

# Annexes to Annex 15 Restriction Report Proposal for a restriction

Substance name(s): Per and polyfluoroalkyl substances (PFAS)

■ EC Number: N/A ■ CAS Number: N/A

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## Annex A Manufacturing methods of PFAS in FFF

Electrochemical fluorination involves replacement of all hydrogen atoms by fluorine with electrolysis of the organic starting material in anhydrous hydrogen fluoride. The process involves free radical production which can cause the carbon chain to break and rearrange, resulting in a mixture of numerous linear and branched chain perfluorinated isomers and homologues. For example, during the production of perfluoroctane sulfonic acid (PFOS) and perfluoroctanoic acid (PFOA), branched chains typically make up 20% to 30% (Buck *et al.*, 2011 and references therein), and different chain lengths can be present as minor constituents (e.g., Environment Agency, 2004) reports around 10% of a C8 commercial product was C5–C7). There may also be partially fluorinated starting materials or intermediates (i.e., polyfluoroalkyl substances), which would be expected to be present as low-level impurities (Environment Agency, 2004).

An important example is the electrofluorination of C<sub>n</sub>H<sub>2n+1</sub>SO<sub>2</sub>F which produces perfluoroalkyl sulfonyl fluoride (C<sub>n</sub>F<sub>2n+1</sub>SO<sub>2</sub>F; PASF), a precursor to the PASF-based substances which are constituents of a number of FFFs. Examples of some major electrofluorination-based PFAS groups reported in FFFs are presented in Table A.1 (D'Agostino and Mabury, 2014; Liu *et al.*, 2024).

Table A.1: Examples of electrofluorination-based PFAS commonly reported to be present in FFF (adapted from Brendel *et al.* (2018) and (D'Agostino and Mabury, 2014, 2017a))

Perfluoroalkyl carboxylic acids (PFCA) $n = 4 \text{ to } 8$	Perfluoroalkylsulfonic acids (PFSAs) $n = 4 \text{ to } 10$ $f = \begin{cases} f & 0 \\ I & S \\ I & I \\ I & O \\ I & O \\ I & I \\ I & O $
Perfluoroalkyl sulfonamide amino carboxylate (PFASaAmA)	Perfluoroalkyl sulfonamido amine (PFASaAm)
n = 3 to 8	n = 3 to 8
$F = \begin{pmatrix} F \\ I \\ C \\ I \\ F \end{pmatrix}_{n} \begin{pmatrix} O \\ I \\ O \\ O \end{pmatrix} = \begin{pmatrix} O \\ O \\ O \\ O \\ C \\ O \\ O$	$F = \begin{pmatrix} F \\ I \\ C \\ I \\ S \\ N \end{pmatrix} = \begin{pmatrix} O \\ I \\ S \\ N \\ O \\ I \\ C \\ I \\ CH_3 \\ CH_3 \\ H \end{pmatrix}$

PASF-based substances such as those belonging to PFASaAm and PFASaAmA groups were present in formulations of products from the early 1990s. However, the use of PASF-based substances in FFFs appears to have mostly been superseded in recent years by fluorotelomer based classes of PFAS (Place and Field, 2012).

The second method of production, fluorotelomerisation, is based on telomerisation where a mixture of longer chain perfluoroalkyl iodides is produced by reaction of a short chain perfluoroalkyl iodide (e.g. pentafluoroethyl iodide) with tetrafluoroethylene (CF<sub>2</sub>=CF<sub>2</sub>). The iodide is then reacted further with ethylene to produce an n:2 fluorotelomer iodide from which fluorotelomer-based FFFs are produced (Buck *et al.*, 2011). The perfluoroalkyl chains are attached to a nonfluorinated carbon chain, with the n:2 nomenclature indicating the fluorocarbon chain length (n) and the hydrocarbon chain length (typically 2), respectively. Although a 6:2 fluorotelomer would have a chain length of C8, they are referred to as C6 fluorotelomers as this is the portion that is fluorinated. The perfluoroalkyl chains do not break during telomerisation and therefore branching does not occur.

Fluorotelomer substances have been reported to have been used in FFF since the mid-1970s (Prevedouros *et al.*, 2006; Ross, 2020). The structures of example

fluorotelomer-based PFAS reported in FFFs are presented in Table A.2. For most of these substances more than one perfluorinated alkyl chain length was reported. Further to this, numerous isomers and analogues differing by one fluorinated carbon in the tail have also been identified.

## Table A.2: Examples of fluorotelomer-based PFAS commonly reported to be present in FFF

## n:2 fluorotelomer sulfonamide betaine (FTAB)

n = 6, 8, 10, 12

$$F = \begin{bmatrix} F \\ I \\ I \\ F \end{bmatrix}_{n} \begin{bmatrix} O \\ II \\ I \\ O \end{bmatrix}$$

n:2 fluorotelomer thioamido sulfonates (FtTAoS)

Alternative name: n:2 fluorotelomer-

mercaptoalkylamido sulfonate (FTSAS)

$$n = 4, 6, 8$$

$$F = \begin{bmatrix} F \\ C \\ F \end{bmatrix}_n S \longrightarrow \begin{bmatrix} O \\ N \\ H \end{bmatrix} S \bigcirc O$$

n:2 fluorotelomer thiohydroxy ammonium (FTTHN)

$$n = 6, 8$$

$$F = \begin{cases} F \\ I \\ C \\ I \\ F \end{cases}$$
 OH 
$$\begin{cases} H \\ I \\ N \\ \\ \\ \end{cases}$$

n:2 fluorotelomer sulfonamide amine (FTSaAm)

n:2 fluorotelomer thioether amido amino carboxylic acid

$$n = 6, 8$$

$$F = \begin{bmatrix} F \\ C \\ F \\ D \end{bmatrix}_{n} \begin{bmatrix} O & O & O \\ N & N \\ N & N \end{bmatrix}$$

n:1:2 fluorotelomer betaine (FTB)

$$n = 5, 7, 9$$

$$F = \begin{bmatrix} F \\ I \\ I \\ F \end{bmatrix}_{n} \begin{bmatrix} O \\ I \\ I \end{bmatrix}_{n} O$$

n:3 fluorotelomer betaine

$$n = 5, 7, 9$$

$$F = \begin{bmatrix} F \\ I \\ F \end{bmatrix}_{n}$$

n:2 fluorotelomer thioalkylamido betaine (FTSAB)

## Annex B Characterisation of PFAS in FFFs and PFAS impacted environments

#### Annex B.1 Overview

The full characterisation of PFAS in any environmental sample is significantly underestimated (McDonough *et al.*, 2019). The following text examines the current analytical techniques available for examining PFAS, and the types of data that they will provide.

Measurement of PFAS in any sample is complicated by the fact that there are thousands of known PFAS (Buck *et al.*, 2011). Products that are released into the environment will contain a proprietary mixture of PFAS and also unknown / unintended PFAS because of their method of production (e.g., Benjamin and Jennifer, 2012; Krista *et al.*, 2017; Liu *et al.*, 2024) (see Annex A). Targeted analysis, which focuses on identifying specific PFAS compounds, may not detect or quantify certain PFAS, including precursors to persistent perfluoroalkyl acids (PFAAs), degradation products, and PFAS without available analytical standards (e.g., Aro *et al.*, 2021a; Houtz *et al.*, 2016; Murakami *et al.*, 2009).

As a result, non-targeted analytical approaches are used to provide additional information. The most general has been to quantify total organic fluorine (TOF) in any sample (e.g., McDonough *et al.*, 2019) to understand the degree to which fluorinated substances are not quantified by targeted analysis. TOF can include fluorinated organic substances that are not PFAS such as pesticides and pharmaceuticals. Practically, studies have more often reported the determination of total extractable fluorine (EOF) (D'Agostino and Mabury, 2014) or total adsorbable fluorine (AOF) (Wagner *et al.*, 2013), sometimes with measurement of inorganic fluorine. This approach has been used to give an indication of the full extent of total PFAS present.

Another non-targeted approach that has been used is the total oxidisable precursor (TOP) assay. This method uses hydroxyl radicals to oxidise PFAA precursors to PFCAs. The concentration of PFCAs is measured in the sample before and after oxidation to determine the PFAA precursors present (Houtz and Sedlak, 2012). The TOP assay quantifies total PFAA precursors and some information on the perfluoroalkyl chain lengths can also be inferred, but the assay is limited to substances that oxidise to PFCAs.

The approaches to a comprehensive analysis of fluorine in samples have been discussed by McDonough *et al.* (2019) and Koch *et al.* (2020). Two or more analysis techniques are often required. For example, Miyake *et al.* (2007) used a mass balance approach to determine the contribution of perfluorinated substances to total fluorine in water, and Dubocq *et al.* (2020) reports the characterisation of the fluorinated components of FFFs by measuring total fluorine, inorganic fluorine, targeted PFAS, and non-target analysis to tentatively identify of unknown PFAS. Several researchers have refined the original TOP assay to characterise FFFs and different impacted environmental compartments (see Annex B.2). In summary, targeted analysis alone is often not sufficient to get a clear picture of PFAS contamination from FFFs and additional information can be obtained from using non-specific methods.

A summary of fluorine speciation and analysis that can be used to help characterise PFAS is presented in Figure B.1.

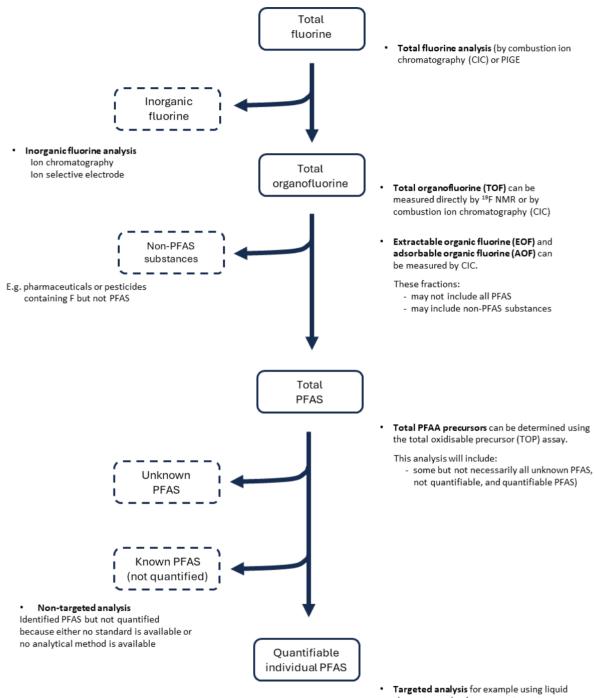
#### **Annex B.2** Chemical Analysis of PFAS in FFFs

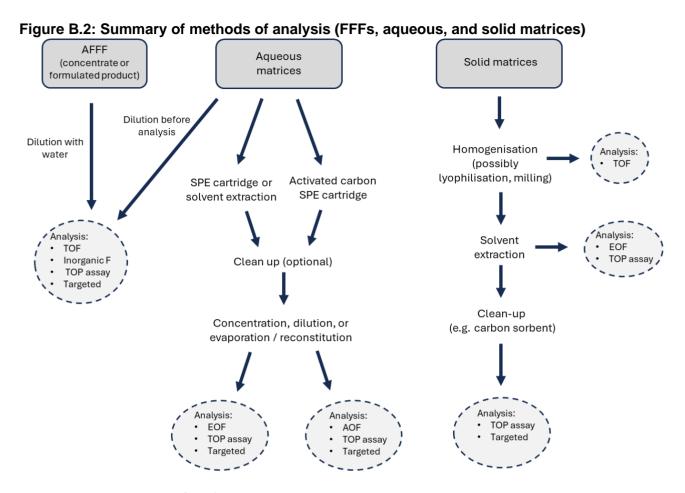
#### **Annex B.2.1 Sample preparation**

Total fluorine analysis (TOF) requires minimal sample preparation before analysis, whereas analysis for extractable organofluorine (EOF) and adsorbable organofluorine (AOF) requires extraction and adsorption respectively as these are part of the operational definitions of the methods.

For more specific analysis such as the TOP assay and targeted analysis, the methodology will vary depending on the matrix, the PFAS being analysed, and the expected concentrations present. For example, FFF concentrates are unlikely to require any extraction but instead significant dilution before analysis (D'Agostino and Mabury, 2014; Liu *et al.*, 2024). Although some impacted waters where there has been extensive contamination have been analysed directly or after dilution (Houtz *et al.*, 2013), most surface waters and groundwaters will require extraction and concentration, and may also benefit from a clean-up procedure before analysis depending on the extent of co-extracted organic matter. Solid samples will require extraction and there are various options in terms of solvents and techniques. Again, after extraction of solid samples, the need either for concentration or dilution, and whether a clean-up step is necessary, will depend on the PFAS concentrations present as well as the extent of co-extraction of organic matter and its likely effect on the final analytical detection method being used. The general approaches to analysis of FFFs, aqueous, and solid matrices is presented in Figure B.2.

Figure B.1: Fluorine speciation and general approaches to the characterisation of fluorinated substances.





#### Annex B.2.1.1 Extraction from water

FFF concentrates and some heavily contaminated aqueous matrices require dilution before analysis for organofluorine analysis (Barzen-Hanson *et al.*, 2017; Martin *et al.*, 2019; Place and Field, 2012). However, most aqueous samples require only an extraction procedure, the most common of which is passage through a solid phase extraction (SPE) cartridge, where the organofluorine substances concentrate on the solid phase. A weak anion exchange cartridge has often been used, as it has been shown to be capable of retaining not only anionic PFAS but also at least some cationic and zwitterionic PFAS substances through secondary binding mechanisms (e.g. D'Agostino and Mabury, 2017a; Houtz *et al.*, 2016; Taniyasu *et al.*, 2005; Tsou *et al.*, 2023). Other types of solid phase have also been used for extraction of PFAS, for example polystyrenedivinylbenzene (US EPA, 2020) and phases with both hydrophilic / lipophilic properties (Taniyasu *et al.*, 2005). An alternative method is liquid-liquid extraction which has been used for example for groundwater samples, for example by Backe *et al.* (2013) and Barzen-Hanson *et al.* (2017).

#### Annex B.2.1.2 Extraction from soils/sediment and sludge

Extraction of organic substances from solid matrices can be carried out using a variety of solvents and extraction techniques, for example Soxhlet extraction, sonication, shaking, and accelerated solvent extraction (ASE). The extraction of organofluorine substances from soils, sediments, and sludges impacted with FFFs has often been based on shaking or sonication with a polar organic solvent such as

methanol modified with different acids or bases. The efficiency of extraction of PFAS from impacted soils has been compared for different solvents. For example, Mejia-Avendaño *et al.* (2017a) found that extraction of some fluorotelomer based PFAS was improved with methanol (MeOH) modified with sodium hydroxide (NaOH) compared to modification with ammonium hydroxide (NH<sub>4</sub>OH) but had the disadvantage of high detection limits. Munoz *et al.* (2018) concluded that MeOH / ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>) provided the most satisfactory extraction for a wide range of PFAS with limited matrix effects. Several reports have used NH<sub>4</sub>OH in MeOH (0.1% to 1.0%) for extraction of sediments (D'Agostino and Mabury, 2017a; Houtz *et al.*, 2013) and soils (Bräunig *et al.*, 2019; Mejia-Avendaño *et al.*, 2017b). There is also a draft EPA method (US EPA, 2024a) that uses 0.3% NH<sub>4</sub>OH in MeOH to extract solid samples in a general PFAS method.

#### Annex B.2.1.3 Clean-up and preparation of samples for analysis

Depending on the extent of co-extracted organic material in the samples and the analytical technique being used, there may be a need for sample clean up before analysis. Methods using weak anion exchange materials or graphitised non-porous carbon have been described (e.g. D'Agostino and Mabury, 2017a; Houtz *et al.*, 2016; Taniyasu *et al.*, 2005; Tsou *et al.*, 2023). The use of graphitised non-porous carbon, either in an SPE cartridge or added directly to the extract either before or after concentration, is a commonly reported clean up step for the extracts of FFF impacted matrices (D'Agostino and Mabury, 2017a; Houtz *et al.*, 2013).

The final step before analysis is either concentration and amendment with solvent, dilution with solvent, or evaporation and reconstitution in solvent. The solvent mixture depends on the analytical detection technique being used and the specific method of analysis.

#### **Annex B.2.2 Methods of analysis**

#### **Annex B.2.2.1 Total fluorine content**

The sample is homogenised if required and then analysed by combustion ion chromatography (CIC). The sample is placed onto a ceramic boat which is then introduced to a furnace at 900 to 1000 °C. Organofluorines are converted to hydrogen fluoride and converted to H<sup>+</sup> and F<sup>-</sup> on dissolution in the absorption unit. Fluoride ion content can then be determined by ion chromatography with detection by conductivity measurement (Aro *et al.*, 2021b) and will be the sum of organofluorine and inorganic fluorine in the sample.

#### Annex B.2.2.2 Inorganic fluorine

Inorganic fluorine can be determined directly in aqueous samples using ion chromatography (IC). Some sample clean-up may be required to remove interfering ions (e.g., Miyake *et al.*, 2007). Where inorganic fluorine has been separated from the organic fluorine, for example after an SPE procedure, then it can be measured by CIC in a similar way to total fluorine content.

Inorganic fluorine can also be determined without separation from organofluorine by ion selective electrode. Typically, the sample is mixed with a buffer solution to obtain a specified pH and ionic strength and then analysed using a fluoride ion-selective electrode under controlled conditions.

#### Annex B.2.2.3 Extractable organofluorine

An extraction procedure is carried out on the sample (see Annex B.2.1). The extract or a subsample of the extract is then placed onto a ceramic boat and analysed using CIC with the same method as described for total organofluorine. The extractable organofluorine (EOF) will be operationally defined by the type of extraction that is carried out and this may complicate any comparison of EOF between studies.

#### Annex B.2.2.4 Adsorbable organic fluorine

Adsorbable organic carbon (AOF) can be determined in aqueous samples using a specific extraction procedure. The sample is acidified with nitric acid / nitrate solution then passed through a SPE cartridge containing activated carbon. The cartridge is washed with nitric acid / nitrate and then the adsorbent transferred to a ceramic boat and analysed by CIC analysis (see Annex B.2.2.1). This approach has been described by various researchers (e.g. Wagner *et al.*, 2013; Willach *et al.*, 2016) and is also a US EPA method (US EPA, 2024b).

#### Annex B.2.2.5 Total oxidisable precursor assay

Degradation of many polyfluorinated substances such as fluorotelomers in the environment results in loss of the non-fluorinated moiety and formation of PFAAs with these substances referred to as PFAA precursors. Houtz and Sedlak (2012) proposed a method to quantify the total of 'difficult to measure and unidentified' PFCA and PFSA precursors in any sample by using hydroxyl radicals produced from thermolysis of persulfate under basic pH conditions, summarised in equations (1) and (2), to oxidise the precursors to PFCAs.

S<sub>2</sub>O<sub>8</sub><sup>2-</sup> + heat 
$$\longrightarrow$$
 2SO<sub>4</sub><sup>-</sup> equation (1)

SO<sub>4</sub><sup>-</sup> + OH<sup>-</sup>  $\longrightarrow$  SO<sub>4</sub><sup>2-</sup> + OH<sup>-</sup> equation (2)

The original method looked at PFAS in urban wastewater samples. Briefly, the water samples were amended with potassium persulfate and sodium hydroxide (10 N) and then heated in a water bath at 85 °C for 6 hours. After cooling to room temperature and addition of isotopically labelled standards, the pH was adjusted to between 5 and 9 using concentrated HCl and then samples extracted using a weak anion exchange solid phase extraction (SPE) cartridge. The eluent from the cartridge was evaporated to dryness and reconstituted in water: methanol (1: 1) before analysis by HPLC/MS-MS. It was found that C8 sulfonamide containing precursors were quantitatively transformed to PFOA but that fluorotelomer precursors produced a

suite of PFCAs of different chain lengths. The direct measurement of common precursors such as perfluorooctane sulfonamide and 8:2 fluorotelomer sulfonate accounted for less than 25% of the observed increase in PFOA on oxidation, indicating the presence of unknown precursors in the samples.

Houtz *et al.* (2013) applied the total oxidisable precursor (TOP) assay to FFFs and impacted soil and groundwater. There was a decline in precursors present in the impacted soil and groundwater compared to the original FFFs indicating that degradation of precursors was occurring naturally. There were still however unidentified precursors present in the soil and groundwater. The assay has been used for example at a site contaminated with FFFs to show the potential for future PFCA contamination and not just the present concentrations (McGuire *et al.*, 2014). Martin *et al.* (2019) showed that the TOP assay was amenable to the oxidation of neutral, zwitterionic, and cationic precursor substances to PFCAs. They observed significant contribution from precursors in groundwater impacted by FFFs. Liu *et al.* (2022) used the TOP assay as part of the investigation of PFAS contamination in soils and groundwaters and concluded that it was useful to estimate total PFAS and unknown precursors, and that it revealed that the background PFAS content in FFF impacted soils may have been underestimated.

There have been a number of reports of use of the TOP assay with modifications of the original method including increased concentration of oxidant or base to counteract high organic matter content in samples (Hutchinson *et al.*, 2020), lengthening the thermal activation time up to 20 h (Janda *et al.*, 2019; Neuwald *et al.*, 2022), addition of a <sup>13</sup>C labelled standard before the assay to verify precursor oxidation was complete (Tsou *et al.*, 2023), and extension of the analytical method to include ultrashort chain PFCAs trifluoroacetic acid and perfluoropropanoic acid (Janda *et al.*, 2019; Tsou *et al.*, 2023).

(Patch *et al.*, 2024) investigated several parts of the TOP assay with the aim of producing a robust quantitative method. Quenching of the reaction immediately with acetic acid / methanol instead of cooling and then quenching with HCl resulted in improved recoveries of PFOS. Addition of labelled PFOS after oxidation but before quenching allowed correction of the majority of the lost PFOS. Dilution of samples 10-fold with a 1:1 water / methanol solution after quenching also improved recovery of PFOS. The use of UV light instead of thermal activation of the oxidant resulted in substantially faster activation (93% within one hour, full activation within 4 hours compared to 86% in 6 hours with thermal activation). The UV activation also resulted in better preservation of the perfluoroalkyl chain in the precursor and improved PFAS yield.

#### Annex B.2.2.6 Total reducible organofluorine

Another method to investigate the unknown organofluorine substances present in a sample is the total reducible organic fluorine (TROF) assay (Fan *et al.*, 2022). This method is based on generation of hydrated electron production using a UV/sulfite

system under alkaline conditions. The hydrated electrons facilitate conversion of PFAS to inorganic fluoride which is then determined by ion chromatography. Measurement of fluoride concentrations before and after reduction allows determination of the TROF content of the sample. Fan *et al.* (2022) used this method to determine that targeted analysis and the TOP assay accounted for 0.12 to 54% of TROF for PFAS impacted environmental waters and 9.7 to 14% of TROF in PFAS impacted wastewaters. They concluded that the TROF assay could be used to infer whether contamination had occurred, the extent of contamination, and to estimate the fraction of uncharacterised PFAS.

#### **Annex B.2.2.7 Targeted sample analysis**

Targeted quantitative analysis can be carried out for substances where specific standards and suitable internal standards are available. It typically involves analysis by liquid chromatography (LC) with triple quadrupole (MS/MS) detection working in multiple reaction (MRM) mode where ideally at least two transitions are monitored for each analyte. Quantitative analysis has occasionally been extended to substances where no specific standard is available. For example, Houtz *et al.* (2013) used the calibration curves prepared from commercially available C6 homologues to estimate the concentrations of non-C6 homologues, correcting for the perfluorinated chain length; this allowed targeted analysis of 42 PFAS. Mejia-Avendaño *et al.* (2017b) carried out quantitative analysis by LC/MS/MS for 55 PFAS with authentic standards available and also semi-quantitatively analysed for a further 56 substances for which there was a standard available for one member of the homologue series.

#### Annex B.2.2.8 Non-targeted analysis

Non-targeted analysis can be carried out without prior separation, for example by fast atom bombardment (FAB) mass spectrometry (MS). However, liquid chromatographic separation followed by high resolution mass spectrometry is generally preferred for identification of unknown PFAS because of the sensitivity of the method. Accurate mass analysis allows elemental formulae to be determined, from which proposed structures can be identified (e.g., D'Agostino and Mabury, 2014). Another reported approach is to qualitatively search in high resolution full scan mode for structures of PFAS substances that have been previously reported and then to confirm identities from spectral information collected from fragmentation of a selected precursor ion with high resolution detection (Mejia-Avendaño et al., 2017a). A further systematic approach first screened molecular features against a database of PFAS structures with mass spectra already available then if no match was identified, priority features were identified by peak intensity, mass defect characteristic of fluorine, and homologous series with mass differences of 50 and 100 Da corresponding to -CF<sub>2</sub>- and -CF<sub>2</sub>- respectively. Unknown features were tentatively identified using a molecular formula generator which then led to proposed formulae. MS/MS fragmentation was then used to help propose structures consistent with the tentative formulae (Houtz et al., 2018).

#### **Annex C Degradation pathways**

## Annex C.1 Proposed degradation pathways of PFAS used in FFFs (examples)

Concern over the persistence and widespread occurrence of perfluorooctane sulfonate (PFOS) in the environment led to its replacement in firefighting foams by a wide variety of other fluorochemicals (Barzen-Hanson *et al.*, 2017; D'Agostino and Mabury, 2014), including fluorotelomers (FT). A large percentage of the organofluorine content of FT-based contemporary aqueous film forming foams have been found to be 6:2 fluorotelomers (Fang *et al.*, 2024; Moe *et al.*, 2012). Many of these novel fluoroalkylated surfactants have been detected in the environment after use of firefighting foams (Houtz *et al.*, 2018; Mejia-Avendaño *et al.*, 2017b).

The initial degradation of polyfluorinated substances, whether abiotic or biotic, usually starts with the functional groups in the non-fluorinated part of the chemical structure. Investigations of the degradation of PFAS in the environment have centred around measuring the presence of some of the suspected degradation products formed and from this presenting a proposed degradation pathway. Three example PFAS known to be used in FFF are presented here as case studies to demonstrate the potential degradation pathways to PFAA arrowheads based on published studies. These are 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB), 6:2 fluorotelomer thioether amido sulfonate (6:2 FtTAoS), and perfluoralkylsulfonamides. Structures for 6:2 FTAB and 6:2 FtTAoS are presented in Figure C.1. The pathways described generally do not distinguish between biotic and abiotic degradation.

Figure C.1: Structures of 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) and 6:2 fluorotelomer thioether amido sulfonate (6:2 FtTAoS).

