoic acid (PFBA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluorpentanoic acid (PFPA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluorhexanoic acid (PFHxA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluorheptanoic acid (PFHpA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluoroctanoic acid (PFOA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluornonanoic acid (PFNA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluordecanoic acid (PFDA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluorundecanoic acid (PFUnDA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluordodecanoic acid (PFDoDA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluortridecanoic acid (PFTrDA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluortetradecanoic acid (PFTeDA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluorhexadecanoic acid (PFHxDA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluoroctadecanoic acid (PFODA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluoro alkane sulfonamides		
Perfluoroctanoic sulfonamide (PFOSA)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluoronated sulfonic acids		
Perfluorbutanoic sulphonate (PFBS)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluorhexanoic sulphonate (PFHxS)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluoroctanoic sulphonate (PFOS)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Perfluordecane sulphonate (PFDS)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
Fluorotelomer sulfonates		
6:2 Fluorotelomer sulfonate (6:2 FTS)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
8:2 Fluorotelomer sulfonate (8:2 FTS)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l
10:2 Fluorotelomer sulfonate (10:2 FTS)	0.5 - 1 µg/kg dm	0.005 - 1.0 µg/l

The reporting limit reported in this study was determined based on the concentration measured in the analysis sample.

Table 35: Overview of analysis parameters and reporting limits

8 RESULTS AND INTERPRETATION

8.1 MEASUREMENT CAMPAIGN

8.1.1 Results of soil and sediment

Within the context of this study, a total of 35 drillings were carried out on 18 selected sites and 40 soil samples and 1 sediment sample were selected for analyses on PFAS. The complete dataset of all measurement results is included in Annex 3: other annexes. Table 38 summarises the data available from the PFAS measurements for the soil and sediment.

In the results table in Annex 11.3 the following limit values were used for an indicative assessment of the results:

	PFOS	**PFOA**	**6:2 FTS**
> target value	*0.5*	*0.5*	
> Risk based value - ecology	8	7	
> Risk based value - leaching GW	**100**	**2.7**	
> Risk based value - Human III	6600	674	
> Risk based Value - Human V	16000	1900	

Table 36: Overview of the toxicological levels used - soil

	PFOS	**PFOA**	**6:2 FTS**
target value	*0.001*	*0.001*	*0.001*
classification criterion	0.1	-	
risk based value - drinking water	0.53	0.39	**0.4**
seriously contaminated	4.7	0.39	

Table 37: Overview of the toxicological levels used – groundwater

	number	% of the total number
number of sampling points with sum of PFAS[6] in soil above reporting limit (1µg/kg dm)	32	78
number of sampling points with sum of PFAS in soil above 10x reporting limit (10 µg/kg dm)	27	66
number of sampling points with sum of PFAS in soil above 100x reporting limit (100 µg/kg dm)	15	37
number of sampling points with sum of PFAS in soil above 1000x reporting limit (1,000 µg/kg dm)	10	24

Table 38: Overview of PFAS in soil and sediment measurement data

At the selected risk locations at 66% of the sampling points a concentration of $PFAS_{sum}$ in soil higher than 10 x reporting limit (> 10 µg/kg dm) is measured.
In 24% of the sampling points PFAS higher than 1000 x reporting limit are measured (> 1,000 µg/kg dm).

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[6] Sum parameter of all PFAS components analysed (see Table 5: Overview of risk locations included in this study)

8.1.2 Groundwater results

	number	**% of total number**
number of sampling points with sum of PFAS in groundwater above reporting limit (0.005 µg/l)	44	92
number of sampling points with sum of PFAS in groundwater higher than 10x reporting limit (0.05 µg/l)	41	85
number of sampling points with sum of PFAS in groundwater higher than 100x reporting limit (0.5 µg/l)	34	71
number of sampling points with sum of PFAS in groundwater higher than 1000x reporting limit (5 µg/l)	20	42

Table 39: Overview of the PFAS in groundwater measurement data

At the selected risk locations at 71% of the sampling points a concentration of $PFAS_{sum}$ in the groundwater higher than 100 x reporting limit (0.5 µg/l) was measured.
In 42% of the sampling points PFAS higher than 1000 x reporting limit (> 5 µg/l) was measured.

8.2 GRAPHICAL PRESENTATION

8.2.1 Soil and sediment

Figures 10-17 graphically show the results for the soil and sediment per risk location in a histogram (results in µg/kg dm). Because of the large variability in total concentrations, in the following figures the y-axis has been reduced to a maximum of 1,000 µg/kg dm and 100 µg/kg dm, with the maximum values being outside the range of the graph.

In addition to a histogram with results from all soil samples, a histogram with results of the top soil samples and deeper samples (soil samples at groundwater level) is also shown.

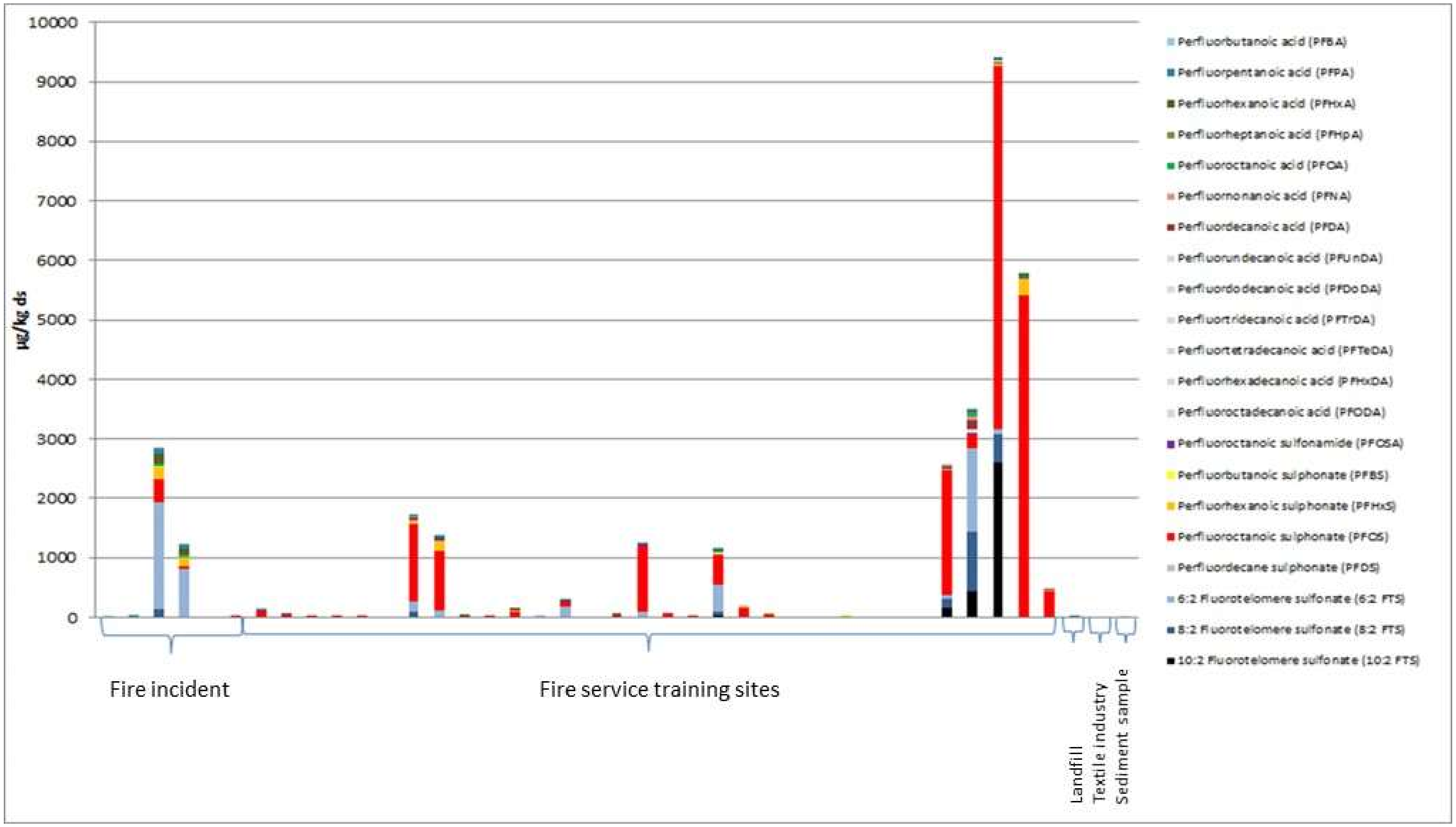

Figure 10: Histogram for PFAS in soil and sediment - all results in µg/kg.dm

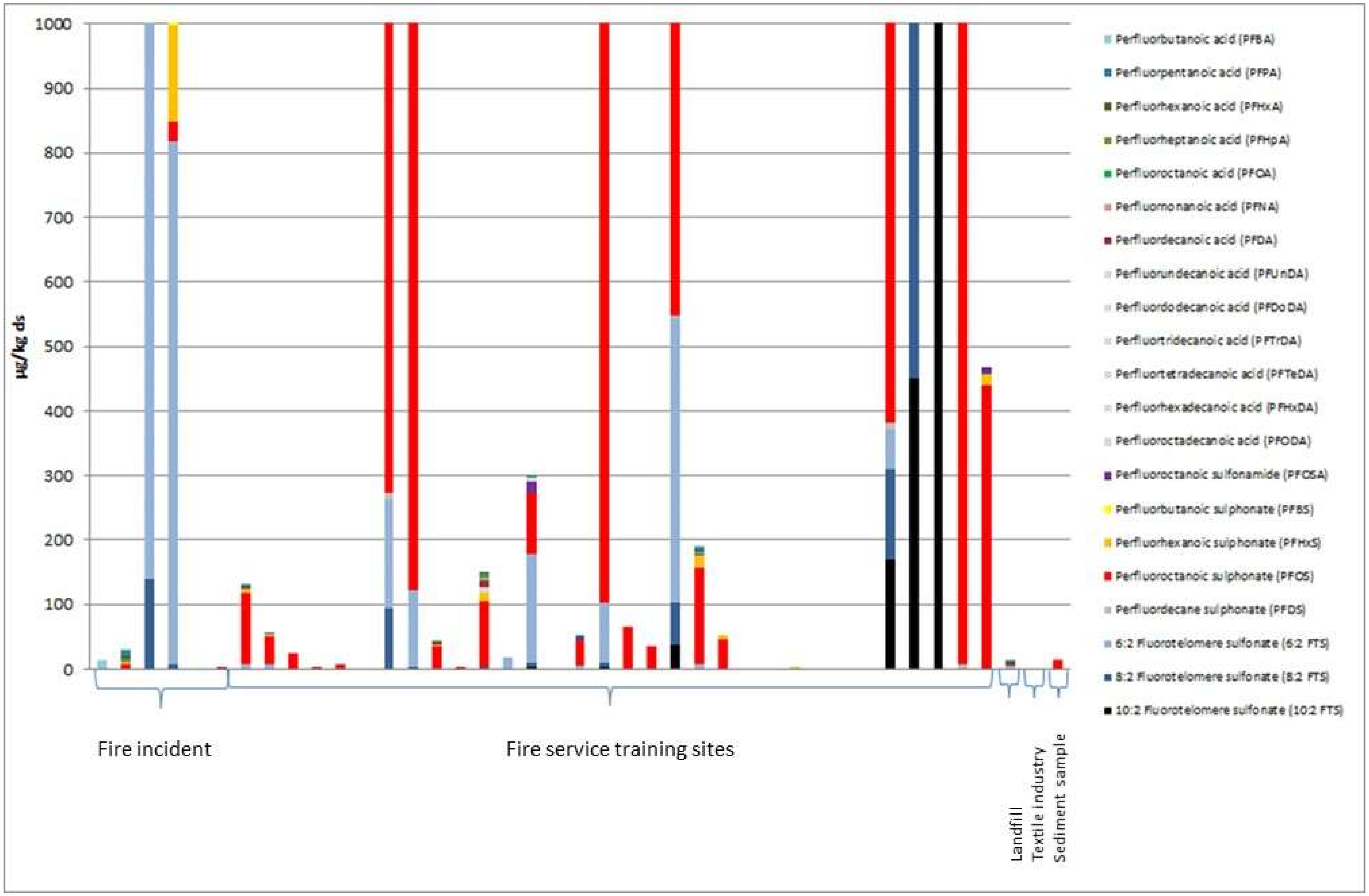

Figure 11: Histogram for PFAS in soil and sediment - all results in µg/kg.dm

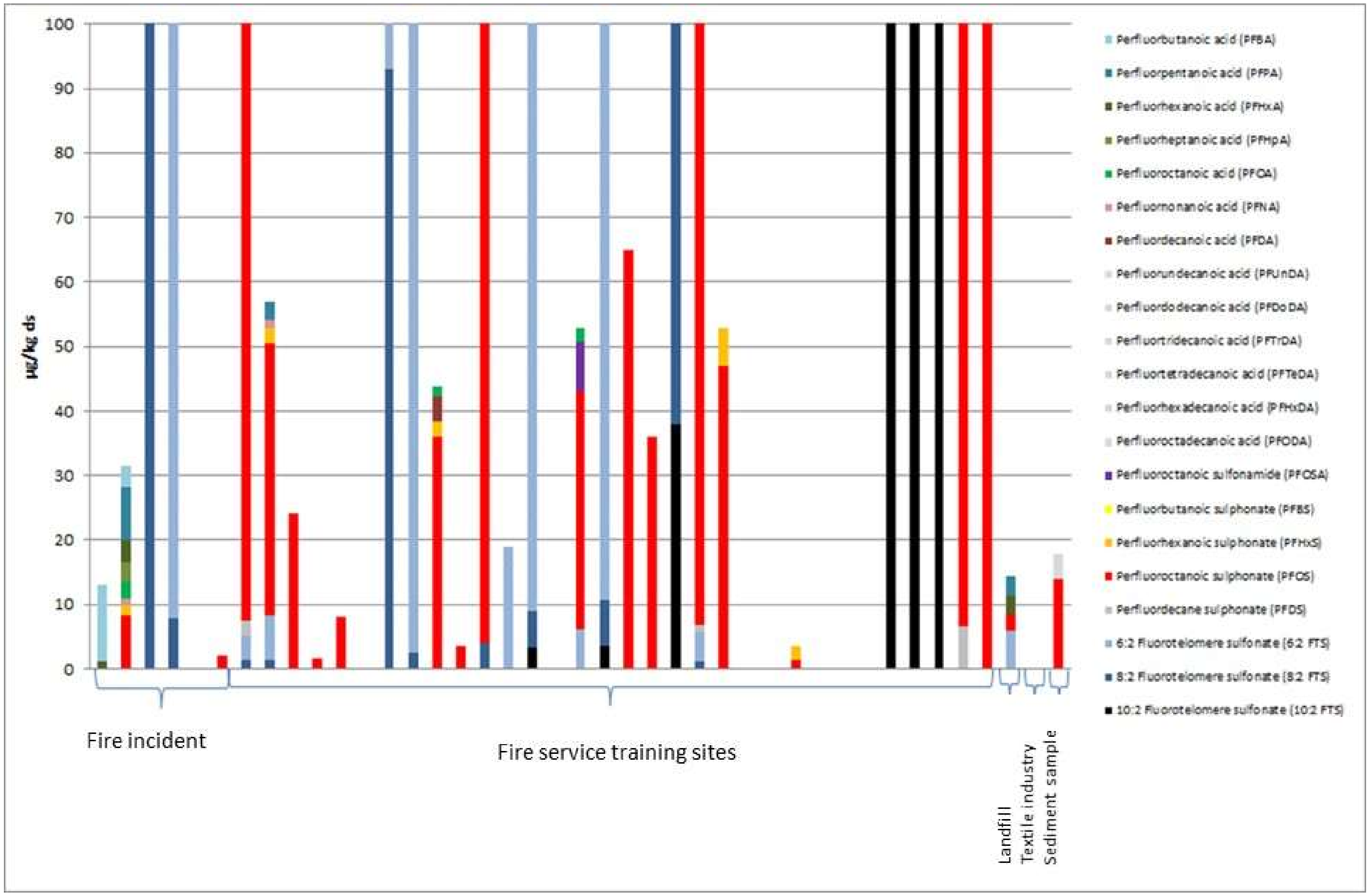

Figure 12: Histogram for PFAS in soil and sediment - all results in µg/kg.dm

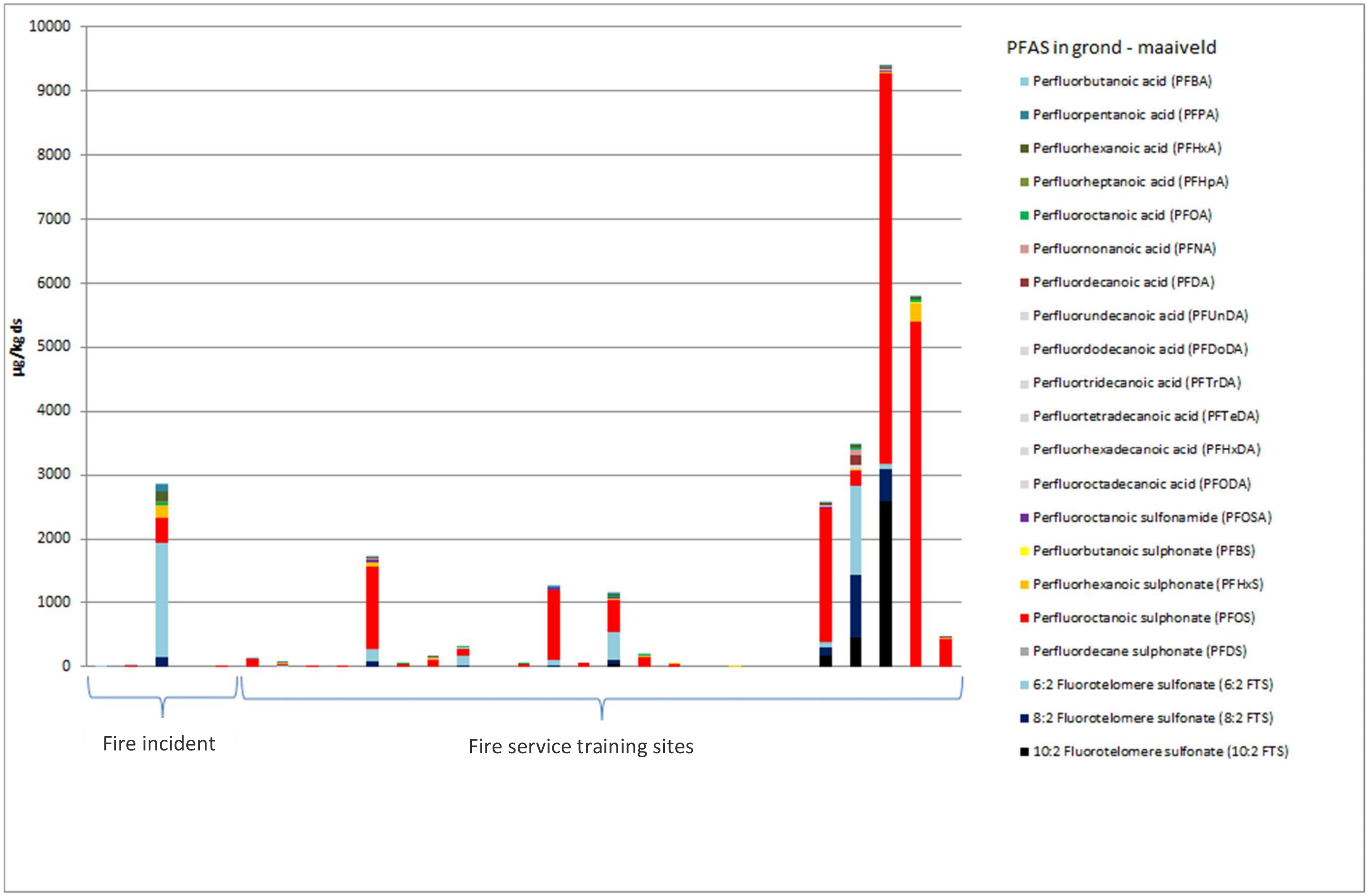