## Annex C.1.1 Case study 1: Environmental degradation of 6:2 fluorotelomer sulfonamide alkylbetaine

The degradation of 6:2 FTAB (CAS no.: 34455-29-3) begins at the sulfonamide functional group. This degradation has been shown to lead to formation of 6:2 fluorotelomer sulfonamide (6:2 FTSAm) and 6:2 fluorotelomer alcohol (6:2 FTOH) in the presence of wastewater treatment plant sludge (D'Agostino and Mabury, 2017b). The same work suggested that there was a possibility that 6:2 fluorotelomer sulfonate (FTSA) could also be a degradation product but that relatively rapid biodegradation to 6:2 FTOH may have prevented it being present at a detectable concentration. 6:2 FTSA was observed in sterile controls, indicating abiotic degradation of 6:2 FTAB could lead to its formation. Shaw et al. (2019) investigated the degradation of 6:2 FTAB using Gordonia sp. strain NB4-1Y cultures, an environmentally ubiquitous bacteria that can be isolated from both soil and water. The study lasted seven days under sulfur-limited conditions and did not observe the formation of 6:2 FTSA. Fang et al. (2024) investigated the degradation in aerobic sludge of several PFAS substances found in firefighting foams and concluded that 6:2 FTSAm hydrolysis to FTSA was very limited. The biodegradation of 6:2 FTSA in activated sludge did not produce 6:2 FTOH (Wang et al., 2011b). Overall, there is little evidence for the formation of 6:2 FTSA on biodegradation. It is noted that Trouborst (2016) observed the formation 6:2 FTSA (as well as of 6:2 FTSAm) when investigating the aqueous photolysis of 6:2 FTAB in synthetic water (prepared waters with different dissolved organic matter, bicarbonate and nitrate ion concentrations, and at different pH values) using artificial light (290 to 800 nm).

The proposed initial degradation of 6:2 FTAB in environmental samples has been summarised by Zhang *et al.* (2021) and is presented in Figure C.2.

Figure C.2: Initial degradation of 6:2 FTAB

D'Agostino and Mabury (2017b) could not quantify the aerobic degradation rate of 6:2 FTAB in the presence of wastewater sludge but concluded that it was relatively slow: the formation of 6:2 FTOH after 109 days was less than 1% on a molar basis (compared to the parent substance) and total degradation product formation was less than 3% on a molar basis. Although Fang *et al.* (2024) found gradual disappearance of 6:2 FTAB from the test system with aerobic sludge over 100 days, the relative contribution of degradation and irreversible sorption could not be determined. Very low amounts of degradation products were seen and it was concluded that overall degradation of 6:2 FTAB was very slow. Trouborst (2016) found the photolytic degradation of 6:2 FTAB to be relatively rapid (< 5 days) in artificially prepared water containing dissolved organic matter. Overall, it seems that the initial degradation of 6:2 FTAB to 6:2 FTOH (Figure C.2) is likely to be slow under environmentally relevant conditions unless there is the possibility for aqueous photolysis to occur.

The degradation of 6:2 FTOH has been investigated in soil and aerobic sludge (Liu et al., 2010; Wang et al., 2012) and summarised by Liu and Mejia Avendano (2013) and Zhang et al. (2021). The proposed degradation pathway starts with transformation of the hydroxyl group of the fluorotelomer alcohol leading to 6:2 fluorotelomer aldehyde (6:2 FTAL) and then 6:2 fluorotelomer carboxylic acid (6:2 FTCA). The first loss of a fluorine atom then occurs as 6:2 fluorotelomer unsaturated carboxylic acid (6:2 FTUCA) is formed (Figure C.3). This degradation pathway has been proposed to occur in both soil and sludge (Liu and Mejia Avendano, 2013).

Figure C.3: Initial biodegradation of 6:2 FTOH; summarised in Ragnarsdottir *et al.* (2024).

Liu and Mejia Avendano (2013), drawing on other studies (Liu *et al.*, 2010; Wang *et al.*, 2012) proposed that the degradation of 6:2 FTUCA leads to the 5:2 ketone and then to perfluorohexanoic acid (PFHxA) via the secondary (s) alcohol 1-perfluoropentyl ethanol (5:2 sFTOH) (Figure C.4). The proposed degradation also includes the formation of perfluoropentanoic aicd (PFPeA) although it does not indicate the pathway. Shaw *et al.* (2019) proposed the formation of the 4:2 ketone from 5:2 sFTOH in what is effectively a chain shortening process (loss of CF<sub>2</sub>) and then PFPeA is formed from degradation of 4:2 ketone in a similar way to formation of PFHxA from the 5:2 ketone. The proposed pathway is summarised in Figure C.4.

There is also a proposed separate pathway of degradation of 6:2 FTUCA to the unsaturated acid 5:3 FTUCA and then the 5:3 fluorotelomer carboxylic acid (5:3 acid). Degradation of 5:3 FTUCA can also occur and leads to the formation of 5:2 FTUCA, another pathway that is effectively chain shortening degradation. The 5:2 FTUCA is then assumed to lead to the 4:2 ketone from which PFCAs including perfluorobutanoic acid (PFBA) are produced in a similar way to that described in Figure C.5.

Figure C.4: Biodegradation of 6:2 FTUCA to PFCAs (including chain shortening of x:2 ketones as intermediates in the formation of PFCAs.

$$F_{3}C \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{O}$$

$$6:2 \text{ FTUCA}$$

$$5:2 \text{ ketone}$$

$$F_{3}C \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{O} \xrightarrow{CH_{3}}$$

$$F_{3}C \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{O} \xrightarrow{CH_{3}}$$

$$F_{3}C \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{O} \xrightarrow{CH_{3}}$$

$$F_{3}C \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{O} \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{CH_{3}}$$

$$4:2 \text{ ketone}$$

$$via 4:2 \text{ sFTOH}$$

$$PFPEA$$

Figure C.5: Biodegradation of 6:2 FTUCA to PFCAs (including chain shortening to x:2 FTUCAs as intermediates in the formation of PFCAs).

$$F_{3}C \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{O} OH$$

$$F_{3}C \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} OH$$

$$F_{3}C \xrightarrow{F} \rightarrow OH$$

$$F_{3}C \xrightarrow{F} \xrightarrow{F} OH$$

$$F_{3}$$

The overall proposed degradation scheme for 6:2 FTAB is summarised in Figure C.6. 6:2 FTAB initially degrades to form 6:2 FTOH and then 6:2 FTUCA. The degradation of 6:2 FTUCA can then proceed via the 5:2 ketone or the 5:3 acid. The 5:2 ketone can form PFHxA or undergo chain shortening to the 4:2 ketone from which PFPeA is formed. The 5:3 acid forms 5:2 FTUCA (again chain shortening) from which the 4:2 ketone can be formed and then PFPeA. It is not clear if further chain shortening occurs by either route; this would lead to the formation of ultra short chain perfluoroalkyl carboxylic acids (PFCAs).

Figure C.6: Summary of the biodegradation of 6:2 FTAB.

Primary degradation of 6:2 FTOH has been observed to be relatively fast (< 2 days) in soil (Liu *et al.*, 2010), water-sediment systems (Zhao *et al.*, 2013a), and activated sludge (Zhao *et al.*, 2013b). The formation of transformation products was observed at relatively high molar percentage values compared to the starting 6:2 FTOH in these studies. For example, 6:2 FTCA, 6:2 FTUCA, and 5:2 sFTOH peaked on a molar basis at 23.5% (day 2), 7% (day 2), and 34.6% (day 28) respectively for a

sediment water system (Zhao *et al.*, 2013a). PFCAs were also observed from degradation of 6:2 FTOH. For example, the combined amounts of PFBA, PFPeA, and PFHxA reached 20.3% on a molar basis in the sediment water system at the end of the study at 100 days (Zhao *et al.*, 2013a). In a soil system (Liu *et al.*, 2010), the intermediate metabolites 6:2 FTCA, 6:2 FTUCA, and the 5:2 ketone all peaked at <10% on a molar basis and were non-detectable after day 7. At the end of the study after 180 days, on a molar basis, PFPeA (30%) and the 5:3 acid (15%) were the two dominant metabolites, while PFHxA (8.1%), 5:2 sFTOH (7.1%), and PFBA (1.8%) were also quantifiable.

#### Annex C.1.1.1 Metabolism of 6:2 FTAB in plants and wildlife

Zhao *et al.* (2022) investigated the behaviour of 6:2 FTAB in wheat seedlings, including biotransformation. After hydroponic exposure for 12 days, 6:2 FTAB was easily taken up into the roots. 6:2 FTSA accounted for a high proportion of all transformation products seen, which in total amounted to less than 6% on a molar basis. 6:2 FTCA was also observed along with a number of PFCAs. It was assumed that PFHpA was formed by  $\alpha$ -oxidation of 6:2 FTCA and shorter chain PFCAs (TFA to PFHxA) by  $\beta$ -oxidation (Figure C.7).

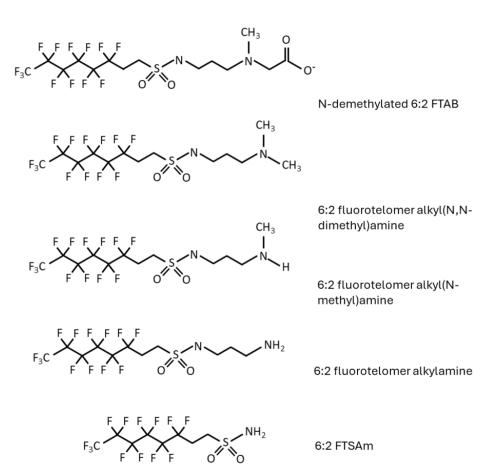
Figure C.7: Metabolism of 6:2 FTAB in wheat plants.

Moe *et al.* (2012) identified five metabolites of 6:2 FTAB in mussels (Figure C.8) that had been exposed in a laboratory study for 96 hours. The major metabolite formed (relative abundance of 94% of total identified metabolites) was the tertiary N,N-dimethylamine formed by deacetylation. The next most abundant was 6:2

fluorotelomer alkylamine (4%). The 6:2 fluorotelomer sulfonamide (2%) was also seen along with trace amounts of N-demethylated 6:2 FTAB and the secondary amine. By contrast, in juvenile turbot exposed to 6:2 FTAB for 48 hours, only the secondary and tertiary amines (56% and 32% respectively) and 6:2 FTSAm (12%) were observed.

The metabolism pathway was suggested to start either by decarboxylation followed by demethylation of the resulting quaternary amine or direct deacetylation, then demethylation of the tertiary amine. Although 6:2 FTSAm was observed, there was no evidence of further metabolism to PFCAs.

Figure C.8: Metabolites observed in mussels and/or turbot.



## Annex C.1.2 Case study 2: Degradation of 6:2 fluorotelomer thioether amido sulfonate

The presence of n:2 fluorotelomer thioether amido sulfonate (FtTAoS) has been reported in FFFs. Houtz et al. (2018) focussed on the most abundant of this series in FFFs (the 6:2 fluorotelomer, CAS: 88992-47-6) and identified the singly oxidised sulfinyl degradation product 6:2 fluorotelomer sulfinylamido sulfonate (6:2 FtSOAoS) in both influent and effluent from a sewage treatment works (design residence time of 3 hours) with much larger amounts in the effluent. The doubly oxidised 6:2 fluorotelomer sulfinylamido sulfonate (6:2 FtSO2AoS) was observed in the effluent but at lower concentrations than 6:2 FtSOAoS. 6:2 fluorotelomer sulfinyl propanoic acid (6:2 FtSOPA) was also observed in influent and effluent, again at much larger concentrations in the effluent. The further oxidised 6:2 fluorotelomer sulfonyl propanoic acid (6:2 FtSO<sub>2</sub>PA) was also observed in the effluent. No reaction rates were calculated but it was noted that 1.7% of the total PFAS in the influent (measured by the TOP assay) were converted to PFCAs in the effluent, with conversion occurring during the trickling filter and clarification section of the treatment. An initial degradation pathway for 6:2 FtTAoS was proposed by Houtz et al. (2018) and this has been extended to formation of PFCAs by Yan et al. (2024). Olivares et al. (2022) proposed a similar degradation pathway for 6:2 FtTAoS in microcosms of FFF impacted surficial solids. The half-life for 6:2 FtTAoS was 6.65 days with 6:2 FTSA the dominant transformation product after 20 days.

6:2 FTSA is assumed to degrade to 6:2 FTOH or directly to 6:2 FTAL. Further degradation then leads to PFCAs (e.g. Harding-Marjanovic *et al.*, 2015, and see case study 1). The proposed degradation scheme is presented in Figure C.9.

Figure C.9: Proposed initial degradation pathway for 6:2 FtTAoS.

The degradation of 6:2 FTSA has been investigated using pure bacterial strain *Gordonia* sp. strain NB4-1Y, known to be capable of degrading organosulfur compounds (Van Hamme *et al.*, 2013), and in activated sludge (Wang *et al.*, 2011b) (Annex C.1.1). In both cases, it was proposed that the initial degradation of 6:2 FTSA occurred by loss of HSO<sub>3</sub>- to form 6:2 FTAL directly, although 6:2 FTAL may not be seen as it quickly degrades to 6:2 FTUCA. However, other studies have presented evidence for the pathway to include degradation to 6:2 FTOH (Shaw *et al.*, 2019; Zhang *et al.*, 2016). There is evidence that degradation of 6:2 FTSA may be a rate limiting step in the degradation pathway to PFCAs, either because of a lack of specific sulfate reductases or the presence of other more easily assimilated sulfur sources (e.g. sulfate) in the environment that suppress desulfonation (Wang *et al.*, 2011b; Zhang *et al.*, 2016).

#### Annex C.1.3 Case study 3: Degradation of perfluoroalkyl sulfonamides

A range of perfluorinated sulfonamides have been identified in FFFs containing different substitutions of the amine group (e.g. Barzen-Hanson *et al.*, 2017; Place and Field, 2012). The degradation of a number of specific substances found in FFFs has been investigated and pathways of degradation proposed. The following examples consider substances with perfluorooctyl chains that are no longer commercially available but which illustrate degradation pathways that are relevant for similar substances with shorter perfluoroalkyl chains.

Mejia-Avendaño *et al.* (2016) investigated the degradation in soil microcosms of perfluorooctane sulfonamide quaternary salt (PFOSAmS), a cationic surfactant that appears in the patents of several FFFs. They proposed three pathways for the formation of PFOS from PFOSAmS from the confirmed or tentative identification of intermediates and by hypothesising others (Figure C.10). Two occur via the formation of perfluorooctane sulfonamide (FOSA) and one directly from PFOSAmS. It was noted that the degradation of PFOSAmS was slow during the 180-day study and a half-life was not calculated. PFOSAm was formed at approximately 10% on a molar basis early in the study and remained approximately constant until 180 days. No other intermediate exceeded 0.001% on a molar basis at any point in the study and the formation of PFOS only reached 0.003% on a molar basis after 180 days.

Figure C.10: Proposed biodegradation of PFOSAmS in soil.

The aerobic degradation of N-ethyl perfluorooctane sulfonamide (EtFOSE) in sludge has been described in a review by Liu and Mejia Avendano (2013) and illustrates how degradation of the amine sidechains leads to FOSA and then to the sulfonic acid PFOS (Figure C.11). Rhoads et al (2008) reported the half-life in activated sludge was less than 1 day (EtFOSE), 7.5 days (EtFOSA acid), 0.75 days (EtFOSA), 1.89 days (FOSA acid), and 9.2 days (FOSA).

Figure C.11: Proposed biodegradation of EtFOSE in sludge.

FOSA acid

OH

F<sub>17</sub>C<sub>8</sub>

$$=$$
 $=$ 

F<sub>17</sub>C<sub>8</sub>
 $=$ 
 $=$ 

F<sub>17</sub>C<sub>8</sub>
 $=$ 

Chen *et al.* (2020) demonstrated that perfluorooctane sulfonamido amine oxide (PFOSNO) degraded in aerobic surface soils to PFOS. Liu *et al.* (2021) proposed a degradation pathway for perfluorooctane sulfonamido betaine (PFOSB) in aerobic soil, again from identification of some transformation products.

Yan *et al.* (2024) summarised the proposed pathways of PFASAmS, PFASNO, and PFASB into a general degradation pathway for perfluoroalkyl sulfonamides, which is presented in Figure C.12. It demonstrates that for perfluoroalkyl sulfonamides, degradation in the environment is likely to lead to the eventual formation of arrowhead perfluoroalkyl sulfonic acids (Figure C.12).

Figure C.12: Initial degradation of three perfluoroalkyl sulfonamides to ETFASA

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#### **Annex C.1.4 Discussion and conclusion**

The case studies have illustrated the degradation pathways of three 6:2 fluorotelomer based PFAS substances found in FFFs and example pathways for the degradation of perfluorosulfonamides also found in FFFs. The information on rates of transformation were limited but there were some clear rate-limiting steps such as initial degradation of 6:2 FTAB to 6:2 FTOH, and the initial degradation of PFOSAmS. The general pattern in all cases is degradation of the non-fluorinated

part of the molecule, which eventually leads to the formation of PFAAs. Transformation processes typically start on the non-fluorinated part of the molecule. Rates are slow, but these processes will eventually lead, via intermediates, to highly stable fluorinated substances, referred to as 'terminal degradation products' or 'arrowheads'. Some shortening of the perfluorinated carbon chain can occur from fluorotelomer based precursors leading to the formation of a range of PFCAs.

Polyfluoroalkyl chains that contain C-H connections are fragile and prone to biotic or abiotic disintegration (Sharifan *et al.*, 2021), resulting in smaller PFAAs or related terminal transformation products, that are highly resistant to further transformation.

## Annex C.2 Consideration of terminal degradation products other than PFAAs

Classical PFCAs and PFSAs may not always be the terminal PFAA degradation products of PFAS. This is a consequence of regulatory actions targeting PFOS and PFOA, which resulted in the development of alternatives such as potassium 9-chlorohexadecafluoro-3oxanonane-1-sulfonate (F53-B) (Environment Agency, 2023b) and perfluoro(2-ethoxy-2-fluoroethoxy)-acetic acid, ammonium salt (EEA-NH4) (Environment Agency, 2023a). Commercial F-53B is dominated by 4:2, 6:2 and 8:2 chlorinated polyfluorinated ether sulfonic acid (CI-PFESA) components (Yao et al., 2020), and EEA-NH4 is a perfluoroalkyl ether carboxylic acid (PFECAs) (Figure C.13).

Oxygen atoms (and/or halogens other than fluorine) have been incorporated within the molecular backbones of such alternatives (Figure C.13), disrupting the continuous chains of perfluorinated carbons. The aim (by industry) was that the insertion of oxygen atoms would make the replacements more susceptible to degradation and less persistent. These substances are however still resistant to transformation under environmentally relevant conditions. PFESAs and PFECAs contain discrete x-CF<sub>2</sub>-x units (which falls in the definition of PFAS in this restriction (Section 1.2.5.4 in Annex 15 report). In particular, PFECAs containing repeating - CF<sub>2</sub>-O- units have been identified (Yao *et al.*, 2020). Figure C.13 presents the variation in associated examples of these structures including F53-B, EEA-NH4, and perfluoro-3,5,7-trioxaoctanoic acid (PFO3OA). As a consequence, PFAAs with up to two additional functional groups may be formed (i.e. a dicarboxylate), which would still be considered a PFAA.

Substances like these are not currently known to be used in FFFs and so are not directly considered in the environmental hazard assessment. However, it is viable that a manufacturer may develop a product based on similar chemistry in the future. We could expect such substances and their degradation products (terminal arrowheads) to have persistence and mobility properties analogous to the PFAAs (Lohmann *et al.*, 2020), due to their inherent similarity in structure – any PFAS

developed for FFFs would have the C-F bond by definition (resulting in persistence) and terminal degradation products would, by design, be of a small size (resulting in increased aqueous mobility potential).

Figure C.13: Structures of PFAS that may transform to non-simple PFAAs.

## Annex D Information on human health hazard and exposure

#### Annex D.1 Classification and Labelling

Screening of Annex VI of EU CLP (Regulation (EC) 1272/2008) (European Commission, 2008) to support the EU restriction of PFAS in firefighting foams ECHA (2023e) identified 43 substances with harmonised classification for carcinogenicity, mutagenicity, reproductive toxicity (including effects on or via lactation) and specific target organ toxicity (STOT RE), the health hazard endpoints with most concern following long term exposure of humans to PFAS. These substances are also included in the GB Mandatory Classification and Labelling (MCL) list with equivalent classifications under GB CLP.

Some of the substances identified during the screening exercise do not meet the OECD definition of PFAS and, therefore, are not considered further in this hazard assessment (e.g., trifluoroiodomethane). In addition, numerous biocide and pesticide active substances with a single (isolated) -CF<sub>3</sub> group were identified. Whilst these are likely to meet the OECD definition of PFAS, they are excluded from this hazard assessment because the hazardous properties of such substances are generally a function of the biological pathways being targeted rather than being specific to the fluorinated part of the molecule. Further, they are not expected to be of relevance to firefighting foams (unless they are used as a preservative). The remaining substances identified in the screening are listed in Table D.1 below.

Table D.1: PFAS (in scope of the hazard assessment) with mandatory classification in the GB MCL list

International Chemical Identification	Carbon chain length	EC No	CAS No	Classification		
PFCAs and precursors – long-chain PFCAs						
Nonadecafluorodecanoic acid; [1]  Ammonium nonadecafluorodecanoate; [2]  Sodium nonadecafluorodecanoate [3]  (PFDA and its sodium and ammonium salts)	10	206-400-3 [1] 221-470-5 [2] [3]	335-76-2 [1] 3108-42-7 [2] 3830-45-3 [3]	Carcinogenicity 2 Reproductive toxicity 1B (development) Effects on or via lactation		
Perfluorononan-1-oic acid [1] and its sodium [2] and ammonium [3] salts  (PFNA and its sodium and ammonium salts)	9	206-801-3 [1] [2] [3]	375-95-1 [1] 21049-39-8 [2] 4149-60-4 [3]	Carcinogenicity 2 Reproductive toxicity (1B development, 2 fertility) Effects on or via lactation Acute Tox. 4 Acute Tox. 4 STOT RE 1 (liver, thymus, spleen) Eye Damage 1		
Perfluorooctanoic acid (PFOA)	8	206-397-9	335-67-1	Carcinogenicity 2 Reproductive toxicity 1B (development) Effects on or via lactation Acute Tox. 4 Acute Tox. 4		

International Chemical Identification	Carbon chain length	EC No	CAS No	Classification		
				STOT RE <sup>\$</sup> 1 (liver) Eye Damage 1		
Ammonium pentadecafluorooctanoate APFO (PFOA Ammonium salt)	8	223-320-4	3825-26-1	Carcinogenicity 2 Reproductive toxicity 1B (development) Effects on or via lactation Acute Tox. 4 Acute Tox. 4 STOT RE\$ 1 (liver) Eye Damage 1		
Perfluoroheptanoic acid (PFHpA)	7	375-85-9	206-798-9	Reproductive toxicity 1B (development) STOT RE\$ 1 (liver)		
PFSAs and precursors – long-chain PFSA	PFSAs and precursors – long-chain PFSAs					
Perfluorooctane sulfonic acid;	8	217-179-8 [1] 220-527-1 [2]	1763-23-1 [1] 2795-39-3 [2]	Carcinogenicity 2 Reproductive toxicity 1B (development)		
Heptadecafluorooctane-1-sulfonic acid; [1]		274-460-8 [3] 249-415-0 [4]	70225-14-8 [3] 29081-56-9 [4]	STOT RE <sup>\$</sup> 1 Acute Tox. 4 *		
Potassium perfluorooctanesulfonate;		249-644-6 [5]	29457-72-5 [5]	Acute Tox. 4 * Effects on or via lactation		
Potassium heptadecafluorooctane-1-sulfonate; [2]				Aquatic Chronic 2		
Diethanolamine perfluorooctane sulfonate; [3]						

International Chemical Identification	Carbon chain length	EC No	CAS No	Classification
Ammonium perfluorooctane sulfonate;				
Ammonium heptadecafluorooctanesulfonate; [4]				
Lithium perfluorooctane sulfonate;				
lithium heptadecafluorooctanesulfonate [5]				
(PFOS and the potassium, ammonium, lithium and diethanolamine salts)				

<sup>\$</sup>STOT RE = specific target-organ toxicity - repeated exposure

Table D.2: PFAS (in scope of the hazard assessment) undergoing mandatory classification and labelling assessment under GB CLP

Substance name	EC number	CAS number	Proposed Classification	Progress
6:2 FTOH	211-447-1	647-42-7	STOT RE Cat. 2; H373 (Teeth and bones)	Agency opinion published August 2023
3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan- 1-ol				
PFHxA  undecafluorohexanoic acid, PFHxA [1]; sodium undecafluorohexanoate, NaPFHx [2]; ammonium undecafluorohexanoate, APFHx [3]; other inorganic salts of undecafluorohexanoic acid [4]	206-196-6[1]; 220-881-7[2]; 244-479-6[3]; - [4]	307-24- 4[1]; 2923- 26-4[2]; 21615-47- 4[3]; -[4]	Repro 1B; H360D (May damage the unborn child)	Technical report published by the Agency November 2024
TFA Trifluoroacetic acid	200-929-3	76-05-1	TBD	Draft
NaTFA [1] and other inorganic salts of trifluoroacetic acid [2]  Sodium trifluoroacetate and other inorganic	220-879-6 [1] - [2]	2923-18-4 [1] - [2]	TBD	Draft
salts of trifluoroacetic acid	700 000 0	000000	TDD	Draft
EEA-NH4  ammonium difluoro[1,1,2,2-tetrafluoro-2-(pentafluoroethoxy)-ethoxy]acetate	700-323-3	908020- 52-0	TBD	Draft

# **Annex D.2** Human health hazard assessment

### **Annex D.2.1** Human health hazard assessment

Table D.3: Summary of human health effects examined in available studies (adopted from HC, 2024)

PFAS groups	PFAS subgroups	Numbe r of PFAS with data	Effec t on body weig ht	Effect on kidney	Effect on immun e system	Effect on liver (except serum lipids)	Effect on reproduc- tion (except ED)	Effect on development (except ED and neurotoxicit y)	Effect on nervous system or neuro- development	Effect on endocrin e system - ED during develop- ment	Effect on endocrine system - Reproductiv e hormones	Effect on endocrin e system - Thyroid gland or hormone s	Effect on endocr ine system - Adrena I gland or hormo nes	Metabo lic disrupt ion - Serum lipids	Metabo lic disrupti on - Glucos e homeo- stasis
PFCAs	C1-C3	≤1	-	A +	A +	A +	A +	A +	-					-	
PFCAs	C4-C7	≤4	H + A +	H ++ A ++	H ++ A +	H+ A ++	H + A +	H ++ A ++	A ++	A +	H +	H ++ A ++		A ++	H ++
PFCAs	≥C8	≤9	H ++ A ++	H ++ A ++	H ++ A ++	H ++ A ++	H ++ A ++	H ++ A ++	H ++ A ++	H ++ A ++	H ++ A ++	H ++ A ++	A ++	H ++ A ++	H ++ A ++
PFSAs	C1-C3	≤1	-			A +	A +					-		A +	A +
PFSAs	C4-C7	≤3	H ++ A ++	H + A ++	H ++ A ++	H ++ A ++	H ++ A +	H ++ A ++	H + A +	A +	H ++ A+	H ++ A ++	A +	H ++ A ++	H ++
PFSAs	≥C8	≤2	H + A +	H ++ A +	H + A +	H + A +	H + A +	H + A +	H + A +	H + A +	H + A +	H + A +	A +	H + A +	H + A +
FASAs and derivatives	FASA	≤1	H+	-	Н+		H+	H+	H+		-	-			
FASAs and derivatives	Derivatives	≤6	H + A +	H + A +	A +	A ++	H + A ++	A ++	-		-	H ++ A +		A ++	H+
FT-based substance s	FTSA (n:2)	≤1	A +	A +		A +			-			-			
FT-based substance s	FTOH (n:2)	≤2	A ++	A ++	A ++	A ++	A +	A +	A +			A ++		A +	
FT-based substance s	FTCA (n:2 and n:3)	≤2	A +	A +	A +	A ++		-	+		-	A +		A +	
Ether- PFAS	PFESA	≤2	A +	H +		H + A +	A +	H+	-		-	A +		H + A +	H +
Ether- PFAS	PFECA	≤12	A ++	H ++ A ++	A ++	H ++ A ++	A +	A ++	1		-	A ++	A ++	H ++ A ++	A ++

#### Legend for Table D.3 above (reproduced from HC, 2024)

Note that carbon chain length refers to perfluorinated carbons.

A: animal data (statistically significant effect and/or adverse effect induced by PFAS); ED: endocrine disruption; H: human data (significant association with exposure to PFAS).

- -- No retrieved data indicating a PFAS-induced effect (A) or an association with exposure to PFAS (H) (that is, effect/association not observed, not evaluated, or not retrieved).
- + Recurrent Effect in the target observed for a single PFAS within the subgroup.
- ++ Recurrent Effect in the target observed for more than 1 PFAS within the subgroup.

**Bold** Indicates cases where (++) were attributed to both human and animal data.

Source: Information for C1-C3 PFCAs (that is, TFA) was taken from ECHA (2023c, 2024) Information for all other PFAS was adapted from Sanexen (2021)

## Annex D.2.2 Toxicokinetics (absorption, metabolism, distribution and elimination)

Table D.4: Summary of available biological half-lives for mouse, rat, monkey, pig and humans (adapted from HC, 2024)

PFAS Group	PFAS	Fully fluorinat ed C atoms (Total C atoms)	Mouse	Rat	Monkey	Pig	Human	Reference
PFCAs (Short Chain)	PFBA	3 (4)	hoursa	hours to days	days	-	days	Chang et al. 2008; Russell et al. 2015b
	PFPeA	4 (5)	-	hours	-	-	-	Choi et al. 2020
	PFHxA	5 (6)	hours	minutes to hours	hours to days	days	weeks	Noker 2001; Ohmori et al. 2003; Himmelstein et al. 2008; Chengelis et al. 2009a, 2009b; Gannon et al. 2009; Iwai 2011; Russell et al. 2013; Numata et al. 2014; Russell et al. 2015b Dzierlenga et al. 2020;
	PFHpA	6 (7)	-	hours	-	months	months to years	Zhang et al. 2013; Numata et al. 2014; Russell et al. 2015b; Xu et al. 2020a
PFCAs (Long Chain)	PFOA <sup>b</sup>	7 (8)	weeks	hours to weeks	weeks to months	months	years to decades	Hanhijärvi et al. 1988; Kemper 2003; Butenhoff et al. 2004a; Benskin et al. 2009; Costa et al. 2009; De Silva et al. 2009; Bartell et al. 2010; Brede et al. 2010; Fu et al. 2016; Gomis et al. 2016, 2017; Dzierlenga et al. 2020; and others <sup>c</sup>

	PFNA	8 (9)	months	days to months	-	-	years	Benskin et al. 2009; De Silva et al. 2009; Ohmori et al. 2003; Tatum-Gibbs et al. 2011; Zhang et al. 2013
	PFDA	9 (10)	-	months	-	-	years	Ohmori et al. 2003; Zhang et al. 2013
	PFUnDA	10 (11)	-	-	-	-	years to decades	Zhang et al. 2013
	PFDoDA	11 (12)	-	months	-	-	-	Kawabata et al. 2017a
PFSAs (Short Chain)	PFBS	4 (4)	hours	hours	hours to days	months	weeks to months	Chengelis et al. 2009a; Olsen et al. 2009; Numata et al. 2014; Rumpler et al. 2016; Huang et al. 2019a; Lau et al. 2020; Xu et al. 2020a
	PFPeS	5 (5)	-	-	-	-	months	Xu et al. 2020a
PFSAs (Long Chain)	PFHxS	6 (6)	weeks	days to weeks	months	years	years to decades	Olsen et al. 2007; Benskin et al. 2009; Zhang et al. 2013; Numata et al. 2014; Fu et al. 2016; Kim et al. 2016; Worley et al. 2017; Li et al. 2018a; Huang et al. 2019a; Sundstrom et al. 2012; Xu et al. 2020a
	PFHpS	7 (7)	-	-	-	years	years	Numata et al. 2014; Xu et al. 2020a
	PFOSd	8 (8)	weeks to months	weeks to months	months	years	years to decades	Seacat et al. 2002; Noker and Gorman 2003; Olsen et al. 2007; Benskin et al. 2009; De Silva et al. 2009; Chang et al. 2012; Numata et al. 2014; Fu et al. 2016; Kim et al. 2016; Gomis et al. 2017; Li et al. 2018a; Huang et al. 2019a; and otherse
FASAs and	FOSA	8 (8)	-	days	-	-	-	Ross et al. 2012

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derivative s								
FT- based	8:2 FTOH	8 (10)	-	hours	-	-	-	Fasano et al. 2006; Huang et al. 2019b
substan ces	5:3 Acid	5 (8)	-	weeks to months	-	-	months	Russell et al. 2015b; Kabadi et al. 2020
PFPAs	C6 PFPA	6 (6)	-	days	-	-	-	D'eon and Mabury 2010
	C8 PFPA	8 (8)	-	hours to days	-	-	-	D'eon and Mabury 2010; Joudan et al. 2017
	C10 PFPA	10 (10)	-	days	-	-	-	D'eon and Mabury 2010
PFPIAs	C6/C6 PFPiA	12 (12)	-	days	-	-	-	D'eon and Mabury 2010
	C6/C8 PFPiA	14 (14)	-	days	-	-	-	D'eon and Mabury 2010; Joudan et al. 2017
	C6/C10 PFPiA	16 (16)	-	days	-	-	-	D'eon and Mabury 2010
	C6/C12 PFPiA	18 (18)	-	days to weeks	-	-	-	D'eon and Mabury 2010
	C8/C8 PFPiA	16 (16)	-	days	-	-	-	D'eon and Mabury 2010; Joudan et al. 2017
	C8/C10 PFPiA	18 (18)	-	days to weeks	-	-	-	D'eon and Mabury 2010
PAPs	4:2 diPAP	8 (12)	-	days	-	-	-	D'eon and Mabury 2011

	6:2 diPAP	12 (16)	-	days	-	-	-	D'eon and Mabury 2011
	8:2 diPAP	16 (20)	-	days	-	-	-	D'eon and Mabury 2011
	10:2 diPAP	20 (24)	-	days	-	-	-	D'eon and Mabury 2011
PFECAs and PFESAs	6:2 CI-PFESA	7 (8)	-	days	-	-	years to decades	Shi et al. 2016; Yi et al. 2021
	6:2 H-PFESA	7 (8)	-	days	-	-	-	Yi et al. 2021
	ADONA	5 (7)	hours	hours to weeks	hours	-	weeks	3M 2007a, 2008a, 2008b, 2008c, 2010; Harlan Laboratories Ltd 2010
	EEA-NH4	6	-	hours	hours to days	-	-	AGC Chemical 2007a, 2007b
	HFPO-DA	5 (6)	hours to days	hours to days	hours to days	-	-	DuPont 2008b, 2011; Gannon et al. 2016
	PFO4DA	5 (6)	hours	-	-	-	-	Chen et al. 2021
	PFO5DoDA	6 (7)	months	-	-	-	-	Chen et al. 2021

Table D.5: Estimated serum half-lives in occupationally- or residentially-exposed people, taken from review data in Nilsson *et al.*, 2022 (Supplementary data Table S10) and Rosato *et al.*, 2024

Study	Study population and exposure scenario	Temporal setting	Type of half-life	Half-lives (Years) and Range/ Confidence Interval				
				PFOA	PFHxS	PFHpS	PFOS	
Nilsson et al., 2022	130 Firefighter staff, occupationally exposed to AFFF, 126 males, 4 females, (aged 27-66 at	First blood sample collected approximately 10 years after beginning of AFFF phase out.	Apparent  All participants <sup>1</sup>	<b>5.0</b> (95% CI, 4.7, 5.4)	<b>7.8</b> (95% CI 7.3, 8.3)	<b>7.4</b> (95% CI 6.8, 8.0)	<b>6.5</b> (95% CI 6.1, 6.9)	
	baseline).	Participants followed for 5 years.	Apparent  Participants with elevated PFAS levels <sup>2</sup>	<b>4.6</b> (95% CI 4.3, 4.9)	<b>7.7</b> (95% CI 7.1, 8.3)	<b>7.6</b> (95% CI 7.0, 8.2)	<b>6.5</b> (95% CI 6.1, 6.9)	
			Apparent  Participants without elevated PFAS levels <sup>3</sup>	<b>5.4</b> (95% CI 4.8, 5.9)	<b>8.2</b> (95% CI 6.7, 9.6)	<b>5.9</b> (95% CI 4.6, 7.3)	<b>6.7</b> (95% CI 4.5, 8.8)	
Li et al., 2022	114 residentially exposed community exposed to AFFF via contaminated drinking water, 56 males, 60 females (aged 4-84 at baseline).	First blood samples collected approximately 6 months after abrupt end of exposure through drinking water. Participants followed for approx. 5 years.	Half-life accounted for background PFAS levels and BMI <sup>4</sup>	<b>2.47</b> (95% CI 2.27, 2.7)	<b>4.52</b> (95% CI 4.14, 4.99)	<b>4.55</b> (95% CI 4.14, 5.06)	<b>2.73</b> (95% CI 2.55, 2.92) (L-PFOS)	

Study	Study population and exposure scenario	Temporal setting	Type of half-life	Hal	f-lives (Years) and R	ange/ Confidence Int	erval
				PFOA	PFHxS	PFHpS	PFOS
Xu et al., 2020	17 airport employees exposed to AFF contaminated drinking water, 11 males, 6 females (aged 24-62 at baseline).	First blood sample collected within 11-14 days after the termination of contaminated drinking water exposure, participants followed for 4 months.	Apparent <sup>5</sup>	<b>1.48</b> (95% CI 1.19, 1.96)	<b>2.84</b> (95% CI 2.08, 4.43)	<b>1.35</b> (95% CI 0.77, 5.71)	<b>1.69</b> (95% CI 0.98, 6.04) (L- PFOS)
Li et al., 2019	108 residentially exposed community exposed to AFFF via contaminated drinking water, 51 males, 57 females (aged 4-84 at baseline).	First blood samples collected approximately 6 months after abrupt end of exposure through drinking water. Participants followed for approx. 5 years.	N/A	<b>3</b> (95% CI 2.8, 3.2)	<b>4.7</b> (95% CI 4.3, 5.2)	<b>4.7</b> (95% CI 4.3, 5.3)	<b>2.9</b> (95% CI 2.7, 3.1)
Li et al., 2018	106 residentially exposed community exposed to AFFF via contaminated drinking water, (aged 4-84 at baseline). 20 males aged 15- 50 presented in this table, followed by male and female mean half-live from Rosato <i>et al.</i> , 2024.	First blood sample collected approximately 6 months after abrupt end of exposure through drinking water. Participants were followed for 27 months.	Apparent, accounting for age, sex and BMI <sup>6</sup>	2.8 (95% CI 2.4, 3.4) (male) 2.7 (95% CI 2.5, 2.9) (male and female)	7.4 (95% CI 6.0, 9.7) (male)  5.3 (95% CI 4.6, 6.0) (male and female)	-	<b>4.6</b> (95% CI 3.7, 6.1) (male) <b>3.4</b> (95% CI 3.1, 3.7) (male and female)

Study	Study population and exposure scenario	Temporal setting	Type of half-life	Hal	nge/ Confidence In	terval	
				PFOA	PFHxS	PFHpS	PFOS
Worley et al., 2017	45 individuals, exposed to PFAS contaminated environment: contaminated biosolid sludge and contaminated drinking water in private water well. 22 males, 23 females, mean age 62 at final collection.	First blood sample was collected three years after detection of contamination. Contamination may still have been ongoing during the sample period. Participants were followed for 6 years.	Apparent	<b>3.9</b> (range 3.5-4.1)	<b>15.5</b> (range 13.4-17.6)	-	<b>3.3</b> (range 3.0-3.6)
Olsen et al., 2007	26 Fluorochemical production workers. 24 male, 2 female aged 55-75 at baseline.	First blood sample was collected within 3 years of retirement from the fluorochemical production plant. Participants were followed for approximately 5 years.	Apparent	3.8 (range 3.1-4.4)  Geometric mean 3.5 (95% CI 3.0-4.1)	8.5 (range 6.4-10.6)  Geometric mean 7.3 (95% CI 5.8- 9.2)	-	<b>5.4</b> (range 3.9-6.9)  Geometric mean <b>4.8</b> (95% CI 4.0-5.8)
Costa et al., 2009`	16 formally exposed workers (PFOA production plant). 16 males, mean age 52 years.	Samples collected over 7 years, annually.		5.1 (range 2.6-9.7)  Geometric mean  4.8	-	-	-

- <sup>1</sup>Participants with longitudinal data, that had a decrease in concentration between the two serum collections.
- <sup>2</sup>Participants with initial serum PFAS concentrations greater than the 95<sup>th</sup> percentile of the general Australian population in 2016-17.
- <sup>3</sup>Participants without initial serum PFAS concentrations greater than the 95<sup>th</sup> percentile of the general Australian population in 2016-17.
- <sup>4</sup>Values presented by Nilsson *et al* (2022) have been replaced by reported half-lives after subtraction of background exposure presented based on Li *et al* data as reported in Rosato *et al* (2024) after review of the data given in the original paper (Li *et al.*, 2022) and review by Rosato *et al.*, (2024).
- <sup>5</sup>Sensitivity analysis accounted for general background PFAS levels and generally showed shorter half-lives. Average mean half-lives reported are after subtraction of background exposure (given in Rosato *et al.*, 2024 and original paper (Xu *et al.*, 2020) to align with reported half-lives with the subtraction of background exposure reported elsewhere in the table.
- <sup>6</sup>The apparent half-life is estimated after documented abrupt end of the dominating source of exposure, thus a reliable estimate of the 'actual' half-life.

Table D.6: Summary of available studies assessing serum PFAS concentrations based on ECHA (2023b) Table B.44 and updated with information from literature searches performed by the Agency in May 2024.

Studies with authors' names in **bold** were assessed by ECHA (Table B.44).

Reference	Study population	Comparison group	Geographic location	PFAS analysed	Sampling timefram e	Limitations identified by study authors	Reliability
Burgess et al. (2023)	N = 256 male, 31 female, Mean age 42	NHANES (N = 771 male , 99 female)	USA – 4 locations (unspecified)	Detected: PFHxS, n-PFOS, Sm-PFOS, n- PFOA, PFNA, PFDA, PFUnDA  Below LOD: Sb-PFOA, MeFOSSA	2016-2019	Lack of concurrent comparison data, leading to potential underestimation of serum PFAS levels in general population.	Reliable with limitations  Cross-sectional study. Analytical data are reliable.  Use of PPE not reported. Some estimation of duration of employment factored into analysis.  Results not consistent between the 4 locations used, potentially indicative of alternative

Reference	Study population	Comparison group	Geographic location	PFAS analysed	Sampling timefram e	Limitations identified by study authors	Reliability
							exposure scenarios or differing AFFF use.
Caban- Martinez et al. (2022)	N = 108 (94.4% male), Mean age 40.3	-	USA- Florida	PFBS, PFHpA, PFHxS, PFOA, PFNA, PFOS, PFOSA	Unknown	-	Unreliable  Cross-sectional study using non-probabilistic sampling. No control population reported. Incidental reporting of serum levels only, no further background information given.
Dobraca et al. (2015)	N = 101 (99 male, 2 female),	NHANES (2009-2010)	USA - California	PFOS, PFOA, PFHxS, PFNA, PFDA, PFHpA,	2010- 2011	Small sample population. Limited data on	Reliable

Reference	Study population	Comparison group	Geographic location	PFAS analysed	Sampling timefram e	Limitations identified by study authors	Reliability
	Mean age 42.8	Age 20+ years (N=876)		PFOSA, N- MeFOSAA, N- EtFOSSA, 2-(N- ethyl-PFOSA), PFUnDA, PFDoDA, PFBS		dietary history, or residential chemical exposure.  No consideration of exposure sources.	Cross-sectional analysis. Analytical data are reliable. Factors such as education, race, BMI and smoking taken into consideration. Sex is not a consideration as only 2 female participants, all data analysed without regard to sex. PPE is considered as a factor as well as duration of service.

Reference	Study population	Comparison group	Geographic location	PFAS analysed	Sampling timefram e	Limitations identified by study authors	Reliability
Gasiorowsk i <i>et al.</i> (2022)	N = 285 (279 male, 6 female), Mean age 53.0		Australia	PFOS, PFHxS, (26 further screened but only PFOA had sufficient data for analysis).	2019-2020	Data unsuitable to assess detailed kinetics due to sampling points. Small sample group.	Reliable with limitations  Longitudinal study. Analytical data are reliable. Open-label randomised clinical trial, targeted to participants with known serum PFOS levels of >5 ng/mL. Changes in serum PFAS levels after whole blood donation or plasma donation compared to background of participants with >5 ng/mL of PFOS but no intervention. Full

Reference	Study population	Comparison group	Geographic location	PFAS analysed	Sampling timefram e	Limitations identified by study authors	Reliability
							blood count, biochemistry, thyroid function and lipid profile also collected.
Goodrich et al. (2021)	N = 197 (176 male, 21 female), Mean age 38.6	NHANES 2015-16 (N= 1640, aged 20+)	USA – Arizona (N = 138), California (N= 52), Massachusett s (N=7)	PFHxS, n-PFOA, Sb-PFOA, n- PFOS, Sm- PFOS, PFNA, PFDA, PFUnDA, MeFOSAA	2016 - 2019	Small sample size – reducing statistical significance of data. Diversity of population studied – most white, non-Hispanic males. By analysing for long-chain and other PFAS used historically, this study may have missed current PFAS relevant to occupation.	Reliable  Cross-sectional study. Analytical data are reliable. Factors such as duration of service, age, BMI, smoking and ethnicity considered.  Use of PPE not reported.

Reference	Study population	Comparison group	Geographic location	PFAS analysed	•	Limitations identified by study authors	Reliability
Graber et al. (2021)	N = 135 (128 male, 7 female), Mean age 47	(2015/16 & 2017/18)	USA – New Jersey	Detected: PFDoDA, PFNA, PFDA, PFOS, MeFOSAA, PFHxS, PFOA, PFUnDA	2019	Community exposure to PFAS from industrial pollution.	Reliable  Cross-sectional study in volunteer firefighters. Analytical data are reliable. Factors considered include length of service, age, call outs (frequency), sex, race/ethnicity and education.  Use of PPE not reported. Assumption that there are similar exposures to AFFF between volunteer and career firefighters.

Reference	Study population	Comparison group	Geographic location	PFAS analysed	Sampling timefram e	Limitations identified by study authors	Reliability
							Analysis of societal status cross-referenced to PFAS levels.
Khalil <i>et al.</i> (2020)	N = 38 (100% male) Age 49-54	NHANES 2009-2010 N = 49	USA (Arizona)	Et-PFOSA-AcOH2, PFOSA-AcOH2, PFBS, PFDA, PFDoDA, PFHPA, PFHXS, PFNA, PFOSA, PFOSA, PFUNDA	2009	Small sample size used and geographical location (subset of larger study focusing on firefighters with >5 years' service). Limited contextual information such as length of service at sites such as airports and background levels of PFAS in drinking water.	Reliable with limitations  Cross-sectional study investigating PFAS and associations with carotid intimamedial thickness. Analytical data are reliable. Targeted, small sample size in a small geographical location.

Reference	Study population	Comparison group	Geographic location	PFAS analysed	Sampling timefram e	Limitations identified by study authors	Reliability
Leary et al. (2020)	N = 38 (100% male), Mean age 41	NHANES 2015-16 (data not shown) study control suburban firefighters (N=10). Mean age 28	USA (Ohio)	21 PFAS screened for in total. Serum PFAS values for PFOS, PFOA, PFHxS, PFNA.	Unknown	-	Reliable Cross-sectional study investigating a fire station associated with an airport vs control suburban firefighting service. Analytical data are reliable. Statistically significant difference in age between the 2 groups, but no other factors.
Nematollahi et al. (2024)	N = 154 (25 female incumbents, 74 male incumbents,	-	US (Arizona)	PFHxS, n-PFOS, Sm-PFOS, n- PFOA, Sb- PFOA, PFNA,	2015- 2018	Limitations include focus on a small number of PFAS, no consideration of	Reliable with limitations  Cross-sectional analysis between

Reference	Study population	Comparison group	Geographic location	PFAS analysed	Sampling timefram e	Limitations identified by study authors	Reliability
	52 male recruits plus 3 female recruits)			PFDA, PFUnDA, MeFOSSA,		training time in relation to PFAS exposure and no consideration of PFAS via turnout gear or dust and other environmental routes. No assessment of longitudinal changes in female recruits due to low sample number.	firefighters based on exposure, followed by longitudinal assessment of PFAS levels in recruits. Analytical data are reliable. Analysis of fire attendance taken into consideration for recruits. Use of PPE not reported.
Nilsson et al. (2022)	N=799 (779 male, 20 female),	General population of Australia from Toms <i>et al.</i> (2019)	Australia	40 analysed.  9 detected in >15% of participants: PFHpA, PFOA,	2018- 2019	Longitudinal study had a smaller sample size than the cross-sectional.	Reliable  Longitudinal study and cross-sectional study using previous

Reference	Study population	Comparison group	Geographic location	PFAS analysed	Sampling timefram e	Limitations identified by study authors	Reliability
	Mean age = 52			PFNA, PFDA, PFUnDA, PFBS, PFHxS, PFHpS, PFOS		Unable to study non-linear kinetics due to only 2 sample points.  Due to self-reporting and complex employment history, grouping of exposure was difficult. No directly comparable reference population.	participants of a cross-sectional study. Analytical data are reliable. Study identifies that transitioning away from AFFF is associated with decreased serum PFAS levels.  Use of PPE not reported.
Rihackova et al. (2023)	N= 111 – 59 new recruits (100% male), 52 professional s (100% male)	General population N=55 (100% male), Mean age 26	Czech Republic	PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFBA, PFHxS, PFHpS, PFOS	2019- 2020	All participants white males aged 18-35. Lack of exposure information such as previous employment.	Reliable with limitations  Longitudinal study for new trainees with cross-sectional samples for

Reference	Study population	Comparison group	Geographic location	PFAS analysed	Sampling timefram e	Limitations identified by study authors	Reliability
						Low participant numbers.	professional and control groups. Analytical data are reliable. No female participants. Factors such as occupational and lifestyle (smoking/genera I health assessment) considered. Consideration to PPE was given.
Rotander et al. (2015)	N = 149	General population of Australia and Canada. Some work comparing to fluorosurfactan t chemical	Australia	PFAS detected above LOD: PFOS, PFHxS, PFOA, PFHpA, PFNA, PFDA, PFUnDA, PFDoDA,	2013	Other routes of exposure not captured, such as during training or in the local environment.	Reliable Cross-sectional study. Analytical data are reliable. Considerations for factors such as age, sex, race as well as

Reference	Study population	Comparison group	Geographic location	PFAS analysed	Sampling timefram e	Limitations identified by study authors	Reliability
		workers (Olsen, 2003)		PFTrDA, PFBS, PFDS			lifestyle (diet, alcohol consumption, exercise) and estimated foam exposure and career history.  Use of PPE not reported.
Tefera <i>et al.</i> (2023)	N=130 (125 male, 4 female), Mean age, 53	-	Australia (South Australia)	28 PFAS screened. Only PFOS, PFHxS, PFOA data was analysed.	2018-2022	Only 2 time points analysed, more frequent sampling required to ascertain PFAS kinetics in serum.  Variables such as blood donation not captured.	Reliable  Longitudinal study. Analytical data are reliable. Takes into account service, employment, PFAS use situations and previous exposure, as well as age and gender. Duration of exposure to

Reference	Study population	Comparison group	Geographic location	PFAS analysed		Limitations identified by study authors	Reliability
						Small sample size.	foams considered as well as activities such as training participation. Regression modelling used to calculate changes in ΣPFAS and PFOA. Use of PPE not reported.
Trowbridg e et al. (2020)	N=86 (100% female), Mean age 47.5	Office workers  – N=84 (100% female), mean age 48.3	US (California)	PFBS, PFHxS, PFHpA, PFOA, PFOS, PFOSA, PFNA, PFDA, PFUnDA, PFDoDA, PFBA, PFHxA	2014- 2015	Female only participants.  Unknown sources of PFAS exposure. Unknown PFAS in foam concentrate. Small sample size.	Reliable with limitations  Women Firefighters Biomonitoring Collaborative, no male participants.  Cross-sectional study with

Reference	Study population	Comparison group	Geographic location	PFAS analysed	Sampling timefram e	Limitations identified by study authors	Reliability
Zheng <i>et al.</i> (2023)	N=81 (36% male, 64% female) 25-88 years, mean age 49 ±16 years	Paired samples of drinking water and dust from households in Indiana. Blood, serum and	Residential homes, Indiana, US	47 PFAS, including 23 PFAAs (14 PFCAs and (PFSAs) and 24 Precursors (3 FTSAs, 7	August – December 2020	Small sample size, with limited diversity in cohort and small geographic coverage.	adjustments for age, race, ethnicity diet and education. Geographically similar locations of sampling. Reliable with limitations Cross-sectional study but small cohort with small geographic
	Note: no participants had occupational PFAS exposure e.g., fire	urine samples from residents.		FOSAs, 7 FOSAs/FOSEs, 5 PAPs, 4 FTOHs and 5 FTACs/FTMACs		Unable to account for contribution of diet.  Biotransformation of PFAA precursors or fluorinated pharmaceuticals	coverage – also exclusion of occupational exposure to PFAS in the sample group.  Issues with standards being available for TFA for analyses,

Reference	Study population	Comparison group	Geographic location	PFAS analysed	Sampling timefram e	identified by study authors	Reliability
	fighters/fire stations.					to total body burden.	also C2-C5 PFAAs potentially coelute in mass spectrometry analyses.  Study finds substantial prevalence of ultrashort (C2- C3) PFAAs in US indoor environment and general population.