Figure 13: Histogram for PFAS in top soil - all results

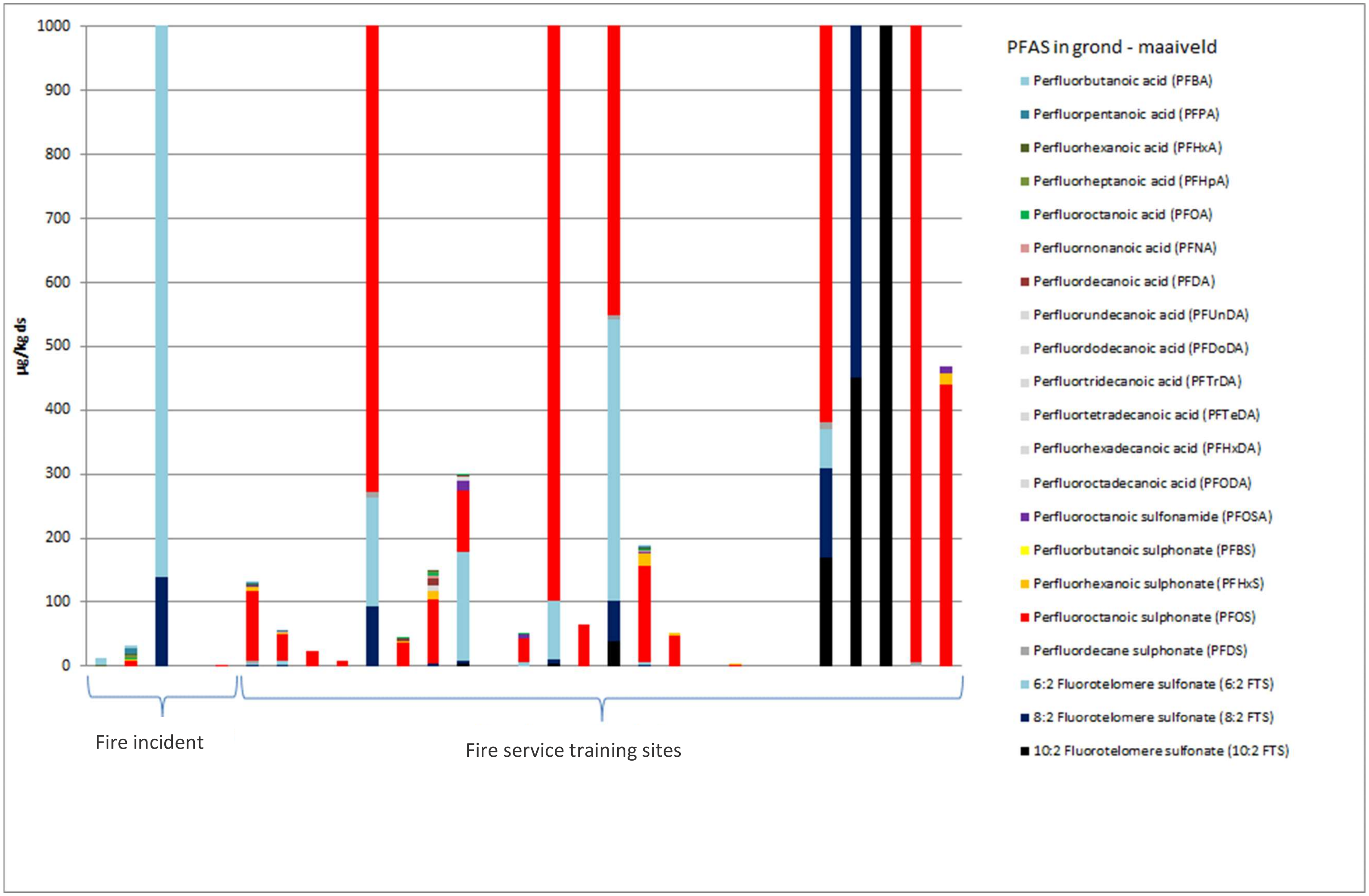

Figure 14: Histogram for PFAS in top soil in µg/kg/dm

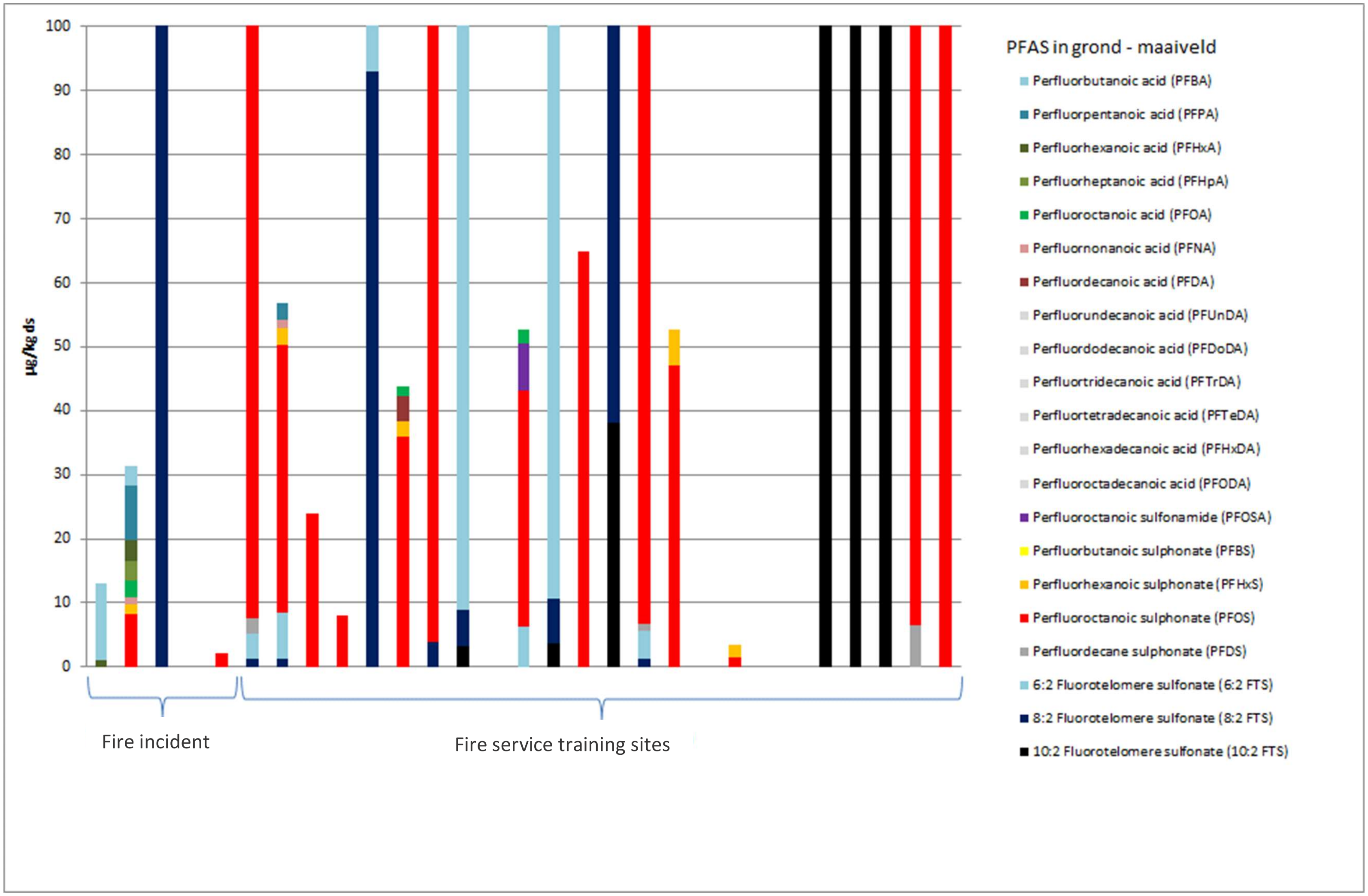

Figure 15: Histogram for PFAS in top soil in µg/kg/dm

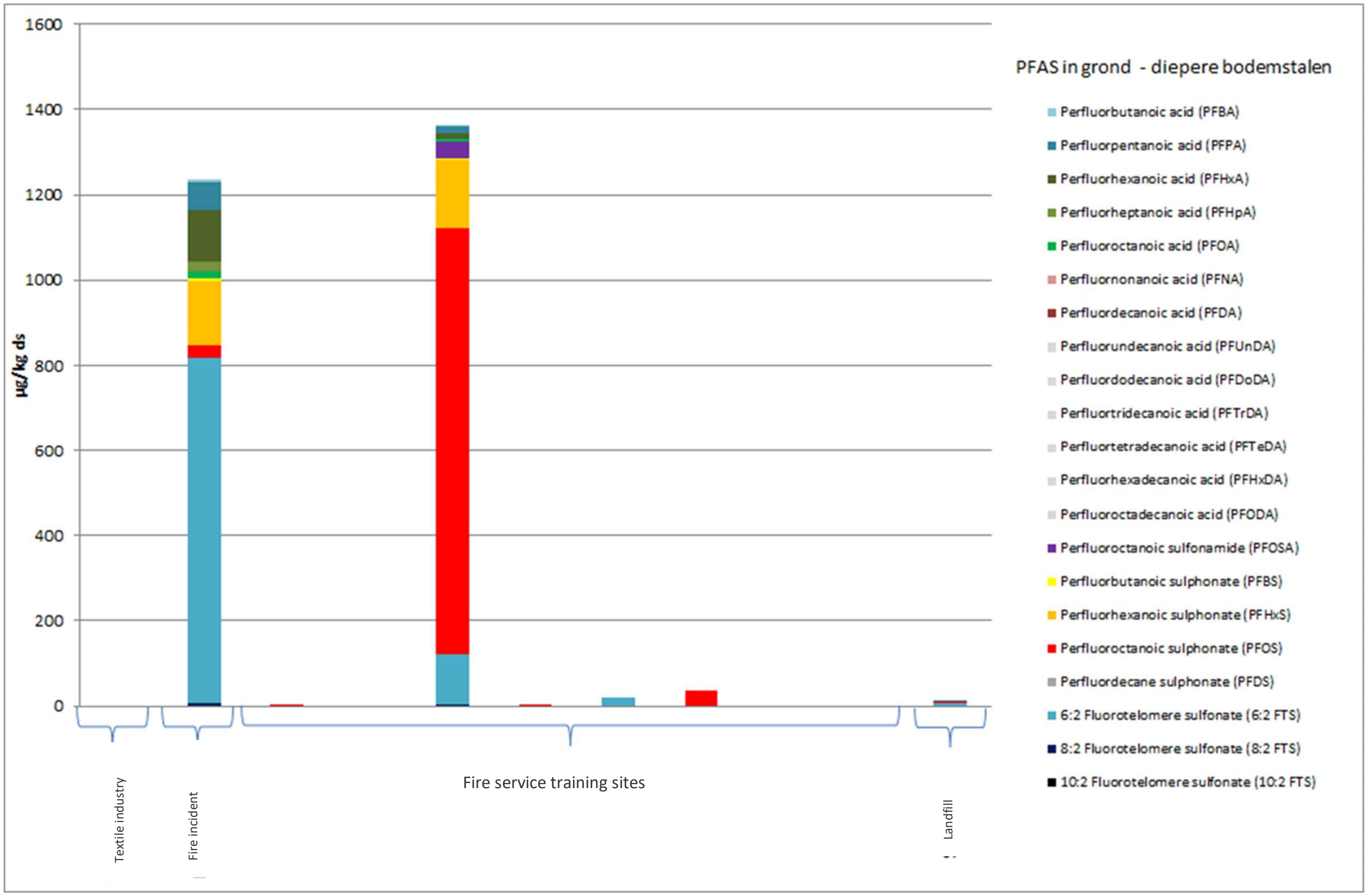

Figure 16: Histogram for PFAS in soil at groundwater level

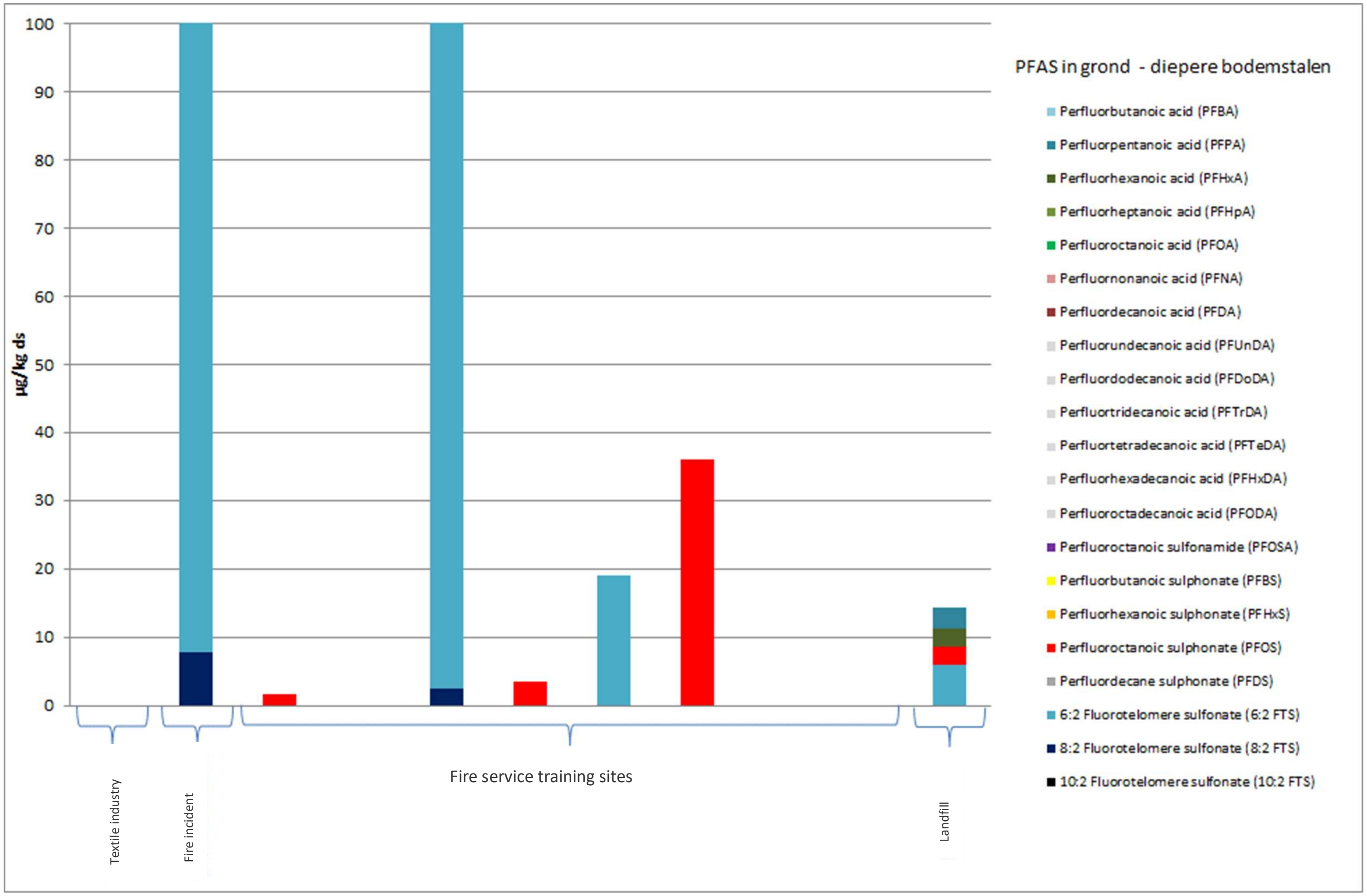

Figure 17: Histogram for PFAS in soil at groundwater level

8.2.1 Groundwater

Figures 18-20 show the groundwater measurement results for each risk location in a histogram (results in µg/l).

In view of the large variability in total concentrations, the y-axis is reduced to a maximum of 100 µg/l and 10 µg/l as a function of readability, with the maximum values falling outside the range of the graph.