# Annex D.2.3 Human-health hazards of components of fluorine-free foam products identified through stakeholder engagement as being on the GB market

Table D.7: Human-health and environmental hazard classifications of components of fluorine-free foam products identified through stakeholder engagement as being on the GB market

Manufacturer	Product name	Ingredient	CAS RN	EC No	Conc (%)	Harmonised HH Classification (EU CLH)	Notified or Registrant HH self- classification	GB MCL HH	ENV hazard classification from ECHA C&L Inventory
Angus Fire	Expando I 3%	2-butoxyethanol	111-76-2	203-905-0	10 - < 25%	Acute Tox. 3 (Inh): H331 Acute Tox. 4 (Oral): H302 Skin Irrit 2: H315 Eye Irrit. 2: H319		Acute Tox. 4* (Inh): H332 Acute Tox. 4 (oral): H302 Skin Irrit. 2: H315 Eye Irrit. 2: H319	
		Sodium laureth sulfate	68891-38-3	500-234-8	4 - < 10%		Skin Irrit. 2: H315 Eye Dam. 1: H318		
		Butanedioic acid, 2(or 3)-sulfo, 4-[2-[(1- oxododecyl)ethyl]est er, sodium salt	75081-73-1	939-648-2	1 - < 10%		Skin Irrit. 2: H315 Eye Irrit. 2: H319		
		1-dodecanol	112-53-8	203-982-0	1 - < 4%		Eye Irrit. 2: H319		Aquatic Acute 1 Aquatic Chronic 2
		1-tetradecanol	112-72-1	204-000-3	0.1 - 1%		Not classified		Aquatic Acute 1 Aquatic Chronic 1
DrSthamer	Sthamex K1% F15	2-(2- butoxyethoxy)ethanol	112-34-5	203-961-6	< 15%	Eye Irrit. 2: H319		Eye Irrit. 2: H319	
		1-butoxy-2-propanol	5131-66-8	225-878-4	< 15%	Eye Irrit. 2: H319 Skin Irrit. 2: H315		Eye Irrit. 2: H319 Skin Irrit. 2: H315	

Manufacturer	Product name	Ingredient	CAS RN	EC No	Conc (%)	Harmonised HH Classification (EU CLH)	Notified or Registrant HH self- classification	GB MCL HH	ENV hazard classification from ECHA C&L Inventory
		Sodium- alkylethersulfate	73665-22-2	161025- 28-1	< 20%		Skin Irrit. 2: H315 Eye Dam. 1: H318		
		Sodium-alpha-olefin sulfonate	68439-57-6	931-534-0	< 15%		Skin Irrit. 2: H315 Eye Dam. 1: H318		
		Sodium alkylsulfosuccinate	577-11-7	209-406-4	< 5%		Skin Irrit. 2: H315 Eye Dam. 1: H318		
3F	Freegen SF-LV	Alkylsulfate	85338-42-7	286-718-7	5 - <10%		Acute Tox. 4: H302 Skin Irrit. 2: H315 Eye Dam. 1: H318		
		Alkylethersulfate	68891-38-3	500-234-8	1 - < 5%		Skin Irrit. 2: H315 Eye Dam. 1: H318		
Cross Plains Solutions	SOYFO AM TF- 1122	Cocamidopropyl betaine	61789-40-0	263-058-8	17 – 32%		Skin Irrit. 2: H315 Skin Sens. 1: Eye Irrit. 2: H319		Aquatic Chronic 3
		N-butanol	71-36-3	200-751-6	3 - <7%	Acute Tox. 4: H302 Skin Irrit. 2: H315 Eye Dam. 1: H318 STOT SE3: H335, H336		Acute Tox. 4: H302 Skin Irrit. 2: H315 Eye Dam. 1: H318	
	ReHeali ng RF1 1%	D-glucopyranose, oligomers, decyl octyl glycosides	68515-73-1	500-220-1	< 3%		Eye Dam. 1: H318		
Solberg		Sodium octyl sulfate	142-31-4	205-535-5	< 10%		Skin Irrit. 2: H315		

Manufacturer	Product name	Ingredient	CAS RN	EC No	Conc (%)	Harmonised HH Classification (EU CLH)	Notified or Registrant HH self- classification	GB MCL HH	ENV hazard classification from ECHA C&L Inventory
							Eye Dam. 1: H318		
		Sodium decyl sulfate	142-87-0	205-568-5	< 3%		Acute Tox. 4: H302 Skin Irrit. 2: H315 Eye Dam. 1: H318		Aquatic Chronic 3
		alpha-sulfo-omega- hydroxy-poly(oxy- 1,2-ethanediyl), C9- 11 alkyl ethers, sodium salts ( -)	96130-61-9		< 3%		Substance not found in ECHA C&L Inventory		Substance not found in ECHA C&L Inventory
		1-Propanaminium, N- (3-aminopropyl)-2- hydroxy-N,N- dimethyl-3-sulfo-, N- coco acyl derivs., hydroxides, inner salts	68139-30-0	268-761-3	0.1 - < 1%		Eye Irrit. 2: H319		Aquatic Acute 1 Aquatic Chronic 2
		Amides, coco, N-[3- (dimethylamino)prop yl]	68140-01-2	268-771-8	< 0.2%		Skin Irrit. 2: H319 Eye Dam. 1: H318		Aquatic Acute 1
		1-propanaminium, 3- amino-N (carboxymethyl)-N,N- dimethyl-, N- coco acyl derivs., hydroxides, inner salts (-)	61789-40-0	263-058-8	0.1 - < 1%		Skin Irrit. 2 Skin Sens. 1 Eye Irrit. 2		Aquatic Chronic 3

Manufacturer	Product name	Ingredient	CAS RN	EC No	Conc (%)	Harmonised HH Classification (EU CLH)	Notified or Registrant HH self- classification	GB MCL HH	ENV hazard classification from ECHA C&L Inventory
		Amides, coco, N-[3- (dimethylamino)prop yl], N-oxides	68155-09-9	268-938-5	< 1%		Acute Tox. 4 (oral): H302 Skin Irrit. 2: H315 Eye Dam. 1: H318 STOT RE 2: H373 (liver, spleen)		
		Sucrose	57-50-1	200-334-9	> 1%		Not classified	Not classified	
		2-(2- butoxyethoxy)ethanol	112-34-5	203-961-6	20 - < 40	Eye Irrit. 2: H319		Eye Irrit. 2: H319	
		Sulfuric acid, mono- C12-14-alkyl esters, compds. with triethanolamine	90583-18-9	292-216-9	< 10%		Acute Tox. 4 (oral): H302 Skin Irrit. 2: H315 Eye Dam. 1: H318		Aquatic Chronic 3
	Rehealin g RF3	2-(2- butoxyethoxy)ethanol	112-34-5	203-961-6	20 - < 40%	Eye Irrit. 2: H319		Eye Irrit. 2: H319	
	3x3	Ethanediol	107-21-1	203-473-3	5 - < 20%	Acute Tox. 4 (oral): H302	Acute Tox. 4: H302 STOT RE 2: H373 (kidney) (oral)	Acute Tox. 4: H302	
		Sodium p- cumenesulfonate	15763-76-5	239-854-6	1- < 5%		Eye Irrit. 2: H319		
		D-glucopyranose, oligomers, decyl octyl glycosides	68515-73-1	500-220-1	0.5 - < 3%		Eye Dam. 1: H318		

Manufacturer	Product name	Ingredient	CAS RN	EC No	Conc (%)	Harmonised HH Classification (EU CLH)	Notified or Registrant HH self- classification	GB MCL HH	ENV hazard classification from ECHA C&L Inventory
		1-Propanaminium, N- (3-aminopropyl)-2- hydroxy-N,N- dimethyl-3-sulfo-, N- coco acyl derivs., hydroxides, inner salts	68139-30-0	268-761-3	0.1 - < 1%		Eye Irrit. 2: H319		Aquatic Acute 1 Aquatic Chronic 2
	3% Mil- Spec	2-(2- butoxyethoxy)ethanol	112-34-5	203-961-6	5 - < 10%	Eye Irrit. 2: H319		Eye Irrit. 2: H319	
	SFFF	(carboxymethyl)dimet hyl-3-[(1- oxododecyl)amino]pr opylammonium hydroxide	4292-10-8	224-292-6	1 - < 5%		Eye Dam. 1: H318		Aquatic Chronic 3
		Sulfonic acids, C14- 16-alkane hydroxy and C14-16-alkene, sodium salts	68439-57-6	270-407-8	1 - < 5%		Skin Irrit. 2: H315 Eye Dam. 1: H318		
		Dodecyldimethylamin e oxide	1643-20-5	216-700-6	1 - < 5%		Acute Tox 4. (oral): H302 Skin Irrit. 2: H319 Eye Dam. 1: H318		Aquatic Acute 1 Aquatic Chronic 2
		Sulfuric acid, mono- C12-14-alkyl esters, compds. with triethanolamine	90583-18-9	292-216-9	0.5 - < 3%		Acute Tox 4. (oral): H302 Skin Irrit. 2: H319 Eye Dam. 1: H318		Aquatic Chronic 3
		Sodium octyl sulfate	142-31-4	205-535-5	0.5 - < 3%		Skin Irrit. 2: H315 Eye Dam. 1: H318		

\*Information from manufacturer's SDS (substance not found in ECHA C&L Inventory)

Table D.8: Hazard classification information for substances identified in F3 products (Sources: stakeholder engagement, Jahura et al. (2024) and Wood et al. (2020))

Substance	CAS RN	EC No	HH Hazard Classification	ENV Classification from ECHA C&L Inventory
alkylamidobetaine <sup>†</sup>	147170-44-3	604-575-4	Eye Dam. 1	Aquatic Chronic 3
alkylethersulfate	68891-38-3	500-234-8	Skin Irrit. 2: H315 Eye Dam. 1: H318	-
alkylsulfate	85338-42-7	286-718-7	Acute Tox. 4: H302 Skin Irrit. 2: H315 Eye Dam. 1: H318	-
alpha-sulfo-omega-hydroxy-poly(oxy- 1,2-ethanediyl), C9-11 alkyl ethers, sodium salts (-)	96130-61-9	-	Substance not found in ECHA C&L Inventory	Substance not found in ECHA C&L Inventory
amides, coco, N-[3- (dimethylamino)propyl]	68140-01-2	268-771-8	Skin Irrit. 2: H319 Eye Dam. 1: H318	Aquatic Acute 1
amides, coco, N-[3- (dimethylamino)propyl], N-oxides	68155-09-9	268-938-5	Acute Tox. 4 (oral): H302 Skin Irrit. 2: H315 Eye Dam. 1: H318 STOT RE 2: H373 (liver, spleen)	-
butanedioic acid, 2(or 3)-sulfo, 4-[2-[(1-oxododecyl)ethyl]ester, sodium salt	75081-73-1	939-648-2	Skin Irrit. 2: H315 Eye Irrit. 2: H319	-
N-butanol	71-36-3	200-751-6	Acute Tox. 4: H302 Skin Irrit. 2: H315 Eye Dam. 1: H318 STOT SE 3: H335, H336	-
2-butoxyethanol	111-76-2	203-905-0	Acute Tox. 3 (Inh): H331 Acute Tox. 4 (Oral): H302	-

			Skin Irrit 2: H315 Eye Irrit. 2: H319	
2-(2-butoxyethoxy)ethanol	112-34-5	203-961-6	Eye Irrit. 2: H319	-
1-butoxy-2-propanol	5131-66-8	225-878-4	Eye Irrit. 2: H319 Skin Irrit. 2: H315	-
(carboxymethyl)dimethyl-3-[(1-oxododecyl)amino]propylammoniumhydroxide	4292-10-8	224-292-6	Eye Dam. 1: H318	Aquatic Chronic 3
N,N-dimethyl-1-tetradecanamine-N-oxide <sup>†</sup>	3332-27-2	222-059-3	Acute Tox. 4 Skin Irrit. 2 Eye Dam. 1	Aquatic Acute 1 Aquatic Chronic 2
1-dodecanol	112-53-8	203-982-0	Eye Irrit. 2: H319	Aquatic Acute 1 Aquatic Chronic 2
dodecyldimethylamine oxide	1643-20-5	216-700-6	Acute Tox 4. (oral): H302 Skin Irrit. 2: H319 Eye Dam. 1: H318	Aquatic Acute 1 Aquatic Chronic 2
ethanediol	107-21-1	203-473-3	Acute Tox. 4 (oral): H302 STOT RE 2: H373 (kidney) (oral)	-
D-glucopyranose, oligomers, decyl octyl glycosides	68515-73-1	500-220-1	Eye Dam. 1: H318	-
1-propanaminium, 3-amino-N (carboxymethyl)-N,N-dimethyl-, N- coco acyl derivs., hydroxides, inner salts (-)	61789-40-0	263-058-8	Skin Irrit. 2: H315 Skin Sens. 1: Eye Irrit. 2: H319	Aquatic Chronic 3
1-Propanaminium, N-(3-aminopropyl)-2- hydroxy-N,N-dimethyl-3-sulfo-, N-coco acyl derivs., hydroxides, inner salt	68139-30-0	268-761-3	Eye Irrit. 2: H319	Aquatic Acute 1 Aquatic Chronic 2
sodium-alkylethersulfate	73665-22-2	161025-28-1	Skin Irrit. 2: H315 Eye Dam. 1: H318	-
sodium alkylsulfosuccinate	577-11-7	209-406-4	Skin Irrit. 2: H315 Eye Dam. 1: H318	-

sodium p-cumenesulfonate	15763-76-5	239-854-6	Eye Irrit. 2: H319	-
sodium-alpha-olefin sulfonate	68439-57-6	931-534-0	Skin Irrit. 2: H315 Eye Dam. 1: H318	-
sodium decyl sulfate	142-87-0	205-568-5	Acute Tox. 4: H302 Skin Irrit. 2: H315 Eye Dam. 1: H318	Aquatic Chronic 3
sodium dodecyl sulfate <sup>†</sup>	151-21-3	205-788-1	Acute Tox. 4 Skin Irrit. 2 Eye Dam. 1	Aquatic Chronic 3
sodium octyl sulfate	142-31-4	205-535-5	Skin Irrit. 2: H315 Eye Dam. 1: H318	-
sucrose	57-50-1	200-334-9	Not classified	Not classified
sulfonic acids, C14-16-alkane hydroxy and C14-16-alkene, sodium salts	68439-57-6	270-407-8	Skin Irrit. 2: H315 Eye Dam. 1: H318	-
sulfuric acid, mono-C12-14-alkyl esters, compds. with triethanolamine	90583-18-9	292-216-9	Acute Tox. 4 (oral): H302 Skin Irrit. 2: H315 Eye Dam. 1: H318	Aquatic Chronic 3
1-tetradecanol	112-72-1	204-000-3	Not classified	Aquatic Acute 1 Aquatic Chronic 1
triethanol ammonium- laurylsulfate <sup>†</sup>	85665-45-8	288-134-8	Acute Tox. 4 (Oral, Inh): H302, H332 Skin Irrit. 2: H315 Eye Dam. 1: H318 STOT SE 3: H335 (respiratory irrit.)	Aquatic Chronic 3

Mandatory / harmonised classifications shown in bold

<sup>&</sup>lt;sup>†</sup> substances identified in Jahura *et al.* (2024) and/or Wood (2020)

# Annex D.3 Human health exposure literature search strategy

A targeted literature search using the Proquest and Web of Science platforms was carried out in May 2024 for the period 2019 onwards. The following search terms were used:

PFAS or fluorochemical\* or "per- and polyfluoroalkyl" or "perfluoroalkyl" or "polyfluoralkyl" or "fluorinated" or \*perfluoro\* or fluorotelemer\* or "aqueous film forming foam" or \*AFFF\* or FFF or "AR-FFF" or F3 or 3F or "fluorine-free" or FP or "fluoro-protein foam" or FFFP or fluoroprotein or "AR-AFFF" or "AR-FFFP" or FPAR or 3M or "Angus Fire" or "OneSeven B-AR" or "ARC Miljö" or Towalex or Sthamex or STHMEX\* or "F-500" or Fomtec or Fomtex or Ansul\* or "National Foam" or Forafac or PROFOAM or NOVEC or Buckeye or Chemquard or Fireade or Chemours or DuPont or GenX or "Gen X" or Adona or "F-53B" or "355-46-4" or "375-92-8" or "1763-23-1" or "68259-12-1" or "335-77-3" or "749786-16-1" or "335-67-1" or "375-95-1" or "335-76-2" or "2058-94-8" or "307-55-1" or "72629-94-8" or "376-06-7" or "16517-11-6" or "354-88-1" or "423-41-6" or "375-73-5" or "2706-91-4" or "375-22-4" or "2706-90-3" or "307-24-4" or "375-85-9" or "13417-01-1" or "167398-54-1" or "647-29-0" or "2991-50-6" or "1336-61-4" or "4151-50-2" or "68298-12-4" or "2806-24-8" or "754-91-6" or "10116-92-4" or "2355-31-9" or "24448-09-7" or "68555-77-1" or "80475-32-7" or "133875-90-8" or "34455-35-1" or "53826-13-4" or "70887-84-2" or "278598-45-1" or "757124-72-4" or "1432486-88-8" or "171184-02-4" or "171184-14-8" or "34455-29-3" or "647-42-7" or "27619-97-2" or "1383438-86-5" or "88992-47-6" or "88992-46-5" or "171184-03-5" or "171184-15-9" or "27854-31-5" or "34455-21-5" or "39108-34-4" or "1383439-45-9" or "171184-04-6" or "171184-16-0" or "1280222-90-3" or "756-13-8" or "161278-39-3" or "70969-47-0" or "70829-87-7" or "13269-86-8" or "34455-29-3" or "80475-32-7" or "62880-93-7" or "88992-45-4" or "76830-12-1" or "34455-29-3" or PFHxS or PFHpS or PFOS or PFNS or PFDS or PFUnDS or PFOA or PFNA or PFDA or PFUnDA or PFDoDA or PFTrDA or PFTeDA or PFODA or PFEtS or PFPrS or PFBS or PFPeS or PFBA or PFPeA or PFHxA or PFEA or FASA or PASF or PBSF or POSF or PFPiA or PTFE or PEPE or ETFE or FEP or PVDF or PFA or PAF or PFPE or PFHxI or POF or PFAI or PENAL or PFAL or PFHpA or PFOSaAm or "C7-FASA" or PFHpSA or "C8-PFSiA" or PFOSI or EtFOSAA or EtFOSE or FBSA or FOSAA or FOSA or FOSE or "N-MeFOSA" or "N-MeFOSE" or PFBSaAm or FTAB or FTCA or FTUCA or FtSaB or FTS or FtTAoS or FTB or FTB or FTOH or FtSaAm or FtTAoS or FtTHN\* or ADONA or OBS or Duxford or Ronneby or Jersey or Copenhagen or Schiphol or Buncefield or Illinois or Ohio or "San Francisco" or California or Australia

and

"fire-fighter" or firefighter or "fire fighter" or "turnout gear" or "protective clothing" or PPE

### **Annex E Environmental hazard and exposure**

# Annex E.1 Thresholds used to assess Persistence, Mobility and Toxicity by different regulatory jurisdictions

Table E.1: Review of thresholds used to assess Persistence, Mobility and Toxicity by different regulatory jurisdictions

Jurisdiction	Persistence criteria	Mobility criteria	Toxicity Criteria
United Kingdom	A substance fulfils the persistence criterion (P) in any of the following situations:  • the degradation half-life in marine water is higher than 60 days (OECD TG 309);  • the degradation half-life in fresh or estuarine water is higher than 40 days (OECD TG 309);  • the degradation half-life in marine sediment is higher than 180 days (OECD TG 308);  • the degradation half-life in fresh or estuarine water sediment is higher than 120 days (OECD TG 308);  • the degradation half-life in soil is higher than 120 days (OECD TG 307).  A substance fulfils the "very persistent" criterion (vP) in any of the following situations:  • the degradation half-life in marine, fresh or estuarine water is higher than 60 days (OECD TG 309);  • the degradation half-life in marine, fresh or estuarine water sediment is higher than 180 days (OECD TG 308);  • the degradation half-life in soil is higher than 180 days (OECD TG 307).	No definitive criteria.	<ul> <li>A substance fulfils the toxicity criterion (T) in any of the following situations**:</li> <li>the long-term no-observed effect concentration (NOEC) or EC10 for marine or freshwater organisms is less than 0.01 mg/L;</li> <li>the substance meets the criteria for classification as carcinogenic (category 1A or 1B), germ cell mutagenic (category 1A or 1B), or toxic for reproduction (category 1A, 1B or 2) according to Regulation EC No 1272/2008;</li> <li>there is other evidence of chronic toxicity, as identified by the substance meeting the criteria for classification: specific target organ toxicity after repeated exposure (STOT RE category 1 or 2) according to Regulation EC No 1272/2008.</li> </ul>

Jurisdiction	Persistence criteria	Mobility criteria	Toxicity Criteria
Stockholm Convention (UNEP, 2023)	Evidence that the half-life of the chemical in water is greater than two months, or that its half-life in soil is greater than six months, or that its half-life in sediment is greater than six months; or     Evidence that the chemical is otherwise sufficiently persistent to justify its consideration within the scope of this Convention.	No definitive criteria.	Evidence of adverse effects to human health or to the environment that justifies consideration of the chemical within the scope of this Convention; or      Toxicity or ecotoxicity data that indicate the potential for damage to human health or to the environment.
Australian (Australian Government, 2022)	<ul> <li>Air</li> <li>Half-life (T½) ≥ 2 days</li> <li>Water</li> <li>Half-life (T½) ≥ 60 days</li> <li>Soil</li> <li>Half-life (T½) ≥ 6 months</li> <li>Sediment</li> <li>Half-life (T½) ≥ 6 months</li> </ul>	No definitive criteria	<ul> <li>Aquatic – Acute</li> <li>Fish 96 h LC50 ≤ 1 mg/L; and/or</li> <li>Invertebrates 48 h EC50 ≤ 1 mg/L; and/or</li> <li>Algae or other aquatic plants 72 or 96 h ErC50 ≤ 1 mg/L</li> <li>Aquatic – Chronic</li> <li>Fish chronic NOEC or ECx ≤ 0.1 mg/L; and/or</li> <li>Invertebrates chronic NOEC or ECx ≤ 0.1 mg/L; and/or</li> <li>Algae or other aquatic plants chronic NOEC or ECx ≤ 0.1 mg/L</li> </ul>

Jurisdiction	Persistence criteria	Mobility criteria	Toxicity Criteria
Canada (Government of Canada, 2019, 2022b, 2023)	A substance is persistent when it has at least one of the following characteristics:  In air:  its half-life is equal to or greater than 2 days, or  it is subject to atmospheric transport from its source to a remote area;  In water:  its half-life is equal to or greater than 182 days; or  In sediments:  its half-life is equal to or greater than 365 days; or  In soil:  its half-life is equal to or greater than 182 days.	No definitive criteria	A substance is toxic if it is entering or may enter the environment in a quantity or concentration or under conditions that:  • have or may have an immediate or long-term harmful effect on the environment or its biological diversity;  • constitute or may constitute a danger to the environment on which life depends; or  • constitute or may constitute a danger in Canada to human life or health.  In determining whether a substance should be declared "toxic" under the Canadian Environmental Protection Act, 1999 (CEPA), the likelihood and magnitude of releases into the environment and the harm it may cause to human health or ecosystems at levels occurring in the Canadian environment are taken into account.
European Union	Same as UK	No definitive criteria <sup>A</sup>	Same as UK
Japan (METI, 2018; Suzuki, 2018)	OECD 301C biodegradation <60%; parent chemicals or metabolites remain. Further consider results from OECD 302C, 301D and 301F.	No definitive criteria	(Eco)toxicity value (e.g., PNEC) <0.001 mg/L, 0.001-0.01 mg/L, 0.01-0.1 mg/L, 0.1-1 mg/L, >1 mg/L (strong toxicity through to weak toxicity threshold levels)

Jurisdiction	Persistence criteria	Mobility criteria	Toxicity Criteria
			combined with exposure tonnage to determine priority.
United States	Transformation half-life	No definitive	Expert judgement 'based upon various factors, including concerns for
(US EPA, 1999)	> 2 months	criteria	persistence, bioaccumulation, other
	> 6 months		physical/chemical factors, and toxicity based on existing data.'
	The EPA approach uses the lower cutoffs for persistence to trigger exposure/release controls and further testing.		
	The higher cutoffs for persistence trigger a ban from commercialization pending testing (which may justify removing a chemical from 'high risk concern'.		

AECHA do not have any definitive criteria with which to assess mobility under EU REACH, but have adopted PMT/vPvM criteria for the EU CLP Regulation, which have subsequently been used in the prioritisation of substances registered under EU REACH. These criteria are: a substance fulfils the mobility criterion (M) when the lowest organic carbon-water coefficient (log K<sub>OC</sub>) over the pH range of 4–9 is less than 3; a substance fulfils the "very mobile" criterion (vM) when the lowest log K<sub>OC</sub> over the pH range of 4–9 is less than 2.

## Annex E.2 Addressing data limitations and uncertainty in the assessment of PFAS physicochemical properties

The OECD Test Guidelines (TG) are recognised internationally as the standards for nonclinical safety testing of chemicals and chemical products for both the environment and human health. Data from the OECD TGs for determining physico-chemical properties are used by the Agency and UK REACH registrants as surrogate indicators in environmental hazard assessment screening, and estimation metrics in exposure modelling. The most commonly used studies to generate surrogate data for environmental endpoints are presented in Table E.2.

The Agency reviewed the chemical applicability domain of experimental studies (as outlined in Table E.2) for substances with surface-active and ionisable properties, including PFAAs. Uncertainties were identified due to the surface-active and permanently ionised nature of PFAAs in the environment.

Limited regulatory guidance exists for amending study designs or analyses during the physical-chemical testing of surface-active or permanently ionised substances (e.g., Guidance Document 23; OECD, 2019), and no guidance is available for substances with both properties. Any study design amendments must ensure the generation of reliable and robust data relevant to the metric of interest. This may not be feasible for PFAAs.

This is discussed further for water solubility, log K<sub>OW</sub>, log K<sub>d</sub>/K<sub>OC</sub> in the following text.

Table E.2: The OECD Test Guidelines for physical chemical testing and their applicability domain for surface active and ionisable substances

Test Guideline	Measures	Applicability for surface active and ionisable substances	Comment with regards to PFAAs
OECD 104	Vapour pressure	No discussion of substance applicability for surface active/ionisable/difficult to test substances.  However, complex mixtures will give a range of vapour pressures rather than a single value.	
OECD 105	Water solubility	No discussion of substance applicability for surface active substances	For surface-active substances the Critical Micelle Concentration (CMC) would be desirable.  For PFAAs, without a reliable CMC to benchmark against it will not be possible to assess whether later aqueous solutions are at surface saturation or whether microscopic micelles have formed.
OECD 106	Adsorption -desorption using a batch equilibrium	For ionisable test substances, the selected soils should cover a wide range of pH, to evaluate the adsorption of the substance in its ionised and unionised forms.  No discussion of substance applicability for surface active/difficult to test substances.	<ul> <li>For surface active substances significant pre-work would be required to assess:</li> <li>The influence of the calcium chloride solution on the CMC.</li> <li>Concentration effects that could lead to aggregation at the soil/water and air/water interface.</li> <li>For PFAAs there will be a high degree of uncertainty in the relevance of results (please see Section E.2.3)</li> </ul>

Test Guideline	Measures	Applicability for surface active and ionisable substances	Comment with regards to PFAAs
OECD 107	Partition coefficient n- octanol/water shake flask method	Measurements should be made on ionisable substances only in non-ionized form.  The shake flask method is not viable to use with surface-active materials as phase separation cannot be guaranteed (for these, a Kow can be calculated from individual solubilities in water and n-octanol).	This is unsuitable for PFAAs as they will be permanently charged unless the pH is adjusted considerably.  The calculation of Kow using solubilities in the water and n-octanol phases is not appropriate for surface active substances which aggregate at different interfaces of the test system, as reliable concentration measurements cannot be made. The recommendation does not account for CMC measurements. See Annex E.2.2.
OECD 111	Hydrolysis	No discussion of substance applicability for surface active/difficult to test substances.	
OECD 115	Surface tension of aqueous solutions	The method notes that the CMC should be known beforehand.	The CMC is determined with a tensiometer by measuring the surface tension (SFT) of a concentration series. With pure surfactants, the SFT is linearly dependent on the logarithm of the concentration over a large range. Above the CMC, the SFT is extensively independent of the concentration.
OECD 117	Partition coefficient-n- octanol-water HPLC method	Measurements can be performed on ionisable substances in their non-ionised form (free acid or free base) only by using an appropriate buffer with a pH below the pKa for a free acid or above the pKa for a free base.  The method is not applicable to strong acids and bases, metal complexes, substances which react with the eluent, or surface-active agents.	For surface active substances, data should not be considered relevant or reliable from this test. This is due to unfavourable interactions with the stationary phase of the HPLC columns.

Test Guideline	Measures	Applicability for surface active and ionisable substances	Comment with regards to PFAAs
OECD 121	Estimation of the adsorption coefficient K <sub>OC</sub> on soil and on sludge using high performance liquid chromatography	Ionisable substances must be measured using a buffered mobile phase, but care must be taken to avoid precipitation of buffer components or test substance.  The method may not work for surface active substances, inorganic compounds and moderate or strong organic acids and bases.	For PFAS there will be a high degree of the uncertainty in the relevance of results.
OECD 123	Partition coefficient n- octanol/water slow stir method	Before carrying out a slow-stirring experiment for determination of K <sub>OW</sub> , the dissociation constant(s) of ionisable substances should be available. The test report should include the aqueous phase pH and the buffers used, when pH is adjusted for ionizable molecules.  No discussion of substance applicability for surface active chemicals.	For PFAS there will be a high degree of the uncertainty in the relevance of results. The shake flask method is not viable to use with surface-active materials as phase separation cannot be guaranteed.

Table E.3: Physico-chemical properties, partition coefficients and indicative thresholds used to screen and rank substances for environmental fate and hazard assessment

The values reported for these properties must correspond to environmentally relevant conditions (temperature 12 - 25 °C; atmospheric pressure; and pH 4–9).

Parameter	Symbol	Units	Thresholds	Indicator for screening
Physical State	-	-	-	Solid, liquid, gas
Vapour pressure	VP	Pa	> 25 kPa	Highly volatile (boiling point < 50 °C)
			< 0.5 kPa	Low volatility (boiling point > 150 °C)
Water solubility	n/a	mg/L	< 10	Low solubility, influences mobility and bioavailability
			10 - 1000	Moderately soluble, influences mobility bioavailability
			> 1000	Highly soluble, influences mobility bioavailability
n-octanol water partition co-efficient	log Kow	unitless	> 2	High potential for bioaccumulation in air-breathing organisms when K <sub>OA</sub> > 5
			> 4.5	High potential for bioaccumulation in aquatic organisms
Organic carbon normalised adsorption	log Koc	unitless	< 3	Mobile <sup>1</sup>
partition co-efficient			< 2	very Mobile <sup>1</sup>

Parameter	Symbol	Units	Thresholds	Indicator for screening
n-octanol air partition co-efficient	log K <sub>OA</sub> <sup>2</sup>	Unitless	> 5	High potential for bioaccumulation in air-breathing organisms when log $K_{\text{OW}} > 2$
Henry's Law Constant (Air water partition co-	HLC	unitless or Pa.m³.mol	0.01	Less volatile than water
efficient - log K <sub>AW</sub> )			> 1	Preferential partitioning to air
			1 - 10	Significant loss to air
			10 - 100	Very significant loss to air
			100	Rapid volatilisation
Acid / base dissociation constant	pK <sub>a</sub> /pK <sub>b</sub>	unitless	-	Influences mobility and bioavailability

<sup>&</sup>lt;sup>1</sup> Criteria used in Europe for classification purposes (European Commission, 2022). Other thresholds are available e.g. <u>US EPA</u> and <u>FAO</u>.

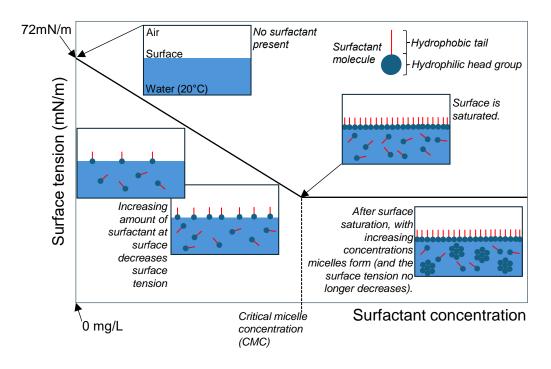
<sup>&</sup>lt;sup>2</sup> K<sub>OA</sub> – this unitless value can be experimentally determined or estimated using QSPR techniques, solvation models or quantum calculations (Baskaran *et al.*, 2021a, 2021b). It describes the distribution of a chemical between octan-1-ol (CAS No. 111-87-5) and the gas phase at equilibrium; K<sub>OA</sub> = C<sub>O</sub>/C<sub>A</sub>, (1) where C<sub>O</sub> and C<sub>A</sub> are the concentrations of a compound in n-octanol and the gas phase in mol.m<sup>-3</sup>, respectively.

### Annex E.2.1 Water solubility

Water solubility can be used to provide an upper limit for dosing concentrations, and refine estimation models for physico-chemical and environmental fate parameters such as  $\log K_{OW}$ ,  $\log K_{OC}$ , n-octanol-air partition coefficient ( $\log K_{OA}$ ) and the Henry's Law Constant (HLC) etc.

Water solubility is defined in the OECD TG 105 as "the saturation mass concentration of the compound in water at a given temperature" (OECD, 1995c). This does not apply to surfactants. At low concentrations they may be true homogenous solutions, but at higher concentrations phase separation occurs (Hodges et al., 2019). Therefore, the term 'water solubility' is not easy to define nor determine for surface-active compounds. The critical micelle concentration (CMC), has been used as a 'surrogate' for water solubility for surface active substances (Hodges et al., 2019), and can be determined using surface tension as per OECD TG 115 (OECD, 1995b). The CMC is the concentration at which surface of an air/water interface is saturated. Above the surface saturation concentration, molecules combine to form micelles (aggregates) and a colloidal solution is formed (Figure E.1).

Figure E.1: Surface tension of a surfactant solution with increasing concentration and the formation of micelles



The CMC should be used with caution as a surrogate for water solubility, especially where the value is being used to model another physical chemical or environmental fate property. The CMC is also unique to a pure substance and should not be determined for substances with multiple components. Surface activity is also sensitive to solution composition, including ionic composition and strength, pH, and the presence of co-solutes. During testing, the nature of any counter ion associated with a PFAS (e.g. sodium, potassium or

ammonium salts) can influence the surface activity (Brusseau, 2019; Brusseau and Van Glubt, 2019) and by default the CMC and partitioning behaviour of these substances (Leung *et al.*, 2023). The role of the fluorinated tail chain length and the presence of electrolytic salts on micelle formation is discussed in detail in in Kancharla *et al.* (2021).

As the chain length of the PFAA increases they display more surface active properties, and water solubility becomes more difficult to operationally define (Leung *et al.*, 2023 and references therein). The CMC is more likely to be reported as a surrogate.

#### Annex E.2.2 n-Octanol/water partition coefficient (log Kow)

Measured and predicted log K<sub>OW</sub> values are used to estimate the partitioning of a substance to environmental and biological matrices (e.g. soils, sludges and lipids etc) and as an indicator of bioavailability. This metric is fundamental to understanding the environmental fate and behaviour of substances at a preliminary level. Direct measurements are usually performed either in de-ionised water (providing the 'ideal' solution) or where ionisable groups are present in pH buffered solutions to generate a log D<sub>OW</sub> (pH specific distribution coefficient).

The OECD TG 107 (OECD, 1995a) and OECD TG 123 (OECD, 2022b) provide direct measurement of log Kow, and the OECD 117 (OECD, 2022a) provides a reference standard benchmarked estimate. The OECD TGs 107, 117 and 123 are not applicable to surface active substances (Table E.2) (Haftka *et al.*, 2015). A working approach for surfactants is noted in ECHA (2017f), where the solubility of the substance in n-octanol and the CMC in pure water can be determined. Hodges *et al.* (2019) notes that using the CMC could prevent the calculation of implausibly low log Kow values but is still of questionable relevance (Hodges *et al.*, 2019).

Hodges *et al.* (2019) provides a comparison of log Kow values for non-ionic, anionic, cationic and amphoteric surfactants, determined using predictions and experimental methods. They recommended newer alternative experimental log Kow methods were developed as well as more biologically relevant and methodologically defensible alternative methods for describing partitioning of surfactants. This is especially important for screening for bioaccumulation potential and understanding bioavailability.

The Agency considers that the log K<sub>OW</sub> value is not relevant for surface active PFAS because they cannot proportionally partition between octanol and aqueous solution. Even at low concentrations they will accumulate at the interface of an equilibrated n-octanol/aqueous buffer solution, forming an emulsion phase in the test system.

Consequently, for polar PFAS log Kow cannot be used for estimating other properties (BCF, soil sorption, aquatic toxicity, etc.), even when it is predicted using QSARs. Until better screening metrics have been developed, these properties require direct measurement.

### Annex E.2.3 Organic carbon normalised soil partition coefficient (log Koc)

Measured and estimated log  $K_{OC}$  (and  $K_d$ ) values are used as a surrogate for estimating the retention of a substance by environmental matrices (e.g. soils, sediments, sludges; Table E.3). The  $K_{OC}$  has been proposed as a metric to screen a substance for potential environmental mobility (Section 2.4.4).

There are two OECD test guidelines, OECD TG 106 (OECD, 2000) and OECD TG 121 (OECD, 2001), that provide direct and estimated measurements, respectively. OECD TG 121 is not suitable for surface active substances (Table E.2). The study design of the batch equilibrium study (OECD TG 106) can be amended to generate a Koc value. These amendments, proposed in Zhang *et al.* (2018), can address the concentration dependence of sorption to prevent colloid formation and phase separation. The concentration at which this occurs was observed to be approaching the CMC but could vary due to the influence of calcium chloride or other salts in the aqueous solution. Precipitation of anionic surfactants through interaction with metal cations was noted in the discussion as a potentially further point of misinterpretation. Subsequently, an understanding of soil characteristics beyond those set out in the OECD TGs is fundamental to understanding whether results are reliable and relevant for a partition coefficient endpoint.

Whether meaningful  $K_d$  or  $K_{OC}$  results can be established for all chain lengths of PFAAs is unclear, due to the mixed sorption phenomena that have been identified. However, as noted in the Mobility Section (Section 2.4.4), experimental data have demonstrated that  $K_d$  values increase with increasing chain length for long chain PFAAs in soils (Chen *et al.*, 2018b; Guelfo and Higgins, 2013; Mejia-Avendano *et al.*, 2020; Nguyen *et al.*, 2020). For shorter chain PFAAs sorption is increasingly dominated by ionic interactions of the polar head group over the hydrophobic interactions of the tail. Similar  $K_d$  values were noted for short chain PFAAs in soils, which indicates a minor role of the fluorinated tail group in sorption (Lyu *et al.*, 2022; Nguyen *et al.*, 2022; Nguyen *et al.*, 2020). Zhou *et al.* (2013) reported similar log  $K_{OC}$  values for PFCAs with carbon chain lengths < 7 in a field study using sediment. Guelfo and Higgins (2013) reported rapid penetration, with no obvious retention, for short chain PFAAs (C  $\leq$  6).

### Annex E.2.4 Alternative methods for estimating the physico-chemical properties of PFAAs and their precursors

Experimental measurements of 'standard' physico-chemical and environmental behaviour properties such as partition coefficients were developed using relatively simple organic substances. However, for the reasons presented in the preceding sections, it is challenging to measure these reliably for highly polar and ionisable PFAS (such as PFAAs). It is therefore difficult to benchmark the values obtained for PFAA against data for other substances, when they have such unique properties.

Similarly, models for predicting these properties, such as EPISuite™ (US EPA, 2012) and other modules in the OECD QSAR Toolbox (OECD, 2023), were developed for the

assessment of less functionalised molecules. Their general applicability to PFAS (including PFAAs) is therefore highly uncertain, because of both a lack of relevant substances in the training set, and uncertainty in the measured properties of any that are included.

Alternative methods and their comparison to standard property estimation tools are provided in Wang *et al.* (2011c), Lampic and Parnis (2020), Brown *et al.* (2024), Endo *et al.* (2013), Droge (2019) and references therein. Data from these references are presented in the following text and tables. These data do show trends as a homologue series with increasing chain length, however due to previously acknowledged uncertainties their value in hazard assessment is considered of unknown reliability.

Wang *et al.* (2011c) used two strategies to calculate and evaluate COSMOTherm property data, these were external comparison and internal consistency checks. External comparison consists of evaluating property estimates for the set of model evaluation compounds against measured property data. For neutral PFAS, results were compared to measured data; for the PFAAs, a comparison of model results with the few available measured data were provided (Table E.4).

Table E.4: Estimated physicochemical data for different groups of PFAAs from COSMOTherm (adapted from Wang et al., 2011c).

Substance	Log K <sub>AW</sub>	Log Kow, dry 1	Log K <sub>OA</sub>	Log P <sub>L</sub> (Pa)	Log S <sub>w</sub> (mol/L)
PFCAs					
PFBA (C4)	-3.23	2.82	6.04	3.59	0.42
PFPeA (C5)	-2.90	3.43	6.33	3.13	-0.37
PFHxA (C6)	-2.58	4.06	6.63	2.66	-1.16
PFHpA (C7)	-2.25	4.67	6.92	2.20	-1.94
PFOA (C8)	-1.93 (-3.0)	5.30	7.23	1.73 (0.62)	-2.73
PFNA (C9)	-1.58	5.92	7.50	1.27 (0.10)	-3.55
PFDA (C10)	-1.27	6.50	7.77	0.82 (-0.64)	-4.31
PFUnDA (C11)	-0.92	7.15	8.08	0.34 (-0.98)	-5.13

Substance	Log Kaw	Log Kow, dry <sup>1</sup>	Log Koa	Log P∟ (Pa)	Log Sw (mol/L)
PFDoDA (C12)	-0.58	7.77	8.36	-0.13 (-2.29)	-5.94
PFTrDA (C13)	-0.38	8.25	8.63	-0.57	-6.59
PFTeDA (C14)	0.03	8.90	8.87	-0.99	-7.42
PFSAs					
PFBS (C4)	-2.59	3.90	6.49	2.80	-1.00
PFHxS (C6)	-2.38	5.17	7.55	1.77	-2.24
PFOS (C8)	-1.65	6.43	8.07	0.83	-3.92
PFDS (C10)	<b>–1.15</b>	7.66	8.82	-0.15	-5.39

<sup>&</sup>lt;sup>1</sup> Log K<sub>OW, dry</sub> – the partition coefficients were calculated using 'dry' octanol; whether 'wet' or 'dry' octanol is used in calculations can affect the results.

Lampic and Parnis (2020), evaluated the accuracy of predicted physicochemical properties for 25 per- and polyfluoroalkyl substances (PFAS) using four different methods: COSMOTherm, EPISuite™ (US Environmental Protection Agency's CompTox Chemicals Dashboard (including OPERA), and Linear Solvation Energy Relationships (LSERs) from the UFZ - LSER Database. Their analysis revealed:

- Acid dissociation constants (pKa) and K<sub>AW</sub> were most accurately predicted by COSMOTherm.
- Vapor pressure and dry K<sub>AW</sub> were best estimated using the OPEn Structure-activity/property Relationship App (OPERA) within the CompTox Dashboard.
- Wet Kow values showed comparable accuracy between OPERA and EPISuite™.
- K<sub>OC</sub> and water solubility were well predicted by both OPERA and COSMOTherm.

Acid dissociation significantly influences the physicochemical properties of perfluoroalkyl acids. Therefore, ionization corrections were included in the analysis.

Brown et al. (2024) reported the development of six new models for predicting physicochemical properties. The models are poly parameter linear free energy

relationships (PPLFER) equations that used experimental parameters and solute descriptors predicted with quantitative structure activity relationships (QSARs) . The predictivity of the models were tested for novel chemicals which are not in the training or external validation datasets. Applicability domain and uncertainty estimates were tested for 9,000 measured partition ratios and 4,000 measured vapour pressure and water solubility values. The prediction accuracy for log Kow, log Kaw and log Koa ranged from 1.7 – 1.8 (root mean squared error). These methods are applicable to any substance whose fate and behaviour (partitioning) is complex and depends on multiple variables, especially those with highly functionalised chemical structures such as PFAAs (Zhang *et al.*, 2024). The descriptor method, algorithms, training and validation sets that have been developed consider the surface active and ionisable properties of PFAAs and other PFAS. Zhang *et al.* (2024) and Endo *et al.* (2023) also provide methods for estimating the physicochemical properties of neutral PFAS.

Endo *et al.* (2013), examined the use of a polyparameter – linear free energy relationship (PP-LFER) system, which estimated how compounds distribute between water and biological tissues (like lipids and proteins). This went further than using a simplified approach that relied on a general relationship between substance behaviour in a simple system (i.e. water-octanol). This simplification can overlook the unique interactions between substances and the diverse components of biological tissues, potentially leading to inaccuracies in predicting a compound's actual distribution. Example PP-LFER systems and quantum methods used to develop equilibrium partition coefficients are provided in Table E.5.

Table E.5: Example PP-LFER systems and quantum methods used to develop equilibrium partition coefficients

Equilibrium partition co- efficient	Models	Reference
storage lipid - water	PP-LFER	Endo et al. (2013)
lipisome-water	PP-LFER, COSMO-RS and COSMOmic	Bittermann et al. (2016)
membrane - water	PP-LFER, COSMO-RS and COSMOmic	Bittermann et al. (2016); Droge (2019); Endo et al. (2013)
albumin – water	PP-LFER	Endo et al. (2013)

protein - water	PP-LFER	Endo et al. (2013)

#### **Annex E.2.5 Conclusions**

Alternative screening partitioning coefficients are considered scientifically more relevant for estimating parameters including bioaccumulation potential and bioavailability for ionic/polar substances. Interpretation beyond screening for bioaccumulation potential is not established, and even then, limited for regulatory purposes. While log  $K_{OW}$  is presently used to judge whether solubility and availability are sufficient for laboratory testing, and to derive log  $K_{OC}$  for neutral organic substances in the absence of empirical data, the applicability of the newly developed partition coefficients for these same purposes remains uncertain especially where  $K_{OW}$  are reported. For the same reasons these metrics may not be suitable for use in exposure models

For ecotoxicity and environmental fate studies (see Table E.2), both study design and analytical methods should ideally consider how the PFAS concentration, pH, and buffers affect the accumulation and aggregation of PFAAs and their precursors at various interfaces e.g., air/water, solid/water, and solid/air.

### Annex E.3 Literature review

The environmental literature review strategy was designed to build upon information already collated during the production of the UK REACH PFAS RMOA (HSE, 2023). National and international regulatory reviews had already been identified during that process and were supplemented by assessments published more recently.

Targeted literature searches were performed using SCOPUS, PubMED and Google Scholar to identify additional published hazard information to inform our assessment of specific topics. The following search terms were used in searches conducted February, August and November 2024, and January 2025. Other relevant sources were harvested from these publications.

Topic	Search terms
Chemical	(PFAS OR perfluoroalkyl substances OR polyfluoroalkyl substance OR perfluoro alkyl acids OR PFAA* OR perfluoro carboxyl* OR perfluoro sulfon* OR perfluoro sulphon*)
Analytical	(measuremen* OR concentrat*OR method* OR total fluorine OR total organic fluorine OR total oxid* fluorine OR total oxid* precursor OR specific analysis OR bulk measur* OR TF OR TOF OR TOP OR mass spectromet* OR MS* OR total inorganic fluorine OR combustion ion chromatography OR chemical

	analysis OR analy* OR fluorocarbon OR fluorine OR identificat* OR quantif* OR quantit*)
Physico- chemical properties	(water solubil* OR solubil* OR octanol water partition coefficient OR soil water partition coefficient OR organic carbon normalised soil water partition coefficient OR vapour pressure OR vapor pressure OR boiling point OR henry's law constant OR hlc OR kow OR koc OR kd OR melting point OR ph OR pka OR pkb OR acid dissociat* const* OR base dissociat* constant* OR indirect photolysis OR atmos* OR air* OR phototransform OR air water (interface) OR soil water (interface) OR air soil (interface) OR surfactant OR surface active OR surfact* OR ionis* OR ioniz* OR oecd tg)  (method* OR laborator* OR measurement* OR estimation* OR predict* OR
	structure activity relationship OR sar OR qsar OR quant * structure activity relationship OR model* OR algor* OR hydrolysis OR photolysis OR direct photolysis OR polyparameter OR single parameter OR linear free energy relationships)
Persistence	(environmental persistence OR persist* OR biodeg* OR biotranformat* OR degrad* OR microbial degrad* OR biotic degrad* OR abiotic degrad* OR hydrolysis OR photolysis OR oxidat* OR reduct* OR redox OR diagentic sequence) AND (sediment OR soil OR water OR lake OR river OR stream OR marin* OR ocean* OR half-life OR kinetics)
Mobility	(environment* OR mobil* OR mobile organ* OR koc OR kd OR leach* OR adsorp* OR adsorb*)
	(monitor* OR detect* OR desorp* OR desorb* OR ionis* OR surfact* OR surface active* OR ioniz*)
	(ground waters OR surface waters OR aquifers OR subsurface transport OR hydrogeol* OR hydraulic transport OR subsurface biogeochemistry OR subsurface soil OR vados* OR diagenesis* OR hysteresis* OR geolog*)
	(water solubil* OR solubil* OR octanol water partition coefficient OR soil water partition coefficient OR organic carbon normalised soil water OR partition coefficient OR vapour pressure OR vapor pressure OR boiling point OR henry's law constant OR HLC OR kow OR koc OR kd OR melting point)
Ecotoxicity	(environmental toxicity OR ecotoxic* OR toxicity in wildlife OR biota* OR adverse effect OR populat* OR individ* OR trophic OR species)

### Annex E.4 UK REACH Environmental Hazard Criteria

Table E.6: Parameters and threshold criteria used to assess persistence, bioaccumulation and toxicity endpoints under UK REACH

	Persistence	Bioaccumulation	Toxicity
Screening	Not readily biodegradable < 70% DOC or < 60% COD/ThOD  Not inherently biodegradable < 70% DOC (7 d) or < 70% COD/ThOD (14 d)	log K <sub>OW</sub> > 4.5 (aquatic organisms) log K <sub>OW</sub> > 2 (air-breathing organisms) log K <sub>OA</sub> > 5 (air-breathing organisms)	Acute aquatic toxicity  E(L)C <sub>50</sub> < 0.1 mg/L  Human health studies
Definitive	Environmental DT <sub>50</sub> > 40 d <sup>1</sup> to > 120 d <sup>2</sup> (P) > 60 d <sup>1</sup> to > 180 d <sup>2</sup> (vP)	Aquatic organisms BCF > 2000 (B) BCF > 5000 (vB)	Chronic aquatic toxicity data  NOEC or EC <sub>10</sub> < 0.01 mg/L  Human health studies
Supporting data	Abiotic data Hydrolysis Aqueous photolysis Atmospheric photolysis Field monitoring Non-standard studies	BMF > 1 ( $\sim$ vB) $k_2 \le 0.181 d^{-1} (\sim B)^3$ $k_2 \le 0.085 d^{-1} (\sim vB)^3$ Biota monitoring Mammalian toxicokinetic data - terminal elimination half-lives $\sim$ 4 days (rat) $\sim$ 50 days (human) Non-standard studies	Non-standard studies

<sup>&</sup>lt;sup>1</sup> Surface waters; <sup>2</sup> Soil; <sup>3</sup> Depuration half-life k<sub>2</sub> (lipid normalised) (Environment Agency, 2012)

Guidance on testing and assessment of the endpoints is provided in (ECHA, 2017a, 2017b, 2017c, 2017d, 2017f).