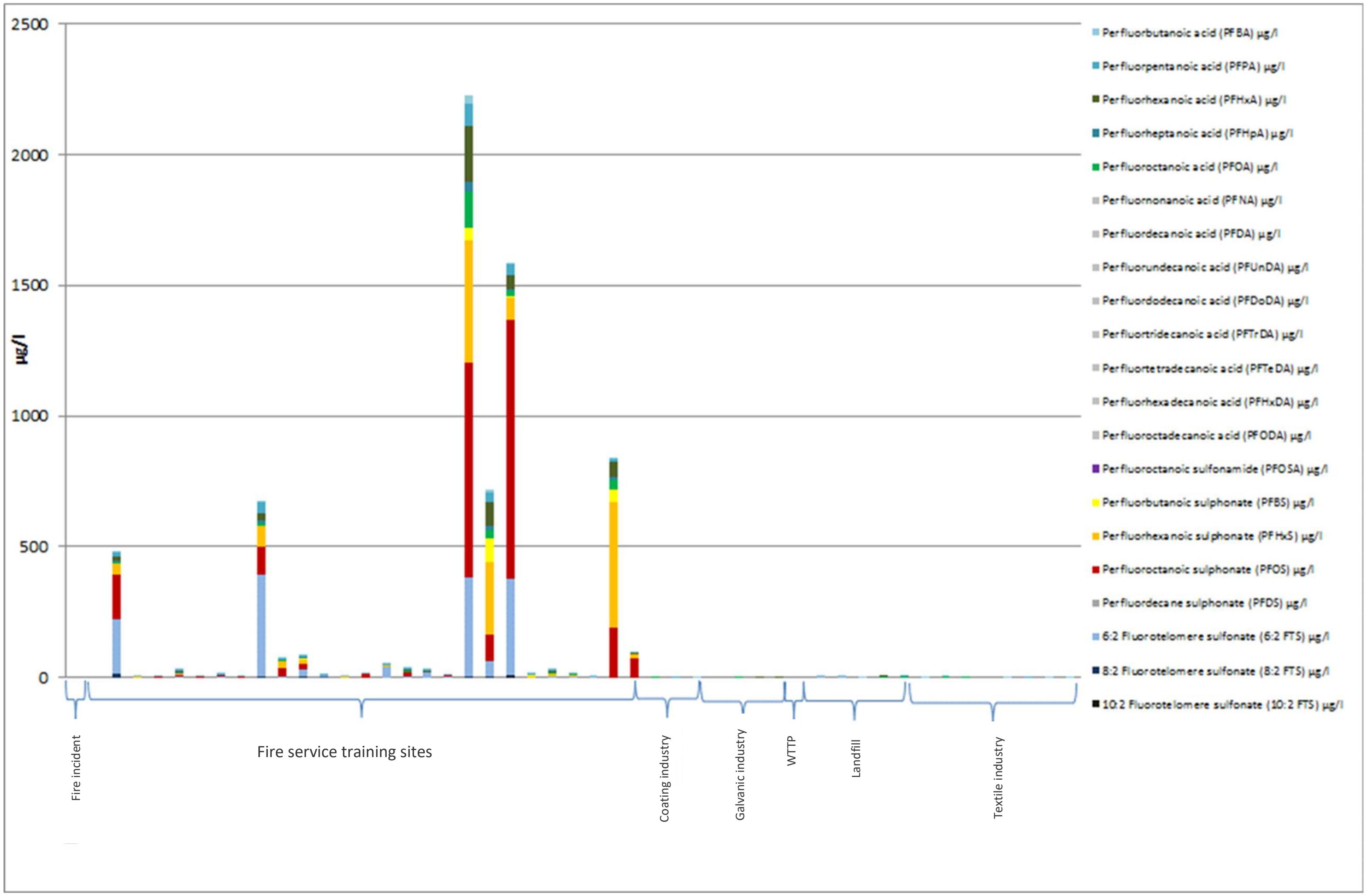

Figure 18: Histogram for PFAS in the groundwater

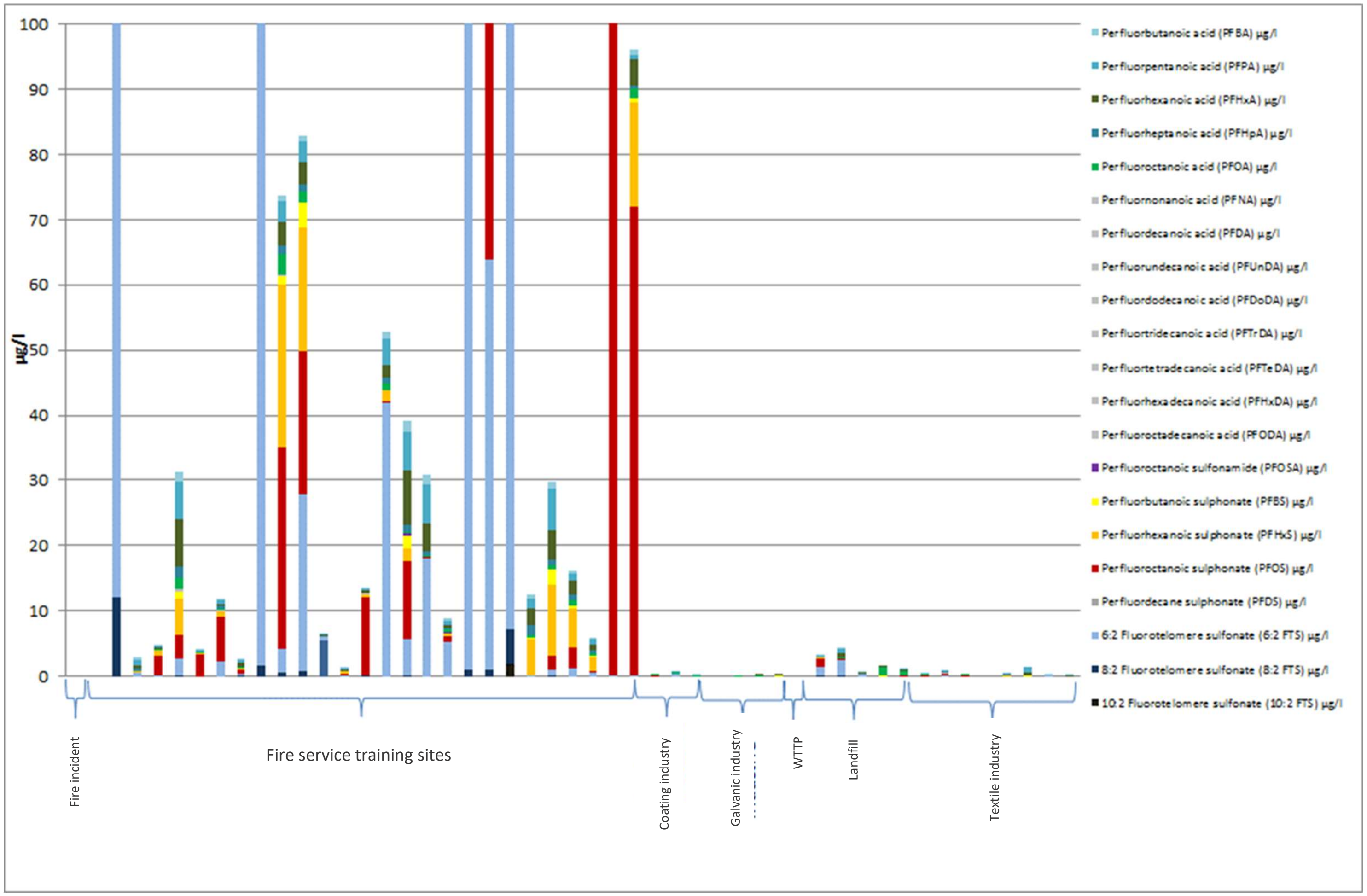

Figure 19: Histogram for PFAS in the groundwater (2)

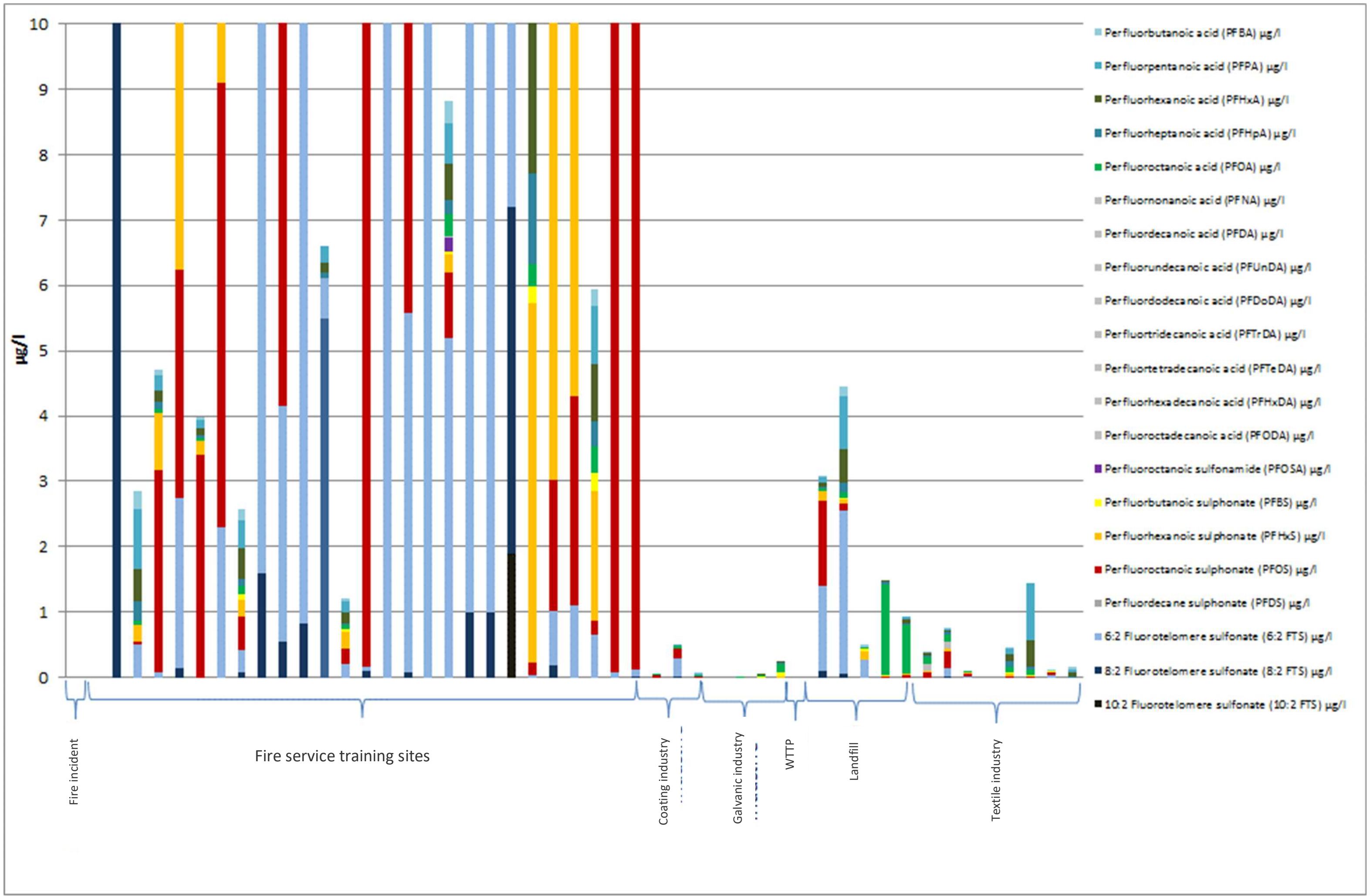

Figure 20: Histogram for PFAS in the groundwater (3)

8.3 INTERPRETATION OF THE RESULTS

8.3.1 Soil

From the results of the sampling campaign at risk locations, it is established for soil and sediment that:

- PFAS was found at all locations with extinguishing activities. In relation to the other activities, the highest concentrations of PFAS were found at the locations with extinguishing activities: maximum concentration is 9392 µg/kg dm.
- At the locations with other activities, one soil/sludge sampling per location was carried out (landfill, textile industry, sludge steel water buffer). The concentrations are maximum 14 µg/kg dm.
- The PFOS parameter is determined relatively in the highest concentrations.
- At locations where calamities have occurred (relatively recent fire incidents), relatively more precursors (FTS[7] components) are measured.
- It is striking that longer PFAS precursors 8:2 and 10:2 FTS are also measured in elevated concentrations (higher than detection limit). These can degrade into, among others, C8 and C10 compounds.
- Based on the results of the sampling campaign, the highest measured PFOS concentration in the soil was 6100 µg/kg dm. The risk limit value for housing with garden of 11 µg/kg dm (leaching to groundwater) is more than exceeded at these sites.
- The highest concentrations of PFAS are determined in the top soil.

8.3.2 Groundwater

From the results of the measurement campaign at risk locations, it is established for the groundwater that:

- PFAS are found in the groundwater in the highest concentrations at sites with extinguishing activities. The maximum concentration was 2226.8 µg/l.
- Increased PFAS concentrations in the groundwater are also found at risk locations with other activities (textile industry, coating industry, landfills).
- The perfluorosulfonates, including PFOS, are found relatively the most.
- Compared to the results for the soil, relatively more carboxylic acids are found in the groundwater and more shorter chains. This is in line with the expectation that perfluorocarboxylic acids are more mobile than perfluorosulfonic acids, and that shorter chains are more mobile than longer chains. For example, the long 10:2-FTS is found in high concentrations in soil at a location, but not or hardly in the groundwater, while the shorter 6:2-FTS is clearly present in both compartments.
- Increased FTS concentrations are also found in the groundwater.

On the basis of the measurement results, it is established that no PFAS was detected in the groundwater at the location where a calamity occurred (groundwater level approx. 7 m bgl). Since this only concerns one monitoring well with a deep groundwater level, this assertion cannot be generalised.

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[7] Fluorotelomere sulfonates (FTS) are used as a replacement for PFOS in fire extinguishing foam

PART C – Conclusions and recommendations

Based on all available data and its interpretation, recommendations are made for further strategy and policy. However, it must be realised that this study was limited in scope and that the knowledge and expertise in this area are still rapidly developing.

Based on the available dataset and the literature study, the following observations can be made:

- The assessment framework for PFAS is still evolving, generally more stringent assessment values are proposed as a function of time. For example, we expect that in time the ADI for PFOS will decrease.
- PFAS occur in elevated concentrations in soil and groundwater. In addition to PFOS and PFOA, other PFAS such as 6:2-FTS also occur in several of the samples analysed. 6:2-FTS is a precursor, which can degrade to persistent perfluoro compounds.
- Increased levels in soil and groundwater are mainly measured at firefighting sites in this study. However, not all types of risk activities were sampled within the framework of this study. A number of locations do not show increased PFAS in soil or groundwater, but this can also be the result of a too limited sampling campaign at each location.
- Risk based values are not available for all common PFAS. RIVM is working on ADIs for approx. 10 compounds, however, they are not available yet and will only be applicable to human risks. They are not accompanied by toxicological levels for ecological risks or for risks resulting from leaching from soil to groundwater.
- No data are available yet for possible background values in soil with PFAS in Flanders.