### Annex E.5 Review of regulatory assessments

This annex includes regulatory conclusions of persistence, mobility, toxicity and LRTP by the UN Stockholm Convention, and by the UK, Australia, Canada, Europe, Japan and the USA. No assessments in English were found for Japan. One assessment carried out in the USA by the Agency for Toxic Substances and Disease Registry was found (ATSDR, 2021) that referred to persistence, bioaccumulation and toxicity; the ATSDR report identified perfluoroalkyls as persistent and mobile with variable bioaccumulation (increases with increasing chain length), LRTP and variable toxicity. However, these were overarching conclusions for perfluoroalkyls (they did not distinguish between different groups) and did not appear to be based on the criteria set out in the US EPA (1999) 'Category for Persistent, Bioaccumulative and Toxic New Chemical Substances. The substances included in the ATSDR report were: PFBA, PFHxA, PFHpA (i.e., short chain PFCAs), PFOA, PFNA, PFDA, PFUnDA, PFDoDA (i.e., long chain PFCAs), PFBS, PFHxS (i.e., short chain PFSAs), PFOS (long chain PFSA).

### **Annex E.5.1 Persistence**

Table E.7: Review of regulatory assessments of persistence performed by the UN Stockholm Convention, and by the UK, Australia, Canada and Europe

Designation	Substances	Report conclusion	Evidence based on	Reference
Long chain F	PFCAs (≥8 carbons) <sup>A</sup>			
Stockholm Convention	PFOA (C <sub>8</sub> PFCA), its salts and PFOA-related compounds	Highly persistent	Chemical properties of PFOA, lack of degradation of PFOA under environmentally relevant conditions, and long PFOA half-lives data in multiple environmental compartments.	UN POPS (2016)
Stockholm Convention	C <sub>9</sub> –C <sub>21</sub> PFCAs, their salts and related compounds  Recommended to COP for inclusion in Annex A (EFSA et al., 2020).	Extremely persistent	Stability of the C–F bond; multiple studies that demonstrate that long-chain PFCAs do not degrade under environmentally relevant conditions.	UN POPS (2023)
Australia	PFOA (C <sub>8</sub> PFCA) and its salts	Highly persistent	Resistance of PFOA to biodegradation, hydrolysis and aqueous photolysis.	NICNAS (2015d). By extension, this also applies to their indirect precursors NICNAS

Designation	Substances	Report conclusion	Evidence based on	Reference
				(2019b, 2019c)
Canada	C <sub>9</sub> –C <sub>20</sub> PFCAs, their salts, and precursors	Extremely persistent	Presence of C <sub>9-11</sub> PFCAs in arctic ( <i>LRTP</i> ); stability of the C–F bond. <b>Read-across</b> due to lack of empirical degradation data for long-chain PFCAs.	Environment Canada (2012); Government of Canada (2022a)
Europe	PFOA (C <sub>8</sub> PFCA)	Very persistent	Abiotic and biotic degradation data showing that PFOA does not degrade under environmentally relevant conditions; stability of the C–F bond.	ECHA (2013)
Europe	PFNA (C <sub>9</sub> PFCA) and its sodium and ammonium salts	Very persistent	One PFNA screening study and <b>read-across</b> from PFOA indicating that PFNA is not degraded under environmentally relevant conditions; stability of the C–F bond.	ECHA (2015)
Europe	PFDA (C10 PFCA) and its sodium and ammonium salts	Very persistent	PFOA, PFNA and C <sub>11–14</sub> PFCA data; <b>read-across</b> because no degradation studies for PFDA available. Stability of the C–F bond.	ECHA (2016)

Designation	Substances	Report conclusion	Evidence based on	Reference
Europe	C11 PFCA	Very persistent	$C_{8,9,12,14}$ PFCA data; <b>read-across</b> because no degradation studies for $C_{11}$ available. Stability of the C–F bond.	ECHA (2012d)
Europe	C12 PFCA	Very persistent	PFOA abiotic and biotic degradation data and C <sub>8,9,14</sub> -PFCA screening studies ( <b>read-across</b> ), as well as one C <sub>12</sub> -PFCA standard screening biodegradation study (no abiotic degradation studies available for C <sub>12</sub> -PFCA), indicate that C <sub>12</sub> PFCA is not degraded in the environment. Stability of the C–F bond.	ECHA (2012c)
Europe	C13 PFCA	Very persistent	PFOA abiotic degradation studies, biodegradation screening tests for C <sub>8,9,12,14</sub> -PFCAs and nonstandard aerobic and anaerobic biodegradation simulation studies with PFOA; and PFOA field monitoring data. Also evidenced the stability of the C–F bond. <b>Read-across</b> because no degradation studies for C <sub>13</sub> -PFCA available.	ECHA (2012b)
Europe	C14 PFCA	Very persistent	Biodegradation screening tests for C <sub>8,9,12</sub> -PFCAs, and PFOA non-standard simulation studies and field monitoring data ( <b>read-across</b> ), as well as one C <sub>14</sub> -PFCA standard biodegradation screening study (no abiotic degradation studies available for C <sub>14</sub> -PFCA) indicate that C <sub>14</sub> PFCA is not degraded in the	ECHA (2012a)

Designation	Substances	Report conclusion	Evidence based on	Reference
			environment. Also evidenced the stability of the C-F bond.	
Short chain I	PFCAs (<8 carbons) <sup>B</sup>			
Australia	PFHpA (C7 PFCA) and ammonium PFHpA	Highly persistent	Multiple studies conducted on a range of perfluorinated substances (does not specify which) showing no evidence of potential for biodegradation, hydrolysis or aqueous photolysis under environmental conditions; focuses on non-biodegradable C <sub>6</sub> and C <sub>8</sub> homologues. Long estimated atmospheric lifetime of PFAAs in the group.	NICNAS (2015b)
Australia	PFHxA (C6 PFCA) and ammonium PFHxA  PFPeA (C5 PFCA) and ammonium PFPeA  PFBA (C4 PFCA) and PFBA anhydride	Highly persistent	Empirical data showing PFHxA is non-biodegradable; multiple studies conducted on a range of perfluorinated substances (does not specify which) showing no evidence of potential for biodegradation, hydrolysis or aqueous photolysis under environmental conditions; long estimated atmospheric lifetime of PFAAs in the group.	NICNAS (2015c); by extension, this also applies to their indirect precursors in NICNAS (2019a)

Designation	Substances	Report conclusion	Evidence based on	Reference
Canada	C4–C7 PFCAs	Extremely persistent	Data showing that degradation of C <sub>4-7</sub> PFCA does not occur under environmentally relevant conditions; stability of the C–F bond.	ECCC (2023)
Europe	PFHpA (C7 PFCA) and its salts	Very persistent	Stability of the C–F bond. <b>Read-across</b> from C <sub>6,8–14</sub> PFCAs degradation data (no PFHpA degradation data available).	ECHA (2022)
Europe	PFHxA (C6 PFCA), its salts and related substances	Very persistent	Stability of the C–F bond. <b>Read-across</b> from PFOA degradation data. Studies showing no degradation of PFCAs including PFHxA.	ECHA (2019b)
Long chain F	PFSAs (≥6 carbons)		<u> </u>	
Stockholm Convention	PFOS (C8 PFSA) and 96 PFOS-related substances	Extremely persistent	Degradation data showing that PFOS does not hydrolyse, photolyse or biodegrade under any environmental conditions.	UN POPS (2006)
Stockholm Convention	PFHxS (C6 PFSA), its salts and PFHxS-related compounds	Very persistent	Chemical properties of PFHxS, and some PFHxS field and monitoring data, indicate persistence.  Read-across from PFOS, PFBS and PFOA.	UN POPS (2018)
UK	PFOS (C8 PFSA)	Very persistent	Degradation data showing no biodegradation, hydrolysis, or photolysis of PFOS.	Environment Agency (2004)

Designation	Substances	Report conclusion	Evidence based on	Reference
Australia	PFOS (C8 PFSA), its salts and PFOSF	Highly persistent	Data showing PFOS is resistant to biodegradation, hydrolysis and aqueous photolysis, and long hydrolysis half-life of PFOS.	NICNAS (2015f); by extension, this also applies to their indirect precursors in NICNAS (2019d)
Australia	PFNS (C9 PFSA) and direct precursors PFDS (C10 PFSA) and direct precursors	Highly persistent	Multiple studies conducted on a range of perfluorinated substances (does not specify which) showing no evidence of potential for biodegradation, hydrolysis or aqueous photolysis under environmental conditions; <b>read-across</b> as no data available for PFNS or PFDS; focuses on C <sub>8</sub> homologue (PFOS).	NICNAS (2015g)
Australia	PFHpS (C7 PFSA) and its salts PFHxS (C6 PFSA) and its salts	Highly persistent	Multiple studies conducted on a range of perfluorinated substances (including the C <sub>4</sub> and C <sub>8</sub> homologues) showing no evidence of potential for biodegradation, hydrolysis or aqueous photolysis under environmental conditions; <b>read-across</b> as no data available for PFHpS or PFHxS; focuses on C <sub>8</sub> homologue (PFOS).	NICNAS (2015a); by extension this also applies to their indirect precursors

Designation	Substances	Report conclusion	Evidence based on	Reference
				in NICNAS (2015h)
Canada	PFOS (C8 PFSA), its salts and precursors that contain the C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> or C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> or C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> N moiety	Extremely persistent	Resistance of PFOS to hydrolysis, photolysis, and biodegradation; stability of the C–F bond; long half-life of PFOS half-life.	Environment Canada (2006)
Canada	C9–C20 PFSAs	Extremely persistent	Stability of the C-F bond.	ECCC (2023)
Canada	PFHxS (C6 PFSA) PFHpS (C7 PFSA) As part of assessment on C4– C7 PFSAs	Extremely persistent	Lack of degradation of C <sub>6</sub> PFSA under environmentally relevant conditions; stability of the C–F bond.	ECCC (2023)
Europe	PFHxS (C6 PFSA) and its salts <sup>B</sup>	Very persistent	Stability of the C–F bond; <b>read-across</b> from PFOS and PFOA data because only one phototransformation study available and no PFHxS biodegradation data.	ECHA (2017e)

Designation	Substances	Report conclusion	Evidence based on	Reference
Australia	PFBS (C4 PFSA) and its precursors	Highly persistent	Multiple studies conducted on a range of analogous perfluorinated substances (does not specify which) showing no evidence of potential for biodegradation, hydrolysis or aqueous photolysis under environmental conditions (read-across).	NICNAS (2015e)
Australia	PFPeS (C5 PFSA) and ammonium PfPeS	Highly persistent	Multiple studies conducted on a range of perfluorinated substances (including the C <sub>4</sub> and C <sub>8</sub> homologues) showing no evidence of potential for biodegradation, hydrolysis or aqueous photolysis under environmental conditions; <b>read-across</b> as no data available for PFPeS.	NICNAS (2015a); by extension this also applies to their indirect precursors in NICNAS (2015h)
Canada	PFBS (C4 PFSA)  PFPeS (C5 PFSA)  As part of assessment on C4– C7 PFSAs.	Extremely persistent	Data showing C <sub>4</sub> and C <sub>6</sub> PFSAs do not degrade under environmentally relevant conditions or undergo photolysis; stability of the C–F bond.	ECCC (2023)
Europe	PFBS (C4 PFSA) and its salts	Very persistent	Stability of the C–F bond; <b>read-across</b> to trifluoromethane sulfonic acid and PFOS data; estimated PFBS QSAR data; presence in remote	ECHA (2019a)

Designation	Substances	Report conclusion	Evidence based on	Reference
			areas; and hydrolysis and screening studies showing no degradation of PFBS.	

A No assessment of any long chain PFCAs was found from the UK

### **Annex E.5.2 Mobility**

Table E.8: Review of regulatory assessments of mobility performed by the UN Stockholm Convention, and by the UK, Australia, Canada and Europe

Designation	Substances	Report conclusion	Evidence based on	Reference		
Long chain PFCAs (≥8	Long chain PFCAs (≥8 carbons) <sup>A</sup>					
Stockholm Convention	PFOA (C8 PFCA), its salts and PFOA-related compounds	Not considered	-	UN POPS (2016)		
Stockholm Convention	C9–C21 PFCAs, their salts and related compounds	Not considered	-	UN POPS (2023)		

<sup>&</sup>lt;sup>B</sup> No assessment of any short chain PFCAs was found from the Stockholm Convention or the UK

<sup>&</sup>lt;sup>C</sup> No assessment of any short chain PFSAs was found from the Stockholm Convention or the UK

Designation	Substances	Report conclusion	Evidence based on	Reference
	Recommended to COP for inclusion in Annex A (Song et al., 2018a).			
Australia	PFOA (C8 PFCA) and its salts	Not considered	-	NICNAS (2015d). By extension, this also applies to their indirect precursors NICNAS (2019b, 2019c)
Canada	C9–C20 PFCAs, their salts, and precursors	Not considered	-	Environment Canada (2012); Government of Canada (2022a)
Europe	PFOA (C8 PFCA)	Not considered	-	ECHA (2013)
Europe	PFNA (C9 PFCA) and its sodium and ammonium salts	Not considered	-	ECHA (2015)
Europe	PFDA (C10 PFCA) and its sodium and ammonium salts	Not considered	-	ECHA (2016)

Designation	Substances	Report conclusion	Evidence based on	Reference
Europe	C11 PFCA	Not considered	-	ECHA (2012d)
Europe	C12 PFCA	Not considered	-	ECHA (2012c)
Europe	C13 PFCA	Not considered	-	ECHA (2012b)
Europe	C14 PFCA	Not considered	-	ECHA (2012a)
Short chain PFCAs (<8	carbons) <sup>B</sup>			
Australia	PFHpA (C7 PFCA) and ammonium PFHpA	Not considered	-	NICNAS (2015b)
Australia	PFHxA (C6 PFCA) and ammonium PFHxA  PFPeA (C5 PFCA) and ammonium PFPeA  PFBA (C4 PFCA) and PFBA anhydride	Highly mobile	Considers LRTP to conclude on the high mobility of the perfluorinated anions.	NICNAS (2015c); by extension, this also applies to their indirect precursors in NICNAS (2019a)

Designation	Substances	Report conclusion	Evidence based on	Reference
Canada	C4–C7 PFCAs	Mobile	Discussed in relation to persistence and LRTP.	ECCC (2023)
Europe	PFHpA (C7 PFCA) and its salts	Very mobile	PFHpA low adsorption potential (Koc), high water solubility, and low volatilisation potential indicate high mobility. Supported by monitoring data (PFHpA present in tap water, bottled drinking water and groundwater).	ECHA (2022)
Europe	PFHxA (C6 PFCA), its salts and related substances	Very mobile	PFHxA low to moderate adsorption potential (Koc), high water solubility, and low to moderate volatilisation potential make PFHxA highly mobile.	ECHA (2019b)
Long chain PFSAs (≥6 o	carbons)			
Stockholm Convention	PFOS (C8 PFSA) and 96 PFOS-related substances	Not considered	-	UN POPS (2006)
Stockholm Convention	PFHxS (C6 PFSA), its salts and PFHxS-related compounds	Not considered	Not considered in detail, however log Koc values are reported as indicators of mobility.	UN POPS (2018)

Designation	Substances	Report conclusion	Evidence based on	Reference
UK	PFOS (C8 PFSA)	Not considered	-	Environment Agency (2004)
Australia	PFOS (C8 PFSA), its salts and PFOSF	Not considered	-	NICNAS (2015f); by extension, this also applies to their indirect precursors in NICNAS (2019d)
Australia	PFNS (C9 PFSA) and direct precursors	Not considered	-	NICNAS (2015g)
Australia	PFHpS (C7 PFSA) and its salts PFHxS (C6 PFSA) and its salts	Not considered	-	NICNAS (2015a); by extension this also applies to their indirect precursors in NICNAS (2015h)
Canada	PFOS (C <sub>8</sub> PFSA), its salts and precursors that contain the C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> or C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> or C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> N moiety	Not considered	Overall not considered, but discussed in relation to uncertainties and presence of PFOS (and precursors) in the Arctic.	Environment Canada (2006)
Canada	C9–C20 PFSAs	Mobile	Discussed in relation to persistence and LRTP.	ECCC (2023)

Designation	Substances	Report conclusion	Evidence based on	Reference
Canada	PFHxS (C6 PFSA) PFHpS (C7 PFSA) As part of assessment on C4–C7 PFSAs	Mobile	Discussed in relation to persistence and LRTP.	ECCC (2023)
Europe	PFHxS (C6 PFSA) and its salts <sup>B</sup>	Not considered	-	ECHA (2017e)
Short chain PFSAs (<6	carbons) <sup>c</sup>			
Australia	PFBS (C4 PFSA) and its precursors	Likely mobile	Discussed as part of LRTP; water solubility and surface-active properties mean likely mobile in aquatic compartment.	NICNAS (2015e)
Australia	PFPeS (C5 PFSA) and ammonium PfPeS	Not considered	-	NICNAS (2015a); by extension this also applies to their indirect precursors in NICNAS (2015h)
Canada	PFBS (C4 PFSA)	Mobile	Discussed in relation to persistence and LRTP.	ECCC (2023)

Designation	Substances	Report conclusion	Evidence based on	Reference
Europe	PFBS (C4 PFSA) and its salts	Very mobile	Highly water soluble, weakly sorbing properties, distribution to the aqueous phase (modelling and field data) and global distribution indicate high mobility.	ECHA (2019a)

A No assessment of any long chain PFCAs was found from the UK

### **Annex E.5.3 Environmental toxicity**

Table E.9: Review of regulatory assessments of environmental toxicity performed by the UN Stockholm Convention, and by the UK, Australia, Canada and Europe

Designation	Substances	Report conclusion	Evidence based on	Reference
Long chain F	PFCAs (≥8 carbons) <sup>A</sup>			
Stockholm Convention	PFOA (C8 PFCA), its salts and PFOA-related compounds	Adverse effects	PFOA has multiple adverse effects in terrestrial organisms (including alterations to liver, endocrine dysfunction, developmental toxicity, and tumour formation). Also shows intergenerational toxicity in first generation offspring of fish and aquatic invertebrates, but generally low to moderate acute	UN POPS (2016)

<sup>&</sup>lt;sup>B</sup> No assessment of any short chain PFCAs was found from the Stockholm Convention or the UK

<sup>&</sup>lt;sup>C</sup> No assessment of any short chain PFSAs was found from the Stockholm Convention or the UK

Designation	Substances	Report conclusion	Evidence based on	Reference
			aquatic toxicity and low chronic toxicity in benthic organisms.	
Stockholm Convention	C9–C21 PFCAs, their salts and related compounds  Recommended to COP for inclusion in Annex A (ECHA, 2023b).	Adverse effects	C <sub>9</sub> –C <sub>14</sub> : human health effects observed in epidemiological studies. C <sub>8–14</sub> , C <sub>16</sub> and C <sub>18</sub> PFCA adverse effects (including developmental, behavioural, hepatotoxicity, immunotoxicity, neurotoxicity, genotoxicity, thyroid effects) across a range of aquatic and air-breathing organisms. <b>Readacross</b> due to lack of empirical evidence for C <sub>15</sub> , C <sub>17</sub> and C <sub>19–21</sub> PFCAs.	UN POPS (2023)
Australia	PFOA (C8 PFCA) and its salts	Toxic	PFOA long-term intergenerational toxicity and endocrine activity data (low acute and chronic toxicity based on standard ecotoxicity testing for PFOA).	NICNAS (2015d). By extension, this also applies to their indirect precursors NICNAS (2019b, 2019c)
Canada	C9–C20 PFCAs, their salts, and precursors	Harmful to organisms	Range of toxicological effects reported in a variety of species for C <sub>9-14</sub> PFCA (in addition to exposure data). <b>Read-across</b> due to lack of empirical data on effects of >C <sub>14</sub> .	Environment Canada (2012); Government of Canada (2022a)

Designation	Substances	Report conclusion	Evidence based on	Reference
Europe	PFOA (C8 PFCA)	Toxic	PFOA reproductive toxicity category 1B and specific target organic toxicity (STOT RE 1) (low acute and chronic toxicity).	ECHA (2013)
Europe	PFNA (C9 PFCA) and its sodium and ammonium salts	Toxic	Data indicating reproductive toxicity of PFNA.	ECHA (2015)
Europe	PFDA (C10 PFCA) and its sodium and ammonium salts	Toxic	Data indicating reproductive toxicity of PFDA.	ECHA (2016)
Europe	C11 PFCA	Not considered	-	ECHA (2012d)
Europe	C12 PFCA	Not considered	-	ECHA (2012c)
Europe	C13 PFCA	Not considered	-	ECHA (2012b)
Europe	C14 PFCA	Not considered	-	ECHA (2012a)
Short chain I	PFCAs (<8 carbons) <sup>E</sup>	3	<u>I</u>	I
Australia	PFHpA (C7 PFCA) and ammonium PFHpA	Uncertain toxicity	Evidenced conflicting data: no evidence of PFHpA acute toxicity based on invertebrate and algal exposure studies. However, noted that the primary concern for other PFAAs, i.e., PFOA, is chronic,	NICNAS (2015b)

Designation	Substances	Report conclusion	Evidence based on	Reference
			intergenerational toxicity, but that studies indicate a decrease in toxicity with decreasing chain length. Concluded insufficient data to reliably interpolate the chronic toxicity of PFHpA from other PFAA homologues. No studies on long-term exposure toxicity available for PFHpA.	
Australia	PFHxA (C6 PFCA) and ammonium PFHxA  PFPeA (C5 PFCA) and ammonium PFPeA  PFBA (C4 PFCA) and PFBA anhydride	Not toxic	Low toxicity based on chronic toxicity of PFHxA to <i>Daphnia magna,</i> fish, and algae, and acute toxicity data for PFHxA and PFBA available for fish, invertebrates and algae. Notes intergenerational toxicity for PFOA and a lack of intergenerational studies for PFHxA, PFPeA, and PFBA, but also that developmental toxicity of PFBA in fish is 100 times lower than that of PFOS.	NICNAS (2015c); by extension, this also applies to their indirect precursors in NICNAS (2019a)
Canada	C4–C7 PFCAs	Toxic	Aquatic acute and chronic toxicity data for C <sub>4–7</sub> PFCAs are summarised, however exposure in airbreathing animals is stated to be more significant. Endocrine related effects data and multi-generational studies indicate toxicity. Concluded likely cumulative toxicity based on continued exposure.	ECCC (2023)

Designation	Substances	Report conclusion	Evidence based on	Reference
Europe	PFHpA (C7 PFCA) and its salts	Toxic	PFHpA reproductive toxicity category 1B and specific target organ toxicity (STOT RE 1).	ECHA (2022)
Europe	PFHxA (C6 PFCA), its salts and related substances	Uncertain toxicity	Generally low acute and chronic environmental toxicity in standard tests, however potentially of limited value due to lack of consideration of intergenerational effects. Some evidence indicating endocrine disrupting properties of PFHxA and potential for developmental and reproductive effects; not sufficient to draw conclusion on T.	ECHA (2019b)
Long chain P	PFSAs (≥6 carbons)			
Stockholm Convention	PFOS (C8 PFSA) and 96 PFOS-related substances	Adverse effects	Data showing PFOS adverse effects and reproductive toxicity in mammals (rats, monkeys, rabbits), moderate acute toxicity to fish and mysid shrimp, and high toxicity to chironomids.	UN POPS (2006)
Stockholm Convention	PFHxS (C6 PFSA), its salts and PFHxS- related compounds	Adverse effects	PFHxS liver and thyroid organ effects in rats; neurotoxicity and reprotoxicity data in mice; epidemiological studies on immune system effects in humans; along with <b>read across</b> from PFBS (multigenerational toxicity in fish) and PFOS (fish toxicity data).	UN POPS (2018)

Designation	Substances	Report conclusion	Evidence based on	Reference
UK	PFOS (C8 PFSA)	Toxic	PFOS chronic bird data (NOAEC); multiple toxicity studies in rats (mortality, carcinogenicity, reprotoxicity), rabbits (reprotoxicity) and monkeys (mortality).	Environment Agency (2004)
Australia	PFOS (C8 PFSA), its salts and PFOSF	Toxic	PFOS chronic toxicity (intergenerational effects) (low to moderate acute and chronic toxicity based on standard ecotoxicity testing for PFOS).	NICNAS (2015f); by extension, this also applies to their indirect precursors in NICNAS (2019d)
Australia	PFDS (C10 PFSA) and direct precursors	Toxic	PFDS acute toxicity data compared with PFOS showing PFDS at least as toxic as PFOS; <b>read-across</b> from PFOS chronic toxicity (intergenerational effects) data; pattern of increasing toxicity of PFAAs with increasing chain length.	NICNAS (2015g)
Australia	PFHpS (C7 PFSA) and its salts PFHxS (C6 PFSA) and its salts	Uncertain toxicity	No measured aquatic toxicity data and limited mammalian toxicity data available. Primary concern may be chronic intergenerational toxicity based on PFOS, but insufficient data available to be certain.	NICNAS (2015a); by extension this also applies to their indirect precursors in

Designation	Substances	Report conclusion	Evidence based on	Reference
				NICNAS (2015h)
Canada	PFOS (C8 PFSA), its salts and precursors that contain the C8F17SO2 or C8F17SO3 or C8F17SO2N moiety	Harmful to the environment (toxicity/exposure analysis)	Multiple effects in laboratory mammals and ecotoxicity in aquatic and terrestrial species described.	Environment Canada (2006)
Canada	C9–C20 PFSAs	Toxic	No acute or chronic toxicity data found for LC-PFSAs, however endocrine-related and other effects observed for PFHxS, PFHpS, PFOS, and PFDS (read-across to higher chain lengths); concluded likely cumulative toxicity based on continued exposure.	ECCC (2023)
Canada	PFHxS (C6 PFSA) PFHpS (C7 PFSA) As part of assessment on C4– C7 PFSAs	Toxic	C <sub>6-7</sub> PFSA acute and chronic toxicity data are summarised, however exposure in air-breathing animals is stated to be more significant. C <sub>6</sub> PFSA multigenerational toxicity data and C <sub>6-7</sub> PFSA endocrine related data indicate toxicity; concluded likely cumulative toxicity based on continued exposure.	ECCC (2023)

Designation	Substances	Report conclusion	Evidence based on	Reference	
Europe	PFHxS (C6 PFSA) and its salts <sup>B</sup>	Uncertain toxicity	No ecotoxicity studies available; some toxic effects in rats and mice noted; insufficient data available to conclude on toxicity.	ECHA (2017e)	
Short chain PFSAs (<6 carbons) <sup>C</sup>					
Australia	PFBS (C4 PFSA) and its precursors	Not toxic	Available aquatic toxicity data for potassium PFBS indicate low toxicity (no PFBS aquatic toxicity data available); developmental toxicity of PFBS 1000 times less than PFOS.	NICNAS (2015e)	
Australia	PFPeS (C5 PFSA) and ammonium PfPeS	Uncertain toxicity	No measured aquatic or mammalian toxicity data available for PFPeS. Primary concern may be chronic intergenerational toxicity based on PFOS, but PFBS has low chronic toxicity, with PFPeS having an intermediate chain length between the two. Overall insufficient data available to be certain.	NICNAS (2015a); by extension this also applies to their indirect precursors in NICNAS (2015h)	
Canada	PFPeS (C5 PFSA)	Toxic	C <sub>4–5</sub> PFSA acute and chronic toxicity data are summarised, however exposure in air-breathing animals is stated to be more significant. C <sub>4</sub> PFSA multigenerational toxicity data and C <sub>6</sub> PFSA endocrine related data ( <b>read-across</b> ) indicate	ECCC (2023)	