This leads to the following recommendations for further strategy and policy:

- Analysing the widest possible package of PFAS is recommended (screening package for PFAS) since not only PFOS and PFOA appear elevated. Even though assessment levels are not yet available, many other perfluorinated compounds are persistent, bioaccumulative and toxic, and the frequently present precursors can degrade into perfluorinated compounds.
- It is recommended to make an inventory of whether precursors other than FTS are present at the risk locations. A TOP analysis (detection limit around 2 ng/l) or AOF analyses (detection limit approximately 1 µg/l) can provide more insight into this. In addition to FTS, many other substances can be used that can degrade in the environment into persistent perfluorosulfonic acids or carboxylic acids.
- The sampling of soil/groundwater/sediment at the identified risk activities (Table 1 in Chapter 2.7, part 1) is recommended to check the occurrence of PFAS compounds (in Orientatieve soil Investigation) and to further limit them if necessary (Descriptive soil Investigation). However, it is not possible to simply link these activities to Vlarebo categories, which makes it difficult to determine the impact/scale in Flanders. For example: fire service training sites are part of chemical companies but are not linked to a Vlarebo category.
- The impact of diffuse pollution must be further evaluated mainly in the context of soil movement (excavation). Based on experience and available data, diffuse impact from PFAS in port areas or in areas in the direct sphere of influence of production sites and sites with frequent use of PFAS products cannot be excluded. Here it may be advisable to carry out a more extensive sampling campaign in the wider

surroundings of the locations where elevated PFAS have been determined in the context of the present study, possibly supplemented by a number of control samples in a non-suspect environment.

- Expanding the sampling campaign to surface water sampling should be considered (several PFAS). An interaction is expected in the entire water system based on international experiences.
- The impact on leaching needs to be investigated further. However, the behaviour of these substances in the soil is very complex.
- The drafting of Flemish assessment levels for soil, groundwater and sediment is recommended, both in the context of soil surveys and soil movement studies. The ADI is currently under review.

PART D – Annexes

9 ANNEX 1: LIST OF TABLES

10 ANNEX 2: LIST OF FIGURES

11 ANNEX 3: OTHER ANNEXES

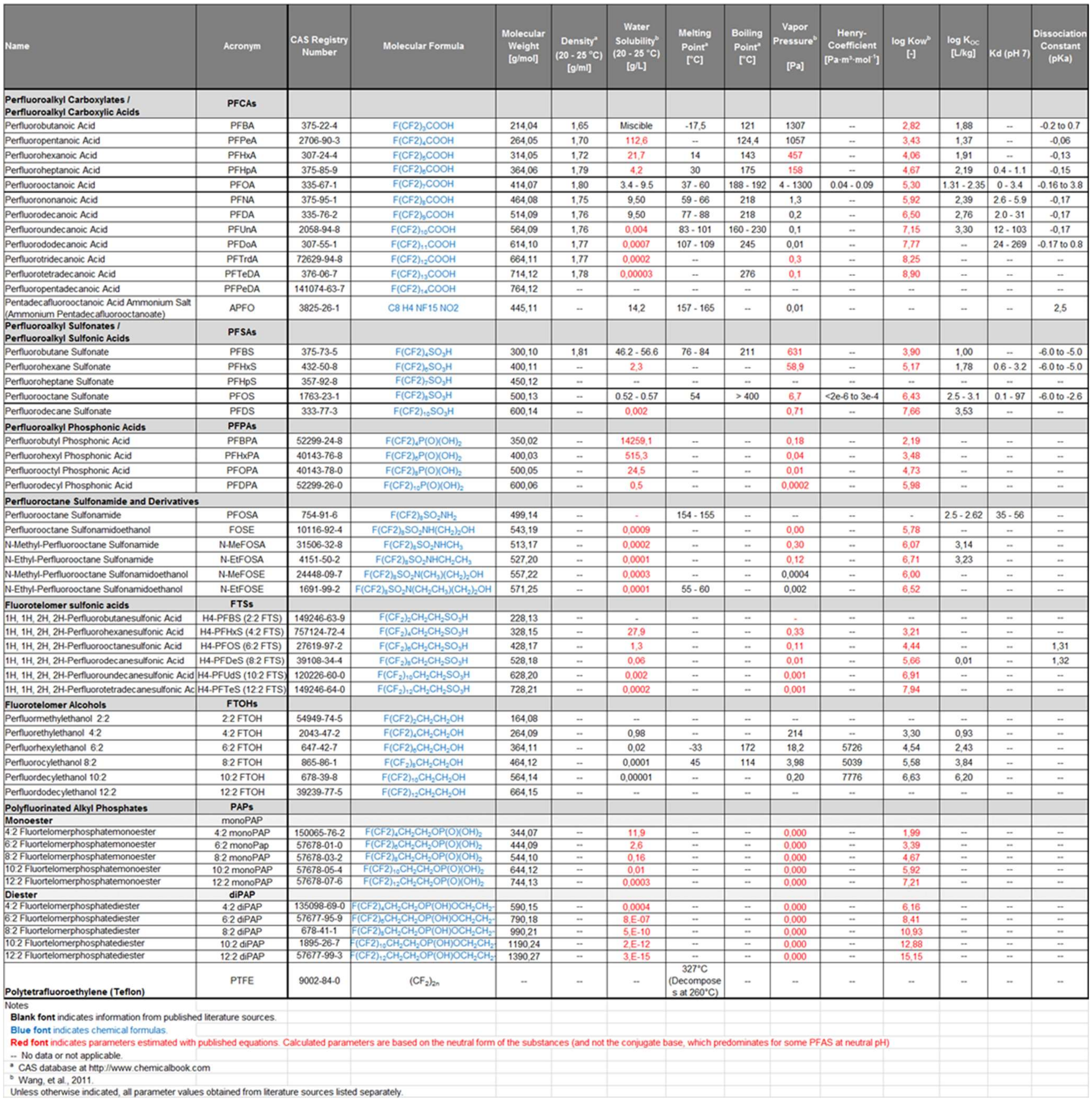
11.1PFAS OVERVIEW

Poly- en geperfluoreerde verbindingen (PFAS)	Geperfluoreerde verbindingen	**Perfluoroalkyl zuren (PFAAs)**						**Fluorpolymeren**
		PFCAs*	**PFSAs***	**PFPAs**	**PFPiAs**	**PFECAs**	**PFESAs**	
		Perfluoroalkyl carboxylzuren	**Perfluoroalkyl sulfonzuren**	**Perfluoralkyl fosfonzuren**	**Perfluoroalkyl fosfinic zuren**	**Perfluoroether carboxylzuren**	**Perhaloether sulfonzuren**	
		$(C_nF_{2n+1}-COOH)$	$(C_nF_{2n+1}-SO_3H)$	$(C_nF_{2n+1}-PO_3H_2)$	$(C_nF_{2n+1}-PO_2H-C_mF_{2m+1})$	$(C_nF_{2n+1}-O-C_mF_{2m}-R-COOH)$	$(X-C_nF_{2n}-O-C_mF_{2m}-SO_3H)$	
		PFBA (n=3, C=4) PFPeA (n=4, C=5) PFHxA (n=5, C=6) PFHpA (n=6, C=7) PFOA (n=7, C=8) PFNA (n=8, C=9) PFDA (n=9, C=10) PFUnA (n=10, C=11) PFDoA (n=11, C=12) PFTrA (n=12, C=13) PFTeA (n=13, C=14)	PFBS (n=4) PFPeS (n=5) PFHxS (n=6) PFHpS (n=7) PFOS (n=8) PFNS (n=9) PFDS (n=10) PFUnS (n=11) PFDoS (n=12) PFTrS (n=13) PFTeS (n=14)	PFBPA (n=4) PFPePA (n=5) PFHxPA (n=6) PFHpPA (n=7) PFOPA (n=8) PFNPA (n=9) PFDPA (n=10) PFUnPA (n=11) PFDoPA (n=12) PFTrPA (n=13) PFTePA (n=14)	C_4/C_4 PFPiA (n,m=4) C_6/C_6 PFPiA (n,m=6) C_8/C_8 PFPiA (n,m=8) C_6/C_8 PFPiA (n=6, m=8)	ADONA (CF3-O-C3F6-O-CHFCF2-COOH) n=1, m=3; R=(O-CHFCF$_2$-) GenX (C3F7-O-CF(CF3)-COOH) n=3, m=2 EEA (C2F5-O-C2F4-O-CF2-COOH) n = 2, m-2, R = O-CF$_2$	F-53B $(Cl-C_6F_{12}-O-C_2F_4-SO_3H)$ X=Cl, n=6, m=2	polytetrafluoretheen (PTFE) $(CF_2)_n$ polyvinylideen fluoride (PVDF) $(CH_2CF_2)_n$ gefluorineerd etheen propeen (FEP) $(C_2F_4)_n-(CF(CF_3)CF_2)_m$ perfluoroalkoxyl polymeer (PFA) $(C_2F_4)_n-(CF_2CF(O-CF_3))_m$ Perfluorpolyether (PFPEs) $(CF(CF_3)CF_2O)_n$ n=10-60
	Gepolyfluoreerde verbindingen	**PFAA precursors**					En duizenden andere...	
		FTOHs	**FTSs**	**mono-PaPs**	**di-PaPs**	**PASF-gebaseerd**		
		Fluortelomeer alcoholen	**Fluorotelomer sulfonzuren**	**Polyfluoralkyl fosforzuur mono-ester**	**Polyfluoralkyl fosforzuur diesters**	**verbindingen**		
		$(C_nF_{2n+1}-C_2H_4-OH)$	$(C_nF_{2n+1}-C_2H_4-SO_3H)$	$(C_nF_{2n+1}-C_2H_4-O-PO_3H_2)$	$(C_nF_{2n+1}-C_2H_4-O-PO_2H-O-C_2H_4-C_mF_{2m+1})$	$(C_nF_{2n+1}-SO_2-R)$		
		4:2 FTOH (n=4) 6:2 FTOH (n=6) 8:2 FTOH (n=8) 10:2 FTOH (n=10) 12:2 FTOH (n=12)	4:2 FTS (n=4) 6:2 FTS (n=6) 8:2 FTS (n=8) 10:2 FTS (n=10) 12:2 FTS (n=12)	4:2 monoPaP (n=4) 6:2 monoPaP (n=6) 8:2 monoPaP (n=8) 10:2 monoPaP (n=10) 12:2 monoPaP (n=12)	4:2 diPaP (n,m=4) 6:2 diPaP (n,m=6) 8:2 diPaP (n,m=8) 10:2 diPaP (n,m=10) 4:2/6:2 diPaP (n=4, m=6) 6:2/8:2 diPaP (n=6, m=8) 8:2/10:2 diPaP (n=8, m=10) 10:2/12:2 diPaP (n=10, m=12)	R=N(CH_3)H MeFBSA (n=4) MeFOSA (n=8) R=N(C_2H_5)H EtFBSA (n=4) EtFOSA (n=8) R=N$(CH_3)C_2H_4OH$ MeFBSE (n=4) MeFOSE (n=8) R=N$(C_2H_5)C_2H_4OH$ EtFBSE (n=4) EtFOSE (n=8) SAmPaP $(C_8F_{17}SO_2N(C_2H_5)C_2H_4-O)_2-PO_2H$		

* Me = methaan/methyl, Et = ethaan/ethyl, Pro = propaan, B = butaan, Pe = pentaan, Hx = hexaan, Hp = heptaan, O = octaan, N = nonaan, D = decaan, Un = undecaan, Do = dodecaan, Tr = tridecaan, Te = tetradecaan

Het waterstofatoom in de COOH- en SO_3H- groep kan ook een NH_3-, K-, Li- etc. groep zijn. Bij dissociatie worden de carboxylzuren en sulfonzuren gevormd, welke door middel van analyse gemeten worden.