Designation	Substances	Report conclusion	Evidence based on	Reference
			toxicity; concluded likely cumulative toxicity based on continued exposure.	
Europe	PFBS (C4 PFSA) and its salts	Toxic	PFBS reprotoxicity data in fish (low acute aquatic toxicity) and multiple other effects (though not sufficient for T individually) in air breathing animals indicate toxicity.	ECHA (2019a)

A No assessment of any long chain PFCAs was found from the UK

## **Annex E.5.4 Long range transport potential**

Table E.10: Review of regulatory assessments of LRTP performed by the UN Stockholm Convention, and by the UK, Australia, Canada and Europe

Designation	Substances	Report conclusion	Evidence based on	Reference		
Long chain I	Long chain PFCAs (≥8 carbons) <sup>A</sup>					
	PFOA (C8 PFCA), its salts and PFOA-related compounds	LRTP	Presence of PFOA in multiple environmental compartments in remote locations, including the Arctic and Antarctica. Persistence of PFOA.	UN POPS (2016)		

<sup>&</sup>lt;sup>B</sup> No assessment of any short chain PFCAs was found from the Stockholm Convention or the UK

<sup>&</sup>lt;sup>C</sup> No assessment of any short chain PFSAs was found from the Stockholm Convention or the UK

Designation	Substances	Report conclusion	Evidence based on	Reference
Stockholm Convention	C9–C21 PFCAs, their salts and related compounds  Recommended to COP for inclusion in Annex A (Saez et al., 2008).	LRTP	C <sub>9–18</sub> PFCAs detected in multiple environmental compartments in remote locations, including the Antarctic and Canadian Arctic. C9-21 PFCAs also expected to have LRTP (based on <b>readacross</b> and modelling data).	UN POPS (2023)
Australia	PFOA (C8 PFCA) and its salts	LRTP	PFOA measurements in Atlantic Ocean, North Polar Sea, Arctic.	NICNAS (2015d). By extension, this also applies to their indirect precursors NICNAS (2019b, 2019c)
Canada	C9–C20 PFCAs, their salts, and precursors	LRTP	Discussed in context of persistence.	Environment Canada (2012); Government of Canada (2022a)
Europe	PFOA (C8 PFCA)	Not considered	-	ECHA (2013)
Europe	PFNA (C9 PFCA) and its sodium and ammonium salts	Not considered	-	ECHA (2015)

Designation	Substances	Report conclusion	Evidence based on	Reference
Europe	PFDA (C10 PFCA) and its sodium and ammonium salts	Not considered	-	ECHA (2016)
Europe	C11 PFCA	Not considered	-	ECHA (2012d)
Europe	C12 PFCA	Not considered	-	ECHA (2012c)
Europe	C13 PFCA	Not considered	-	ECHA (2012b)
Europe	C14 PFCA	Not considered	-	ECHA (2012a)
Short chain	PFCAs (<8 carbons) <sup>B</sup>	1		
Australia	PFHpA (C7 PFCA) and ammonium PFHpA	LRTP	Evidenced presence of PFHpA in remote locations including Antarctica and the European Alps.	NICNAS (2015b)
Australia	PFHxA (C6 PFCA) and ammonium PFHxA	LRTP	Evidenced presence of PFHxA, PFPeA and PFBA worldwide, including in the Arctic Ocean, Antarctica and the European Alps.	NICNAS (2015c); by extension, this also applies to their indirect

Designation	Substances	Report conclusion	Evidence based on	Reference
	PFPeA (C5 PFCA) and ammonium PFPeA PFBA (C4 PFCA) and PFBA anhydride			precursors in NICNAS (2019a)
Canada	C4–C7 PFCAs	LRTP	C2–13 PFCAs detected in remote locations including Devon Ice Cap. Note: discussion around precursors being dominant source of arrowheads in remote areas.	ECCC (2023)
Europe	PFHpA (C7 PFCA) and its salts	LRTP	PFHpA extreme persistence and mobility leads to high LRTP. Presence of PFHpA in remote areas including the Arctic, Antarctic and European Alps.	ECHA (2022)
Europe	PFHxA (C6 PFCA), its salts and related substances	LRTP	PFHxA modelling data indicate high LRTP; presence of PFHxA in remote regions.	ECHA (2019b)
Long chain I	PFSAs (≥6 carbons)			
Stockholm Convention	PFOS (C8 PFSA) and 96 PFOS-related substances	LRTP	PFOS has low volatility but is transported in the atmosphere bound to particles because of surface-active properties. Presence in	UN POPS (2006)

Designation	Substances	Report conclusion	Evidence based on	Reference
			multiple environmental compartments in remote locations, including the Canadian Arctic.	
Stockholm Convention	PFHxS (C6 PFSA), its salts and PFHxS-related compounds	LRTP	PFHxS presence in multiple environmental compartments in remote locations, including the Arctic, Antarctica and Latin America.	UN POPS (2018)
UK	PFOS (C8 PFSA)	Not considered	-	Environment Agency (2004)
Australia	PFOS (C8 PFSA), its salts and PFOSF	LRTP	High volatility and persistence of PFOS; PFOS presence globally including in remote regions (Alaska, Northern Baltic Sea, Arctic, Antarctica).	NICNAS (2015f); by extension, this also applies to their indirect precursors in NICNAS (2019d)
Australia	PFNS (C9 PFSA) and direct precursors	LRTP	PFDS presence in Antarctica; <b>read-across</b> from PFHxS and PFOS which have also been detected worldwide in remote locations.	NICNAS (2015g)
Australia	PFHpS (C7 PFSA) and its salts	LRTP	PFHxS presence in Arctic, Atlantic Ocean and Antarctic. Limited data for PFHpS, but presence in Arctic foxes noted.	NICNAS (2015a); by extension this also applies to their indirect

Designation	Substances	Report conclusion	Evidence based on	Reference
	PFHxS (C6 PFSA) and its salts			precursors in NICNAS (2015h)
Canada	PFOS (C8 PFSA), its salts and precursors that contain the C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> or C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> or C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> N moiety	Not considered	Overall not considered, but discussed in relation to persistence (explaining presence in remote areas) and environmental concentrations in seawater.	Environment Canada (2006)
Canada	C9–C20 PFSAs	LRTP	C8,10-PFSAs detected in remote locations.  Note: discussion around precursors being dominant source of arrowheads in remote areas.	ECCC (2023)
Canada	PFHxS (C6 PFSA) PFHpS (C7 PFSA) As part of assessment on C4–C7 PFSAs	LRTP	C6–7 PFSAs detected in remote locations including Devon Ice Cap. Note: discussion around precursors being dominant source of arrowheads in remote areas.	ECCC (2023)
Europe	PFHxS (C6 PFSA) and its salts <sup>B</sup>	Not considered	-	ECHA (2017e)

Designation	Substances	Report conclusion	Evidence based on	Reference
Australia	PFBS (C4 PFSA) and its precursors	LRTP	PFBS presence in remote locations, including Greenland Sea.	NICNAS (2015e)
Australia	PFPeS (C5 PFSA) and ammonium PfPeS	LRTP	No monitoring data available for PFPeS; read-across based on monitoring data available for PFBS.	NICNAS (2015a); by extension this also applies to their indirect precursors in NICNAS (2015h)
Canada	PFBS (C4 PFSA)  PFPeS (C5 PFSA)  As part of assessment on C4–C7 PFSAs.	LRTP	C4–5 PFSAs detected in remote locations including Devon Ice Cap. Note: discussion around precursors being dominant source of arrowheads in remote areas.	ECCC (2023)
Europe	PFBS (C4 PFSA) and its salts	LRTP	Presence of PFBS in remote locations including the Arctic and Antarctic; estimated travel distance and persistence.	ECHA (2019a)

A No assessment of any long chain PFCAs was found from the UK

<sup>&</sup>lt;sup>B</sup> No assessment of any short chain PFCAs was found from the Stockholm Convention or the UK

<sup>&</sup>lt;sup>C</sup> No assessment of any short chain PFSAs was found from the Stockholm Convention or the UK

# Annex E.6 Review of regulatory data relating to mobility

This annex identifies the organic carbon normalised adsorption coefficient ( $K_{OC}$ ), adsorption coefficient ( $K_{d}$ ), vapour pressure and water solubility data presented for the PFAAs within regulatory reports and the OECD fact cards (OECD, 2022c). The original sources of the data are identified, but have not been assessed for reliability by the Agency.

### Annex E.6.1 Organic carbon normalised adsorption coefficient (log K<sub>OC</sub>) data

Table E.11: Log Koc data available for the PFAAs from regulatory reports and the OECD fact cards

Substance	Value	Additional information	Regulatory Reference(s)	Original Reference
Short chain	PFCAs			
PFBA (C4)	2.62 L/kg	Experimental (field)	ECCC (2023)	Zhang et al. (2012)
PFBA (C4)	1.88	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Guelfo and Higgins (2013)
PFBA (C4)	0.7	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Campos Pereira et al. (2018)
PFPeA (C5)	2.54 L/kg	Experimental (field)	ECCC (2023)	Zhang et al. (2012)
PFPeA (C5)	1.37	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Guelfo and Higgins (2013)
PFPeA (C5)	1.2	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Campos Pereira et al. (2018)
PFPeA (C5)	1.70– 2.11 L/kg	Experimental (field)	ECCC (2023)	Zhao et al. (2012)
PFHxA (C6)	2.72 L/kg	Experimental (field)	ECCC (2023)	Zhang et al. (2012)
PFHxA (C6)	1.31	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Guelfo and Higgins (2013)
PFHxA (C6)	1.63–2.35	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Sepulvado <i>et al.</i> (2011)
PFHxA (C6)	1.3	Desorption experiments; study reliability 2 (according to ECHA)	ECHA (2022)	Campos Pereira et al. (2018)
PFHxA (C6)	3.1–3.7	Field monitoring (sediment); study reliability 2 (according to ECHA)	ECHA (2022)	Li et al. (2011)

Substance	Value	Additional information	Regulatory Reference(s)	Original Reference
PFHxA (C6)	1.3–3.6		ECHA (2019b)	'Values reported in the literature'
PFHpA (C7)	1.63	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Guelfo and Higgins (2013)
PFHpA (C7)	1.8 ± 0.20	Similar to OECD 106; study reliability 2 (according to ECHA).  Value derived from K <sub>f</sub> data reported by original study	ECHA (2022)	Zhang et al. (2013)
PFHpA (C7)	1.7	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Campos Pereira et al. (2018)
PFHpA (C7)	2.22–2.82	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Sepulvado <i>et al.</i> (2011)
PFHpA (C7)	2.9	Field monitoring (suspended matter); study reliability 2 (according to ECHA)	ECHA (2022)	Ahrens et al. (2010)
PFHpA (C7)	3.0–3.6	Field monitoring (sediment); study reliability 2 (according to ECHA)	ECHA (2022)	Li et al. (2011)
PFHpA (C7)	1.72–2.05 L/kg	Experimental (field)	ECCC (2023)	Zhang et al. (2012)
Long chain F	PFCAs			
PFOA (C8)	1.89	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Guelfo and Higgins (2013)
PFOA (C8)	2.1	Average derived from multiple studies	OECD (2022c)	Zareitalabad <i>et al.</i> (2013)
PFOA (C8)	2.11	Similar to OECD 106; study reliability 4 (according to ECHA)	ECHA (2022)	Higgins and Luthy (2006)

Substance	Value	Additional information	Regulatory Reference(s)	Original Reference
PFOA (C8)	2.2	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Campos Pereira et al. (2018)
PFOA (C8)	2.42–2.59	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Sepulvado et al. (2011)
PFOA (C8)	1.9	Field monitoring (sediment); study reliability 2 (according to ECHA)	ECHA (2022)	Ahrens et al. (2010)
PFOA (C8)	3.1–3.7	Field monitoring (sediment); study reliability 2 (according to ECHA)	ECHA (2022)	Li et al. (2011)
PFNA (C9)	2.3–2.48	Experimental	Environment Canada (2012)	Higgins and Luthy (2006)
PFNA (C9)	2.36	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Guelfo and Higgins (2013)
PFNA (C9)	3.1	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Campos Pereira <i>et al.</i> (2018)
PFNA (C9)	2.42–2.59	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Sepulvado <i>et al.</i> (2011)
PFDA (C10)	2.65 - 2.87	Experimental	Environment Canada (2012)	Higgins and Luthy (2006)
PFDA (C10)	2.96	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Guelfo and Higgins (2013)
PFDA (C10)	4.4	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Campos Pereira <i>et al.</i> (2018)
PFDA (C10)	3.14–3.32	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Sepulvado <i>et al.</i> (2011)
PFUnDA (C11)	3.19 - 3.41	Experimental	Environment Canada (2012)	Higgins and Luthy (2006)

Substance	Value	Additional information	Regulatory Reference(s)	Original Reference
PFUnDA (C11)	2.96	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Guelfo and Higgins (2013)
PFUnDA (C11)	3.47	Similar to OECD 106; study reliability 4 (according to ECHA)	ECHA (2022)	Higgins and Luthy (2006)
PFUnDA (C11)	4.7	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Campos Pereira <i>et al.</i> (2018)
PFUnDA (C11)	4.8	Field monitoring (sediment); study reliability 2 (according to ECHA)	ECHA (2022)	Ahrens et al. (2010)
PFUnDA (C11)	5.1	Field monitoring (suspended matter); study reliability 2 (according to ECHA)	ECHA (2022)	Ahrens <i>et al.</i> (2010)
PFUnDA (C11)	3.19-3.41	Experimental	Environment Canada (2012)	Higgins and Luthy (2006)
PFDoDA (C12)	4.3	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Campos Pereira <i>et al.</i> (2018)
PFTeDA (C14)	4.3	Similar to OECD 106; study reliability 2 (according to ECHA)	ECHA (2022)	Campos Pereira <i>et al.</i> (2018)
Short chain I	PFSAs			
PFBS (C4)	<2	potassium salt; Experimental (OECD 106)	ECHA (2019a)	ECHA dissemination website
PFBS (C4)	1.2	Experimental; Sorption in soils	ECHA (2019a)	(Campos Pereira et al., 2018) Milinovic et al 2015)
PFBS (C4)	1.79 ± 0.10	Experimental; Batch sorption in soils	ECHA (2019a)	Guelfo and Higgins (2013)
PFBS (C4)	2.2	Experimental; Sorption in PFAS contaminated soils	ECHA (2019a)	Kwadijk et al. (2010)

Substance	Value	Additional information	Regulatory Reference(s)	Original Reference
PFBS (C4)	2.7	Experimental; Sediment column	ECHA (2019a)	Vierke et al. (2014)
PFBS (C4)	1.2	Experimental; sorption in soils	ECHA (2019a)	Milinovic et al. (2015)
PFBS (C4)	1.75–2.09	Experimental	ECCC (2023)	Zhao et al. (2012)
Long chain F	PFSAs		·	
PFHxS (C6)	2.05	Experimental	ECCC (2023); UN POPS (2018)	Guelfo and Higgins (2013)
PFHxS (C6)	2.4	Experimental	ECCC (2023); UN POPS (2018)	D'Agostino and Mabury (2017a)
PFHxS (C6)	0.74–1.70	Experimental	ECCC (2023)	Zhao et al. (2014)
PFHxS (C6)	1.8 - 2.76	Experimental (field-based)	ECCC (2023); UN POPS (2018)	Chen et al. (2018c)
PFHxS (C6)	2.02 - 2.14	Experimental	ECCC (2023)	Zhao et al. (2012)
PFHxS (C6)	2.6	Extrapolated (extrapolated - read-across)	ECHA (2019a)	-
PFOS (C8)	2.68	Experimental (sediment)	OECD (2022c)	Higgins and Luthy (2006)
PFOS (C8)	3.0	Experimental	ECHA (2019a)	Zareitalabad <i>et al.</i> (2013)
PFOS (C8)	3.4	Extrapolated (extrapolated - read-across)	ECHA (2019a)	-
PFDS (C10)	3.53–3.66	Experimental	ECCC (2023)	Higgins and Luthy (2006)

## Annex E.6.2 Adsorption coefficient (log K<sub>d</sub>) data

Table E.12: Log K<sub>d</sub> data available for the PFAAs from regulatory reports and the OECD fact cards

Substance	Value	Additional information	Regulatory Reference(s)	Original Reference
Short chain	PFCAs			
PFBA (C4)	1.18	Experimental (field)	ECCC (2023)	Zhang et al. (2012)
PFPeA (C5)	1.14	Experimental (field)	ECCC (2023)	Zhang et al. (2012)
PFHxA (C6)	1.33	Experimental (field)	ECCC (2023)	Zhang et al. (2012)
PFHpA (C7)	1.24	Experimental (field)	ECCC (2023)	Zhang et al. (2012)
Long chain F	PFCAs			
PFOA (C8)	-1.40	Experimental (field)	OECD (2022c)	Lam et al. (2014)
PFDoDA (C12)	-0.14	Experimental (field)	OECD (2022c)	Lam et al. (2014)
Short chain	PFSAs			
PFBS (C4)	-0.55- 0.21	Batch sorption in soils	ECHA (2019a)	Guelfo and Higgins (2013)
PFBS (C4)	1.42 ± 0.50	Sorption in PFAS contaminated soils	ECHA (2019a)	Kwadijk et al. (2010)
Long chain F	PFSAs			•
PFHxS (C6)	-1.52	Experimental (field)	OECD (2022c)	Lam et al. (2014)
PFOS (C8)	-1.15	Experimental (field)	OECD (2022c)	Lam et al. (2014)
PFOS (C8)	0.87 L/kg	River sediment; Experimental, method based on OECD 106	Environment Agency (2004)	3M (2003)
PFOS (C8)	0.99 L/kg	Clay loam soil; Experimental, method based on OECD 106	Environment Agency (2004)	3M (2003)

PFOS (C8)	1.26 L/kg	Clay soil; Experimental, method based on OECD 106	Environment Agency (2004)	3M (2003)
PFOS (C8)	1.55 L/kg	Sandy loam soil; Experimental, method based on OECD 106	Environment Agency (2004)	3M (2003)

## Annex E.6.3 Vapour pressure data

Table E.13: Vapour pressure data available for the PFAAs from regulatory reports and the OECD fact cards

Subst ance	Value	Additional information	Regulatory Reference(s)	Original Reference
Short c	hain PFCAs	<b>3</b>		
PFBA (C4)	2.63 Pa	Experimental	ECCC (2023)	Kim <i>et al.</i> (2015)
PFBA (C4)	2.93 Pa	Experimental	ECCC (2023)	Bhhatarai and Gramatica (2011)
PFBA (C4)	849 Pa	Experimental	NICNAS (2015c)	-
PFBA (C4)	1333 Pa	Experimental	ECCC (2023)	MSDS (2004)
PFHxA (C6)	264 Pa	Experimental	NICNAS (2015c)	-
PFHxA (C6)	264 Pa at 25°C	Estimated using EPISuite	ECHA (2019b)	-
PFHp A (C7)	1.32 Pa	Experimental	ECCC (2023)	Bhhatarai and Gramatica (2011)
PFHp A (C7)	1.88 Pa	Experimental	ECCC (2023)	Kim et al. (2015)

Subst ance	Value	Additional information	Regulatory Reference(s)	Original Reference
PFHp A (C7)	17.7 Pa	Experimental	NICNAS (2015b)	-
PFHp A (C7)	17.7 Pa at 15°C	Experimental	ECHA (2022)	US EPA Chem Dashboard
Long c	hain PFCAs			·
PFOA (C8)	2.3 Pa at 20°C	Extrapolated from measured	ECHA (2013); UN POPS (2016)	Washburn <i>et al.</i> (2005)
PFOA (C8)	4.2 Pa	Experimental	NICNAS (2015b, 2015d)	Nielsen (2012)
PFOA (C8)	4.2 Pa at 25°C	Extrapolated from measured	ECHA (2013); UN POPS (2016)	Kaiser <i>et al.</i> (2005); Washburn <i>et al.</i> (2005)
PFNA (C9)	0.1 Pa at 25°C	Experimental	Environment Canada (2012)	Arp et al. (2006)
PFDA (C10)	-0.64 Pa at 25°C	Experimental	Environment Canada (2012)	Arp et al. (2006)
PFDA (C10)	0.1 Pa at 25°C	Experimental	Environment Canada (2012)	Arp et al. (2006)
PFUn DA (C11)	-0.98 Pa at 25°C	Experimental	Environment Canada (2012)	Arp et al. (2006)
PFDo DA (C12)	9.40E-03 Torr at 25°C	Calculated ACD/Labs	ECHA (2012c)	Calculated for report

Subst ance	Value	Additional information	Regulatory Reference(s)	Original Reference
PFTrD A (C13)	0.479 Pa at 25°C	Calculated ACD/Labs	ECHA (2012b)	Calculated for report
PFTeD A (C14)	0.183 Pa at 25°C	Calculated ACD/Labs	ECHA (2012a)	Calculated for report
Short c	hain PFSAs			
PFBS (C4)	2.8 Pa	Estimated - Cosmotherm	ECHA (2019a)	Wang <i>et al.</i> (2011c)
PFBS (C4)	<1.22 <b>x</b> 10 <sup>-5</sup> Pa at 20°C	Potassium salt; Experimental	ECHA (2019a); NICNAS (2015a, 2015e)	ECHA dissemination website
PFBS (C4)	7 Pa at 20°C	Experimental	ECHA (2019a)	ECHA dissemination website
Long cl	hain PFSAs			
PFHxS (C6)	58.9 Pa	Estimated – Cosmotherm (neutral species from log pressure in liquid phase)	(ECHA, 2017e); UN POPS (2018)	Wang <i>et al.</i> (2011c)
PFOS (C8)	213 Pa at 20°C	Experimental	NICNAS (2015f)	Lanners (2010); OECD (2002)
PFOS (C8)	3.31 × 10 <sup>-4</sup> Pa at 20°C	Potassium salt; Experimental (OECD 104)	Environment Agency (2004); Environment Canada (2006); NICNAS (2015f); UN POPS (2006)	Lanners (2010); OECD (2002)

## Annex E.6.4 Water solubility data

Table E.14: Water solubility data available for the PFAAs from regulatory reports and the OECD fact cards

Substa nce	Value	Additional information	Regulatory Reference(s)	Original Reference
Short ch	nain PFCAs			
PFHxA (C6)	15.7 g/L at ambient temperature	Experimental	ECHA (2019b)	Zhao et al. (2014)
PFHpA (C7)	0.00365 g/L	Estimated using EPISuite	ECHA (2022)	-
Long ch	ain PFCAs			
PFOA (C8)	3.727 g/L	Experimental	NICNAS (2015d)	Nielsen (2012)
PFOA (C8)	4.14 g/L at 22°C	Experimental	ECHA (2013); UN POPS (2016)	(Prokop et al., 1989)
PFOA (C8)	9.5 g/L at 25°C	Experimental	ECHA (2013); UN POPS (2016)	Kauck and Diesslin (1951)
PFNA (C9)	1.3 g/L	Critical micelle concentration; Experimental	Environment Canada (2012)	Kunieda and Shinoda (2002)
PFDA (C10)	0.4 g/L	Critical micelle concentration; Experimental	Environment Canada (2012)	Bernett and Zisman (2002)
PFDA (C10)	5.14 g/L	Experimental	Environment Canada (2012)	Kauck and Diesslin (1951)
PFDA (C10)	5.14 g/L at 25°C	Experimental	ECHA (2016)	Kauck and Diesslin (1951)
PFUnD A (C11)	1.2 × 10 <sup>-4</sup> – 0.16 g/L at 25°C	Calculated ACD/Labs	ECHA (2012d)	Calculated for report

Substa nce	Value	Additional information	Regulatory Reference(s)	Original Reference
	2.9 × 10 <sup>-5</sup> – 0.041 g/L at 25°C	Calculated ACD/Labs	ECHA (2012c)	Calculated for report
	7.3 × 10 <sup>-6</sup> – 0.0100 g/L at 25°C	Calculated ACD/Labs	ECHA (2012b)	Calculated for report
	1.9 × 10 <sup>-6</sup> – 2.6 × 10 <sup>-3</sup> g/L at 25°C	Calculated ACD/Labs	ECHA (2012a)	Calculated for report
Short cl	nain PFSAs			
PFBS (C4)	52.6 g/L at 22.5– 24°C	Potassium salt; Experimental	ECHA (2019a)	ECHA dissemination website
PFBS (C4)	67 g/L	Experimental	ECCC (2023)	Kim <i>et al</i> . (2015)
PFBS (C4)	52.6 - 56.6 mg/L	Potassium salt; Experimental	(NICNAS, 2015a, 2015e)	ECHA dissemination website
PFBS (C4)	Fully miscible at 20°C	Experimental	ECHA (2019a)	ECHA dissemination website
Long ch	ain PFSAs			
PFHxS (C6)	1.4 g/L at 20- 25°C	Potassium salt; Experimental	UN POPS (2018)	Campbell <i>et al.</i> (2009)
PFHxS (C6)	2.3 g/L	Estimated – Cosmotherm (neutral species)	(ECHA, 2017e); UN POPS (2018)	Wang <i>et al.</i> (2011c)
PFOS (C8)	0.00029 g/L	Experimental	NICNAS (2015f)	Lanners (2010); OECD (2002)

Substa nce	Value	Additional information	Regulatory Reference(s)	Original Reference
PFOS (C8)	0.519 g/L at 20 ± 0.5°C	Potassium salt; Experimental	Environment Agency (2004); Environment Canada (2006); UN POPS (2006)	OECD (2002)
PFOS (C8)	0.57 g/L	Potassium salt; Experimental	NICNAS (2015f)	Lanners (2010); OECD (2002)
PFOS (C8)	0.68 g/L at 24– 25°C	Potassium salt; experimental (validity rating of 1 by Environment Agency)	Environment Agency (2004); Environment Canada (2006); UN POPS (2006)	OECD (2002)

# Annex E.7 Long range transport potential

### Annex E.7.1 What is long range transport potential (LRTP)?

An additional property of concern that is not defined under UK REACH but is interlinked with concerns around mobility is long-range transport potential (LRTP). This concept has been developed primarily for the purposes of the United Nations (UN) Stockholm Convention on Persistent Organic Pollutants (POPs) but provides a useful reference framework when considering the scale of pollution that can arise because of a substance's properties.