11.2PFAS PHYSICAL AND CHEMICAL PROPERTIES



Name	Acronym	CAS Registry Number	Molecular Formula	Molecular Weight [g/mol]	Density[a] (20 - 25 °C) [g/ml]	Water Solubility[b] (20 - 25 °C) [g/L]	Melting Point[a] [°C]	Boiling Point[a] [°C]	Vapor Pressure[b] [Pa]	Henry-Coefficient $[Pa\cdot m^3\cdot mol^{-1}]$	log Kow[b] [-]	log K_{OC} [L/kg]	Kd (pH 7)	Dissociation Constant (pKa)
Perfluoroalkyl Carboxylates / Perfluoroalkyl Carboxylic Acids	**PFCAs**													
Perfluorobutanoic Acid	PFBA	375-22-4	$F(CF2)_3COOH$	214,04	1,65	Miscible	-17,5	121	1307	--	2,82	1,88	--	-0.2 to 0.7
Perfluoropentanoic Acid	PFPeA	2706-90-3	$F(CF2)_4COOH$	264,05	1,70	112,6	--	124,4	1057	--	3,43	1,37	--	-0,06
Perfluorohexanoic Acid	PFHxA	307-24-4	$F(CF2)_5COOH$	314,05	1,72	21,7	14	143	457	--	4,06	1,91	--	-0,13
Perfluoroheptanoic Acid	PFHpA	375-85-9	$F(CF2)_6COOH$	364,06	1,79	4,2	30	175	158	--	4,67	2,19	0.4 - 1.1	-0,15
Perfluorooctanoic Acid	PFOA	335-67-1	$F(CF2)_7COOH$	414,07	1,80	3.4 - 9.5	37 - 60	188 - 192	4 - 1300	0.04 - 0.09	5,30	1.31 - 2.35	0 - 3.4	-0.16 to 3.8
Perfluorononanoic Acid	PFNA	375-95-1	$F(CF2)_8COOH$	464,08	1,75	9,50	59 - 66	218	1,3	--	5,92	2,39	2.6 - 5.9	-0,17
Perfluorodecanoic Acid	PFDA	335-76-2	$F(CF2)_9COOH$	514,09	1,76	9,50	77 - 88	218	0,2	--	6,50	2,76	2.0 - 31	-0,17
Perfluoroundecanoic Acid	PFUnA	2058-94-8	$F(CF2)_{10}COOH$	564,09	1,76	0,004	83 - 101	160 - 230	0,1	--	7,15	3,30	12 - 103	-0,17
Perfluorododecanoic Acid	PFDoA	307-55-1	$F(CF2)_{11}COOH$	614,10	1,77	0,0007	107 - 109	245	0,01	--	7,77	--	24 - 269	-0.17 to 0.8
Perfluorotridecanoic Acid	PFTrdA	72629-94-8	$F(CF2)_{12}COOH$	664,11	1,77	0,0002	--		0,3	--	8,25	--	--	--
Perfluorotetradecanoic Acid	PFTeDA	376-06-7	$F(CF2)_{13}COOH$	714,12	1,78	0,00003	--	276	0,1	--	8,90	--	--	--
Perfluoropentadecanoic Acid	PFPeDA	141074-63-7	$F(CF2)_{14}COOH$	764,12	--	--	--	--	--	--	--	--	--	--
Pentadecafluorooctanoic Acid Ammonium Salt (Ammonium Pentadecafluorooctanoate)	APFO	3825-26-1	C8 H4 NF15 NO2	445,11	--	14,2	157 - 165	--	0,01	--	--	--	--	2,5
Perfluoroalkyl Sulfonates / Perfluoroalkyl Sulfonic Acids	**PFSAs**													
Perfluorobutane Sulfonate	PFBS	375-73-5	$F(CF2)_4SO_3H$	300,10	1,81	46.2 - 56.6	76 - 84	211	631	--	3,90	1,00	--	-6.0 to -5.0
Perfluorohexane Sulfonate	PFHxS	432-50-8	$F(CF2)_6SO_3H$	400,11	--	2,3	--	--	58,9	--	5,17	1,78	0.6 - 3.2	-6.0 to -5.0
Perfluoroheptane Sulfonate	PFHpS	357-92-8	$F(CF2)_7SO_3H$	450,12	--	--	--	--	--	--	--	--	--	--
Perfluorooctane Sulfonate	PFOS	1763-23-1	$F(CF2)_8SO_3H$	500,13	--	0.52 - 0.57	54	> 400	6,7	<2e-6 to 3e-4	6,43	2.5 - 3.1	0.1 - 97	-6.0 to -2.6
Perfluorodecane Sulfonate	PFDS	333-77-3	$F(CF2)_{10}SO_3H$	600,14	--	0,002			0,71	--	7,66	3,53	--	--
Perfluoroalkyl Phosphonic Acids	**PFPAs**													
Perfluorobutyl Phosphonic Acid	PFBPA	52299-24-8	$F(CF2)_4P(O)(OH)_2$	350,02	--	14259,1	--	--	0,18	--	2,19	--	--	--
Perfluorohexyl Phosphonic Acid	PFHxPA	40143-76-8	$F(CF2)_6P(O)(OH)_2$	400,03	--	515,3	--	--	0,04	--	3,48	--	--	--
Perfluorooctyl Phosphonic Acid	PFOPA	40143-78-0	$F(CF2)_8P(O)(OH)_2$	500,05	--	24,5	--	--	0,01	--	4,73	--	--	--
Perfluorodecyl Phosphonic Acid	PFDPA	52299-26-0	$F(CF2)_{10}P(O)(OH)_2$	600,06	--	0,5	--	--	0,0002	--	5,98	--	--	--
Perfluoroctane Sulfonamide and Derivatives														
Perfluorooctane Sulfonamide	PFOSA	754-91-6	$F(CF2)_8SO_2NH_2$	499,14	--	-	154 - 155	--	--	--	-	2.5 - 2.62	35 - 56	--
Perfluorooctane Sulfonamidoethanol	FOSE	10116-92-4	$F(CF2)_8SO_2NH(CH_2)_2OH$	543,19	--	0,0009	--	--	0,00	--	5,78	--	--	--
N-Methyl-Perfluorooctane Sulfonamide	N-MeFOSA	31506-32-8	$F(CF2)_8SO_2NHCH_3$	513,17	--	0,0002	--	--	0,30	--	6,07	3,14	--	--
N-Ethyl-Perfluorooctane Sulfonamide	N-EtFOSA	4151-50-2	$F(CF2)_8SO_2NHCH_2CH_3$	527,20	--	0,0001	--	--	0,12	--	6,71	3,23	--	--
N-Methyl-Perfluorooctane Sulfonamidoethanol	N-MeFOSE	24448-09-7	$F(CF2)_8SO_2N(CH_3)(CH_2)_2OH$	557,22	--	0,0003	--	--	0,0004	--	6,00	--	--	--
N-Ethyl-Perfluorooctane Sulfonamidoethanol	N-EtFOSE	1691-99-2	$F(CF2)_8SO_2N(CH_2CH_3)(CH_2)_2OH$	571,25	--	0,0001	55 - 60	--	0,002	--	6,52	--	--	--
Fluorotelomer sulfonic acids	**FTSs**													
1H, 1H, 2H, 2H-Perfluorobutanesulfonic Acid	H4-PFBS (2:2 FTS)	149246-63-9	$F(CF_2)_2CH_2CH_2SO_3H$	228,13	--	-	--	--	-	--	--	--	--	--
1H, 1H, 2H, 2H-Perfluorohexanesulfonic Acid	H4-PFHxS (4:2 FTS)	757124-72-4	$F(CF_2)_4CH_2CH_2SO_3H$	328,15	--	27,9	--	--	0,33	--	3,21	--	--	--
1H, 1H, 2H, 2H-Perfluorooctanesulfonic Acid	H4-PFOS (6:2 FTS)	27619-97-2	$F(CF_2)_6CH_2CH_2SO_3H$	428,17	--	1,3	--	--	0,11	--	4,44	--	--	1,31
1H, 1H, 2H, 2H-Perfluorodecanesulfonic Acid	H4-PFDeS (8:2 FTS)	39108-34-4	$F(CF_2)_8CH_2CH_2SO_3H$	528,18	--	0,06	--	--	0,01	--	5,66	0,01	--	1,32
1H, 1H, 2H, 2H-Perfluoroundecanesulfonic Acid	H4-PFUdS (10:2 FTS)	120226-60-0	$F(CF_2)_{10}CH_2CH_2SO_3H$	628,20	--	0,002	--	--	0,001	--	6,91	--	--	--
1H, 1H, 2H, 2H-Perfluorotetradecanesulfonic Ac	H4-PFTeS (12:2 FTS)	149246-64-0	$F(CF_2)_{12}CH_2CH_2SO_3H$	728,21	--	0,0002	--	--	0,001	--	7,94	--	--	--
Fluorotelomer Alcohols	**FTOHs**													
Perfluormethylethanol 2:2	2:2 FTOH	54949-74-5	$F(CF2)_2CH_2CH_2OH$	164,08	--	--	--	--	--	--	--	--	--	--
Perfluorethylethanol 4:2	4:2 FTOH	2043-47-2	$F(CF2)_4CH_2CH_2OH$	264,09	--	0,98	--	--	214	--	3,30	0,93	--	--
Perfluorhexylethanol 6:2	6:2 FTOH	647-42-7	$F(CF2)_6CH_2CH_2OH$	364,11	--	0,02	-33	172	18,2	5726	4,54	2,43	--	--
Perfluorocylethanol 8:2	8:2 FTOH	865-86-1	$F(CF_2)_8CH_2CH_2OH$	464,12	--	0,0001	45	114	3,98	5039	5,58	3,84	--	--
Perfluordecylethanol 10:2	10:2 FTOH	678-39-8	$F(CF2)_{10}CH_2CH_2OH$	564,14	--	0,00001	--	--	0,20	7776	6,63	6,20	--	--
Perfluordodecylethanol 12:2	12:2 FTOH	39239-77-5	$F(CF2)_{12}CH_2CH_2OH$	664,15	--	--	--	--	--	--	--	--	--	--
Polyfluorinated Alkyl Phosphates	**PAPs**													
Monoester	monoPAP													
4:2 Fluortelomerphosphatemonoester	4:2 monoPAP	150065-76-2	$F(CF2)_4CH_2CH_2OP(O)(OH)_2$	344,07	--	11,9	--	--	0,000	--	1,99	--	--	--
6:2 Fluortelomerphosphatemonoester	6:2 monoPap	57678-01-0	$F(CF2)_6CH_2CH_2OP(O)(OH)_2$	444,09	--	2,6	--	--	0,000	--	3,39	--	--	--
8:2 Fluortelomerphosphatemonoester	8:2 monoPAP	57678-03-2	$F(CF2)_8CH_2CH_2OP(O)(OH)_2$	544,10	--	0,16	--	--	0,000	--	4,67	--	--	--
10:2 Fluortelomerphosphatemonoester	10:2 monoPAP	57678-05-4	$F(CF2)_{10}CH_2CH_2OP(O)(OH)_2$	644,12	--	0,01	--	--	0,000	--	5,92	--	--	--
12:2 Fluortelomerphosphatemonoester	12:2 monoPAP	57678-07-6	$F(CF2)_{12}CH_2CH_2OP(O)(OH)_2$	744,13	--	0,0003	--	--	0,000	--	7,21	--	--	--
Diester	**diPAP**													
4:2 Fluortelomerphosphatediester	4:2 diPAP	135098-69-0	$F(CF2)_4CH_2CH_2OP(OH)OCH_2CH_2$-	590,15	--	0,0004	--	--	0,000	--	6,16	--	--	--
6:2 Fluortelomerphosphatediester	6:2 diPAP	57677-95-9	$F(CF2)_6CH_2CH_2OP(OH)OCH_2CH_2$-	790,18	--	8,E-07	--	--	0,000	--	8,41	--	--	--
8:2 Fluortelomerphosphatediester	8:2 diPAP	678-41-1	$F(CF2)_8CH_2CH_2OP(OH)OCH_2CH_2$-	990,21	--	5,E-10	--	--	0,000	--	10,93	--	--	--
10:2 Fluortelomerphosphatediester	10:2 diPAP	1895-26-7	$F(CF2)_{10}CH_2CH_2OP(OH)OCH_2CH_2$	1190,24	--	2,E-12	--	--	0,000	--	12,88	--	--	--
12:2 Fluortelomerphosphatediester	12:2 diPAP	57677-99-3	$F(CF2)_{12}CH_2CH_2OP(OH)OCH_2CH_2$	1390,27	--	3,E-15	--	--	0,000	--	15,15	--	--	--
Polytetrafluoroethylene (Teflon)	PTFE	9002-84-0	$(CF_2)_{2n}$	--	--	--	327°C (Decomposes at 260°C)	--	--	--	--	--	--	--

Notes

Blank font indicates information from published literature sources.

Blue font indicates chemical formulas.

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

-- No data or not applicable.

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

[b] Wang, et al., 2011.

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

11.3GLOBAL TOXICITY LEVELS

Drinking water, groundwater and soil criteria around the world. Values in brackets are values that give a guideline based on the total PFAS.

Drinking Water Criteria in µg/l in European Countries, Australia

	PFOS	PFOA	PFOSA	PFBS	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	6:2 FTS	PFHpS	PFHxS	PFPeS
Denmark[1]	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	-	(0.1)	-
Germany[2]	(0.1)	(0.1)	-	-	-	-	-	-	-	-	-	-	-	-
The Netherlands	0.53[3]	0.0875[4]	-	-	-	-	-	-	-	-	-	-	-	-
Sweden[5]	(0.09)	(0.09)	-	(0.09)	-	(0.09)	(0.09)	(0.09)	-	-	-	-	(0.09)	-
U.K.[6]	0.3	0.3	-	-	-	-	-	-	-	-	-	-	-	-
Italy[7]	0.03	0.5		0.5	0.5	(0.5)	(0.5)	(0.5)	(0.5)	(0.5)			(0.5)	
Australia[8]	(0.07)	0.56											(0.07)	

Drinking Water Criteria in µg/l in North America

	PFOS	PFOA	PFOSA	PFBS	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	6:2 FTS	PFHpS	PFHxS	PFPeS
Michigan[9]	0.07	0.07												
Minnesota[10]	0.027	0.035	-	7	7	-	-	-	-	-	-	-	-	-
New Jersey[11]	-	0.014	-	-	-	-	-	-	0.013	-	-	-	-	-
Vermont[12]	(0.02)	(0.02)												
U.S. EPA[13]	(0.07)	(0.07)	-	-	-	-	-	-	-	-	-	-	-	-
Canada[14]	0.6	0.2	-	15	30	0.2	0.2	0.2	0.2	-	-	-	0.6	-

Groundwater Criteria in µg/l in European Countries, U.S.

	PFOS	PFOA	PFOSA	PFBS	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	6:2 FTS	PFHpS	PFHxS	PFPeS
Denmark[1]	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	-	(0.1)	-
State of Bavaria[15]	0.23/(0.3)	(0.3)	-	3	7	3	1	0.3	0.3	0.3	-	-	(0.3)	-
State of Baden – Württemberg[16]	0.23/(0.3)	0.3/(1)	-	3/(1)	7/(1)	3/(1)	1/(1)	0.3/(1)	0.3/(1)	0.3/(1)	0.3/(1)	0.3/(1)	0.3/(1)	1/(1)
The Netherlands[17]	4.7	0.39	-	-	-	-	-	-	-	-	-	-	-	-
Michigan (surface water interface)[9]	0.012	12												
New Jersey[18]	-	-	-	-	-	-	-	-	0.01	-	-	-	-	-
New Hampshire[19]	(0.07)	(0.07)												
Texas, Residential[20]	0.56	0.29	0.29	34	71	0.093	0.093	0.56	0.29	0.37	-	-	0.093	-

Soil Criteria in mg/kg in European Countries, U.S.

	PFOS	PFOA	PFOSA	PFBS	PFBA	PFPeA	PFHxA	PFHpA	PFNA	PFDA	6:2 FTS	PFHpS	PFHxS	PFPeS
Denmark[1]	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	-	(0.4)	-
Norway[21]	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-
Italy (residential, industrial)[22]		0.5/5												
Michigan, Residential Drinking Water Protection[9]	0.0014	0.059												
Texas, Residential[20]	1.5	0.6	0.058	73	150	5.1	5.1	1.5	0.76	0.96	-	-	4.8	-
U.S., Residential[23]	1.26	1.26		1.260										

Notes:

1 = Σ12 PFASs = 0.100 µg/L (aqueous) or 0.4 mg/kg (soil); includes PFBS, PFHxS, PFOS, PFOSA, 6:2 FTS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA; Provisional Values Issued by Danish Ministry of the Environment in 2015

2 = Σ PFOS and PFOA = 0.100 µg/; Composite precautionary guidance value for long term exposure issued in 2006 by Umweltbundesamt (UBA) and the Drinking Water Commission (TWK) of the Federal Ministry of Health

3 Proposed by National Institute for Public Health and the Environment (RIVM Report) in 2010

4 Proposed by National Institute for Public Health and the Environment (RIVM Report) in 2017

5 = Σ7 PFAS = 0.090 µg/L, includes PFBS, PFHxS, PFOS, PFPeA, PFHxA, PFHpA, PFOA; recommended in 2015 by DEP

6 = Tier 2 values published in 2009 by Drinking Water Inspectorate

7 = Σ8 PFAS = 0.500 µg/L, includes PFHxS, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoA; Separate standards for PFBA, PFBS, PFOA, PFOS; Recommended values from Ministero della Salute and Instituto Superiore di Sanita (ISS) issued in 2014 and 2015

8 = Σ PFOS and PFHxS = 0.070 µg/L; Recommended values from Commonwealth Department of Health issued in 2017

9 = Michigan Department of Environmental Quality Proposed Values, Updated in 2017

10 = Minnesota Dept. of Health 2011 Chronic Health Risk Limits for PFBS, PFBA; PFOS and PFOA current values are 300 µg/L, values in table were proposed updates in 2017

11 = Maximum Contaminant Levels, currently proposed (PFNA in 2016, PFOA in 2017) and under review

12 = Health Advisory: Σ PFOS and PFOA = 0.020 µg/L; Issued in 2016

13 = Lifetime health advisory; Σ PFOS and PFOA = 0.070 µg/L; Established May 2016

14 = Health Canada Drinking Water Screening Values Issued in 2017

15 = Σ PFOS, PFOA, PFHxS = 0.3 µg/l issued by Bavarian State Office for Environment in 2015

16 = Σ12 PFAS < 1 µg/L, includes PFBS, PFHxS, PFOS, PFOSA, 6:2 FTS, PFB, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA; PFOS standard changes to 0.3 µg/L if multiple PFASs present; Issued by State of Baden-Württemberg (Ministerium für Umwelt, Klima und Energiewirtschaft) in 2015

17 = Level intervention value

18 = Interim Specific Ground Water Quality Criterion Proposed in 2014

19 = Ambient Groundwater Quality Standard: Σ PFOS and PFOA = 0.070 µg/L; Proposed in 2016

20 = Residential Protective Concentration Levels, protective of drinking water; Proposed in 2016

21 = Norway Pollution Control Agency

22 = Proposed by Instituto Superiore di Sanita, ISS in 2015

23 = Based on 2017 U.S. EPA RSL Calculator, default assumptions

11.4ANALYSIS RESULTS

This annex contains overviews of the analysis results in soil and groundwater.

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