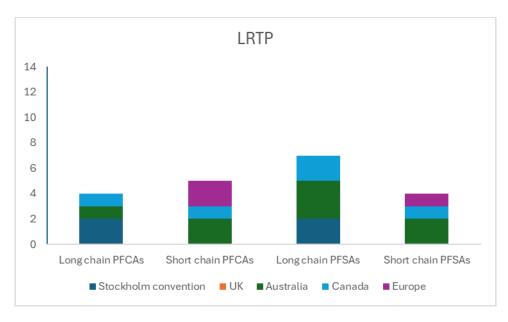
LRTP considers the likelihood of substances moving to locations remote from their source. It is one of the criteria for identifying POPs, which aims to protect polar regions and the deep oceans. Long-range transport (LRT) can occur due to one or more of the following mechanisms:

- movement of a substance within air currents either as vapour, aerosol or adsorbed to particulates, followed by wet or dry deposition;
- movement along rivers and via oceanic currents either as the substance itself or contained within plastic particles; or
- presence within migratory wildlife.

#### **Annex E.7.2 Regulatory landscape**

Relatively few national / international regulatory assessments have been carried out for LTRP, as summarised in Figure E.2.

Figure E.2: Conclusions of LRTP for each group of PFAAs, broken down by regulatory jurisdiction



Regulatory assessments of the LRTP of PFCAs cover chain lengths from C4 to C21 (Table D.15). In summary:

- Long chain: The LRTP of C8 to C21 PFCAs has been confirmed at UN level (UN POPS, 2021, 2024). The Australian regulator concluded that PFOA has LRTP and Canada (regulator and federal government) discussed the LRTP of C9 to C20 PFCAs in the context of persistence (Environment Canada, 2012; Government of Canada, 2022a; NICNAS, 2015d).
- Short chain: The Australian and Canadian regulators both concluded that C4 to C7
  PFCAs each have LRTP (ECCC, 2023; NICNAS, 2015b, 2015c). ECHA concluded
  PFHxA (while the UK was a member) and PFHpA have LRTP (ECHA, 2019a, 2023a).
- Ultra-short chain: No regulatory assessment for ultra-short chain PFCAs was identified.

Regulatory assessments of the LRTP of PFSAs cover chain lengths from C4 to C20 (Table D.16). In summary:

- Long chain: The LRTP of PFOS and PFHxS was confirmed at UN level (UN POPS, 2006, 2018). By interpolation, the C7 PFSA would have the same LRTP. Australia concluded that C7 to C9 PFCAs have LRTP (NICNAS, 2015a, 2015f, 2015g), while Canada has concluded that C6 to C20 PFSAs have LRTP (ECCC, 2023; Environment Canada, 2006).
- Short chain: Australia and Canada have both concluded that PFBS and PFPeS have LRTP (ECCC, 2023; NICNAS, 2015a, 2015e). Europe has also concluded that PFBS has LRTP (ECHA, 2019a).
- Ultra-short chain: No regulatory assessment for ultra-short chain PFCAs was identified.

Regulatory assessments generally used monitoring data for the substance(s) being assessed, but some read-across was used; for example for PFPeS, PFNS and PFDS by Australia, due to a lack of data.

Table E.15: Number of LRTP assessment conclusions\* reached by international/national regulatory jurisdictions at each chain length for PFCAs. Shading provides heatmap visualisation of where conclusions have been made\*

PFCA group UI		Ultra-short chain			Short chain				Long chain												
Carbon chain length		2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
	LRTP	0	0	2	2	3	3	2	2	2	2	2	2	2	2	2	2	2	2	2	2
sior	Uncertain LRTP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
oort	Not LRTP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Rep	Not considered	0	0	0	0	0	0	1	1	1	1	1	1	1	0	0	0	0	0	0	0

<sup>\*</sup>Orange shading highlights where a conclusion of mobility was made; pink shading highlights where assessments have been conducted but mobility has not been considered (darker shading means more assessments).

Table E.16: Number of LRTP assessment conclusions\* reached by international/national regulatory jurisdictions at each chain length for PFSAs. Shading provides heatmap visualisation of where conclusions have been made\*

PFSA group Ultra-short c		rt chain	Sho	rt cha	Long chain																	
Carbon chain length		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
	LRTP	0	0	0	3	2	3	2	2	2	2	1	1	1	1	1	1	1	1	1	1	0
sion	Uncertain LRTP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ort Slu	Not LRTP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Rep	Not considered	0	0	0	0	0	1	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0

<sup>\*</sup>Orange shading highlights where a conclusion of mobility was made; pink shading highlights where assessments have been conducted but mobility has not been considered (darker shading means more assessments).

#### Annex E.7.3 Field data

PFAS with surfactant properties may accumulate in the upper layers of seawater and are therefore quite likely to be present in marine aerosols (i.e., sea spray formation) (Johansson *et al.*, 2019; Prevedouros *et al.*, 2006; Sha *et al.*, 2022). Their presence in the upper layers of seawater means that, although atmospheric deposition is one of the major transport pathways of PFAS (Lyu *et al.*, 2022), LRT of some PFAS may occur by movement in both atmospheric and oceanic currents (ECCC and Health Canada, 2024).

The LRTP of PFAS has sometimes been modelled, for example using the OECD long-range transport model, and used to provide additional evidence of LRTP. The reliability of such modelling is limited because reliable input parameters are not always available. Therefore, in general, LRTP has been demonstrated using monitoring data. For example:

#### Long chain PFCAs:

- PFOA and PFDA were found in seawater from an Arctic Fjord (Kongsfjorden) that receives Atlantic currents, attributed to LRTP (Ademollo *et al.*, 2021).
- C8 to C14 PFCAs were found in ice cores from the Devon Ice Cap (Arctic) (MacInnis et al., 2017).
- C8 to C13 PFCAs were detected in sediments from Lake Hazeon (Arctic circle) (MacInnis *et al.*, 2019).
- C8 to C14 and C16 PFCAs were detected in an ice core from Lomonosovfonna (a remote ice cap in the Svalbard Archipelago, Arctic), although C18 PFCA was below the MQL (2.3 pg/L) (Hartz et al., 2023).
- C8 to C12 PFCAs were detected in seawater, snow, snowmelt and lake water, while PFTrDA (C13) was detected snow, from Deception Island, Antarctica (Casas et al., 2023).
- PFOA, PFNA, PFUnDA and PFDoDA were detected in seawater, snow and snowmelt, PFDA was detected in snow and snowmelt, and PFTrDA was detected in seawater and snowmelt from Livingston Island, Antarctica (Casas et al., 2023).
- C8 to C14 PFCAs were detected in snow samples from Dome C, Antarctica (Xie et al., 2020).
- PFOA was detected in atmospheric samples above an area of the Amazon rainforest that was considered pristine, although it should be noted that C9 to C12 PFCAs were not found above the LOD (0.18 pg/mL) (Kourtchev et al., 2024).

#### Short chain PFCAs:

- PFHxA was found in seawater from an Arctic Fjord (Kongsfjorden) that receives Atlantic currents (Ademollo et al., 2021).
- C4 to C7 PFCAs were found in ice cores from the Devon Ice Cap (Arctic) (MacInnis et al., 2017).
- PFHxA and PFHpA were detected in sediments from Lake Hazen (Arctic circle) (MacInnis et al., 2019).

- PFBA was detected in surface snow at the summit of the Foxfonna ice cap (a remote location on Svalbard, Arctic) (Bjornsdotter *et al.*, 2021).
- C4 to C7 PFCAs were detected in an ice core from Lomonosovfonna (a remote ice cap in the Svalbard Archipelago, Arctic) (Hartz et al., 2023).
- PFBA was detected in seawater, snow, snowmelt and lake water, PFPeA was in snow and snowmelt, PFHxA was in seawater and snow, while PFHpA was in snow, snowmelt and lake water from Deception Island, Antarctica (Casas *et al.*, 2023).
- PFBA was detected in seawater, snow and snowmelt, PFPeA and PFHxA were in seawater and snow and PFHpA was in seawater, snow and snowmelt from Livingston Island, Antarctica (Casas *et al.*, 2023).
- C5 to C7 PFCAs were detected in snow from Dome C, Antarctica (PFBA was not analysed) (Xie *et al.*, 2020).
- It should be noted that each of the short chain PFCAs were screened for in atmospheric samples above the Amazon rainforest, but were not found above the LOD (0.18 pg/mL) (Kourtchev et al., 2024).

#### Ultra-short chain PFCAs:

- TFA and PFPrA were detected in ice cores from the Devon Ice Cap and Mount Oxford icefield, in the High Arctic of Canada (Pickard *et al.*, 2020).
- TFA and PFPrA were detected in surface snow at the summit of the Foxfonna ice cap (a remote location on Svalbard in the Arctic) (Bjornsdotter *et al.*, 2021).
- TFA and PFPrA were detected in an ice core from Lomonosovfonna (a remote ice cap in the Svalbard Archipelago, in the Arctic) (Hartz *et al.*, 2023).
- TFA was found in ocean water from the Southern Ocean and Mid-Atlantic Ocean (Frank *et al.*, 2002).

#### Long chain PFSAs:

- PFOS and PFDS were found in ice cores from the Devon Ice Cap (Arctic) (although PFHxS and PFHpS were not found above the LOD in the same samples) (MacInnis et al., 2017).
- PFHxS and PFOS were detected in sediments from Lake Hazen (Arctic circle) (MacInnis et al., 2019).
- PFOS was detected in seawater, snow, snowmelt and lake water from Deception Island, Antarctica, and seawater, snow and snowmelt from Livingston Island, Antarctica (where lake water was not analysed) (Casas *et al.*, 2023).
- C6 to C8, and C10 PFCAs were detected in snow samples from Dome C, Antarctica (PFNA was not analysed) (Xie *et al.*, 2020).
- PFHxS and PFOS were detected in an ice core from Lomonosovfonna (a remote ice cap in the Svalbard Archipelago, in the Arctic), while PFHpS, PFNS, PFDS and PFDoS were below the MQLs (9.3, 9.3, 2.3 and 2.3 pg/L, respectively) (Hartz *et al.*, 2023).
- It should be noted that PFHxS, PFHpS and PFOS were screened for in atmospheric samples above the Amazon rainforest, but were not found above the LOD (0.18 pg/mL) (Kourtchev *et al.*, 2024).

#### Short chain PFSAs:

- PFBS was found in seawater samples from an Arctic Fjord (Kongsfjorden) that receives Atlantic currents (Ademollo *et al.*, 2021).
- PFBS was found in ice cores from the Devon Ice Cap (Arctic) (MacInnis et al., 2017).
- PFBS was detected in sediments from Lake Hazen (Arctic circle) (MacInnis et al., 2019).
- PFBS and PFPeS were detected in an ice core from Lomonosovfonna (a remote ice cap in the Svalbard Archipelago, in the Arctic), while PFPrS was below the MQL (9.3 pg/L) (Hartz *et al.*, 2023).
- It should be noted that PFBS and PFPrS were below the limit of detection (<0.009 and 0.01 ng/L, respectively) in surface snow, at the summit of the Foxfonna ice cap (a remote location on Svalbard, Arctic) (Bjornsdotter et al., 2021).</li>
- PFBS was detected in seawater, snow, snowmelt and lake water from Deception Island, Antarctica, and seawater, snow and snowmelt from Livingston Island, Antarctica (where lake water was not analysed) (Casas *et al.*, 2023).
- PFBS was detected in snow samples from Dome C, Antarctica (Xie et al., 2020).
- It should be noted that PFBS and PFPeS were screened for in atmospheric samples above the Amazon rainforest, but were not found above the LOD (0.18 pg/mL) (Kourtchev *et al.*, 2024).

#### Ultra-short chain PFSAs:

- TFMS was detected in surface snow, while PFEtS was below the limit of detection (0.05 ng/L), at the summit of the Foxfonna ice cap (a remote location on Svalbard, in the Arctic) (Bjornsdotter *et al.*, 2021).
- PFEtS was below the MQL (9.3 pg/L) in an ice core from Lomonosovfonna (a remote ice cap in the Svalbard Archipelago, in the Arctic), while TFMS contamination to the ice core samples was identified as a result of cutting and processing highlighting the complexity of analysis for the ultra-short chain PFSAs (Hartz *et al.*, 2023).
- Few field data are available for the ultra-short chain PFSAs, possibly because of analytical limitations. With recent improvements in analytical techniques and an increase in the ultra-short chain PFAAs, it is likely that more data will become available in the near future.

It should be noted that, in some cases, the presence of PFAAs in remote areas around the world could be partly due to transport of volatile PFAA precursors (e.g., FTOHs) which subsequently transform to PFAAs either during transport or once deposition has occurred (Ellis *et al.*, 2003; MacInnis *et al.*, 2017; Pickard *et al.*, 2020; Shimizu *et al.*, 2021).

### Annex E.7.4 Conclusion on long range transport potential

Although there are few field data for the ultra-short chain PFSAs, given (a) the detection rates of the long chain and short chain PFSAs and (b) the detection rates of the ultra-short chain PFCAs, the Agency consider it likely that the ultra-short chain PFSAs will also be found in remote areas like the Arctic and Antarctic. The Agency considers that the field

data demonstrate the LRTP of all PFAAs, resulting in their presence in remote and pristine areas that are a long way from known sources. The LRT of these PFAAs may occur by movement in both atmospheric and oceanic currents.

# Annex E.8 Environmental toxicity

### Annex E.8.1 Ecotoxicological threshold values reported by ECHA (2023b)

ECHA (2023b) provide an overview of ecotoxicological threshold values taken from the PFAS-Tox Database (Pelch *et al.*, 2022), accessed on 7th October 2021; the effects relevant to the PFAAs are shown in Table E.17. The studies reported include long chain, short chain and ultra-short chain PFCAs, and long chain and short chain PFSAs. They show a wide variation in effects, across orders of magnitude. Although the Agency has not reviewed the studies for reliability and they do not appear to be standardised studies, the data do not indicate a level of toxicity that would be classified as 'T' under UK REACH. However, some of the concentrations shown are environmentally relevant. Although this review does not include any ultra-short chain PFSAs, given their likely lower toxicity levels than their longer chain counterparts, data on these have not been sought.

Table E.17: Ecotoxicological threshold values for PFAAs taken from the PFASTox database. Adapted from ECHA (2023b).

PFAA Grouping	Substance	Study type	Effect value	Effect	Endpoint	Species / Cell line	Reference
Long chain PFCA	PFDoDA	in vivo	1.2 mg/L	upregulated gene expression levels of thyrotropin-releasing hormone (trh)	LOEC	Danio rerio	Zhang <i>et al.</i> (2019)
Long chain PFCA	PFDoDA	in vivo	1.2 mg/L	upregulated gene expression levels of corticotrophin- releasing hormone (crh)	LOEC	Danio rerio	Zhang <i>et al.</i> (2019)
Long chain PFCA	PFDoDA	in vivo	6 mg/L	upregulated gene expression levels of iodothyronine deiodinases (dio2)	LOEC	Danio rerio	Zhang <i>et al.</i> (2019)
Long chain PFCA	PFDoDA	in vivo	1.2 mg/L	downregulated gene expression levels of thyroglobulin (tg)	LOEC	Danio rerio	Zhang <i>et al.</i> (2019)
Long chain PFCA	PFDoDA	in vivo	6 mg/L	downregulated gene expression levels of	LOEC	Danio rerio	Zhang <i>et al.</i> (2019)

PFAA Grouping	Substance	Study type	Effect value	Effect	Endpoint	Species / Cell line	Reference
				thyroid receptor (trbeta)			
Long chain PFCA	PFDA	in vivo	78 μg/L (95 % CI, Range 73– 84 μg/L)	genotoxicity (DNA strand breaks and fragmentation, chromosomal breaks and apoptosis)	EC50	Perna viridis	Liu <i>et al.</i> (2014)
Long chain PFCA	PFDA	in vivo	31.1 ± 5.2 mg/L	behaviour: prolonged backward swimming (indicating modified cellular cadmium conductance)	EC50	Paramecium caudatum	Matsubara <i>et al.</i> (2006)
Long chain PFCA	PFDA	in vitro	3.6 mg/L	inhibition of p- glycoprotein (p-gp) cellular efflux transporter	IC50	gill cells from Mytilus californianus	Stevenson et al. (2006)
Long chain PFCA	PFDA	in vivo	5.0 mg/L (95 % CI, Range 3.8– 6.6 mg/L)	sublethal endpoints (edema, malformations, non- hatched eggs, lack of circulation, reduced	EC50	Danio rerio	Ulhaq <i>et al.</i> (2013)

PFAA Grouping	Substance	Study type	Effect value	Effect	Endpoint	Species / Cell line	Reference
				pigmentation, spinal curvature)			
Long chain PFCA	PFDA	in vivo	8.4 mg/L (95% CI, Range 5.3– 15 mg/L)	mortality	LC50	Danio rerio	Ulhaq et al. (2013)
Long chain PFCA	PFNA	in vitro	2.2 mg/L	inhibition of p- glycoprotein (p-gp) cellular efflux transporter	IC50	gill cells from Mytilus californianus	Stevenson <i>et al.</i> (2006)
Long chain PFCA	PFNA	in vivo	100000 µg/kg dw	Significant weight loss	LOEC	Eisenia fetida	Karnjanapiboonwong et al. (2018)
Long chain PFCA	PFNA	in vivo	195 µg/L (95 % CI, Range 144–265 µg/L)	genotoxicity (DNA strand breaks and fragmentation, chromosomal breaks and apoptosis)	EC50	Perna viridis	Liu <i>et al.</i> (2014)
Long chain PFCA	PFNA	in vivo	45.8 ± 9.3 mg/L	behaviour: prolonged backward swimming (indicating modified	EC50	Paramecium caudatum	Matsubara et al. (2006)

PFAA Grouping	Substance	Study type	Effect value	Effect	Endpoint	Species / Cell line	Reference
				cellular cadmium conductance)			
Long chain PFCA	PFNA	in vivo	16 mg/L (95 % CI, Range 7.7– 450 mg/L)	sublethal endpoints (edema, malformations, non- hatched eggs, lack of circulation, reduced pigmentation, spinal curvature)	EC50	Danio rerio	Ulhaq <i>et al.</i> (2013)
Long chain PFCA	PFNA	in vivo	>10 mg/L	mortality	LC50	Danio rerio	Ulhaq et al. (2013)
Long chain PFCA	PFNA	in vivo	100000 µg/kg dw	increased mortality	LOEC	Eisenia fetida	Karnjanapiboonwong et al. (2018)
Long chain PFCA	PFOA	in vivo	594 μg/L (95 % CI, Range 341– 1063 μg/L)	genotoxicity (DNA strand breaks and fragmentation, chromosomal breaks and apoptosis)	EC50	Perna viridis	Liu <i>et al.</i> (2014)
Long chain PFCA	PFOA	in vivo	182.8 ± 53.5 mg/L	behaviour: prolonged backward swimming (indicating modified	EC50	Paramecium caudatum	Matsubara <i>et al.</i> (2006)

PFAA Grouping	Substance	Study type	Effect value	Effect	Endpoint	Species / Cell line	Reference	
				cellular cadmium conductance)				
Long chain PFCA	PFOA	in vivo	350 mg/L (95 % CI, Range 290–430 mg/L)	sublethal endpoints (edema, malformations, non- hatched eggs, lack of circulation, reduced pigmentation, spinal curvature)	EC50	Danio rerio	Ulhaq <i>et al.</i> (2013)	
Long chain PFCA	PFOA	in vivo	430 mg/L (95 % CI, Range 290–710 mg/L)	mortality	LC50	Danio rerio	Ulhaq <i>et al.</i> (2013)	
Short chain PFCA	PFHpA	in vivo	100000 µg/kg dw	Significant weight loss	LOEC	Eisenia fetida	Karnjanapiboonwong et al. (2018)	
Short chain PFCA	PFHpA	in vivo	100000 μg/kg dw	increased mortality	LOEC	Eisenia fetida	Karnjanapiboonwong et al. (2018)	
Short chain PFCA	PFHxA	in vivo	0.1 mg/L	reduction in the overall length and yolk sac size	LOEC	Danio rerio	Annunziato <i>et al.</i> (2019)	

PFAA Grouping	Substance	Study type	Effect value	Effect	Endpoint	Species / Cell line	Reference
				(however not observed at higher doses)			
Short chain PFCA	PFHxA	in vivo	140 mg/L	mortality	LC50	Brachionus calyciflorus	Wang <i>et al.</i> (2014)
Short chain PFCA	PFPeA	in vivo	130 mg/L	mortality	LC50	Brachionus calyciflorus	Wang <i>et al.</i> (2014)
Short chain PFCA	PFBA	in vivo	2200 mg/L (95 % CI, Range 1200–2200 mg/L)	sublethal endpoints (edema, malformations, non- hatched eggs, lack of circulation, reduced pigmentation, spinal curvature)	EC50	Danio rerio	Ulhaq <i>et al.</i> (2013)
Short chain PFCA	PFBA	in vivo	110 mg/L	mortality	LC50	Brachionus calyciflorus	Wang <i>et al.</i> (2014)
Short chain PFCA	PFBA	in vivo	>3000 mg/L	mortality	LC50	Danio rerio	Ulhaq <i>et al.</i> (2013)

PFAA Grouping	Substance	_	Effect value	Effect	Endpoint	Species / Cell line	Reference
Ultra-short- chain PFCA	PFPrA	in vivo	80 mg/L	mortality	LC50	Brachionus calyciflorus	Wang <i>et al.</i> (2014)
Ultra-short- chain PFCA	TFA	in vivo	>3000 mg/L	mortality	LC50	Danio rerio	Ulhaq <i>et al.</i> (2013)
Ultra-short- chain PFCA	TFA	in vivo	700 mg/L (95 % CI, Range 460–1000 mg/L)	sublethal endpoints (edema, malformations, non- hatched eggs, lack of circulation, reduced pigmentation, spinal curvature)	EC50	Danio rerio	Ulhaq <i>et al.</i> (2013)
Ultra-short- chain PFCA	TFA	in vivo	70 mg/L	mortality	LC50	Brachionus calyciflorus	Wang <i>et al.</i> (2014)
Long chain PFSA	PFOS	in vivo	16.0 ± 2.2 mg/L	behaviour: prolonged backward swimming (indicating modified cellular cadmium conductance)	EC50	Paramecium caudatum	Matsubara <i>et al.</i> (2006)

PFAA Grouping	Substance	Study type	Effect value	Effect	Endpoint	Species / Cell line	Reference
Long chain PFSA	PFOS	in vivo	0.7 mg/L (95 % CI, Range 0.6– 0.8 mg/L)	mortality	LC50	Caenorhabditis elegans	Chen <i>et al.</i> (2018a)
Long chain PFSA	PFOS	in vivo	% CI,	genotoxicity (DNA strand breaks and fragmentation, chromosomal breaks and apoptosis)	EC50	Perna viridis	Liu <i>et al.</i> (2014)
Long chain PFSA	PFOS	in vivo	1.5 mg/L (95 % CI, Range 1.1– 1.9 mg/L)	sublethal endpoints (edema, malformations, non- hatched eggs, lack of circulation, reduced pigmentation, spinal curvature)	EC50	Danio rerio	Ulhaq <i>et al.</i> (2013)
Long chain PFSA	PFOS	in vivo	<10 mg/L	mortality	LC50	Danio rerio	Ulhaq et al. (2013)
Long chain PFSA	PFHxS	in vivo	0.9 mg/L	morphometric effects in the larvae, specifically increased	LOEC	Danio rerio	Annunziato et al. (2019)

PFAA Grouping	Substance		Effect value	Effect	Endpoint	Species / Cell line	Reference
				length and yolk sac area			
Long chain PFSA	PFHxS	in ovo	38000 ng/g (egg w)	decreased tarsus length and embryo mass	LOEC	Gallus gallus domesticus	Cassone et al. (2012)
Long chain PFSA	PFHxS	in vivo	100000 µg/kg dw	increased mortality	LOEC	Eisenia fetida	Karnjanapiboonwong et al. (2018)
Short chain PFSA	PFBS	in vivo	238 mg/L (95 % CI, Range 187–303 mg/L)	mortality	LC50	Caenorhabditis elegans	Chen et al. (2018a)
Short chain PFSA	PFBS	in vivo	450 mg/L (95 % CI, Range 350–600 mg/L)	sublethal endpoints (edema, malformations, non- hatched eggs, lack of circulation, reduced pigmentation, spinal curvature)	EC50	Danio rerio	Ulhaq <i>et al.</i> (2013)
Short chain PFSA	PFBS	in vivo	1500 mg/L (95 % CI,	mortality	LC50	Danio rerio	Ulhaq <i>et al.</i> (2013)

PFAA Grouping	Substance	Study type	Effect value	Effect	Endpoint	Species / Cell line	Reference
			Range 1100–1900 mg/L)				
Short chain PFSA	PFBS	in vivo	100000 μg/kg dw	increased mortality	LOEC	Eisenia fetida	Karnjanapiboonwong et al. (2018)

LOEC – lowest observed effect concentration (lowest concentration that has a statistically significant adverse effect on the tested organisms); LC50 – median lethal concentration (concentration where 50% of the organisms tested died); EC50 – median effective concentration (concentration where 50% of the organisms tested showed the effect); IC50 – median inhibitory concentration (concentration where 50% inhibition of the measured biological process occurred).

# Annex E.8.2 Adverse ecotoxicological effects reviewed by ECCC and Health Canada (2024)

ECCC and Health Canada (2024) provides a general overview of effects that have been observed for PFAAs; effects relevant to environmental toxicology are summarised in Table E.18. Some of the reported effects (e.g. lysosome damage, behavioural changes, etc.) are not straightforward to assess in the context of an assessment that aims to protect population viability, because the level of effect that is considered relevant, and the consistency / repeatability of measurements, has not been established. Nevertheless, the list indicates that PFAAs are associated with a wide range of effects in many taxonomoic groups. It should be noted that the effect concentrations recorded are not necessarily above T thresholds under UK REACH (see Table E.6).

Table E.18: Adverse ecotoxicological effects, as reviewed by ECCC and Health Canada (2024)

Biota	Data availability	PFAAs	Types of effect
Aquatic invert-ebrates	Most data available	PFOA, PFOS and/or PFHxS	PFSAs typically more toxic than PFCAs.  Longer perfluorinated chain typically more toxic than shorter.  Growth, development, reproduction, oxidative stress, immune-related cell viability, immune fitness, lysosomal damage, genotoxic, neurotoxic (altered brain morphology, locomotor velocity, gene expression), and multigenerational effects (reductions in growth and individual fitness across generations).
Terres- trial invert- ebrates	Fewer than aquatic invert-ebrates	PFOA, PFOS and/or PFHxS	Longer perfluorinated chain typically more toxic than shorter.  Developmental, behavioural, reproductive, neurotoxic, developmental, genotoxic, growth, physiological, locomotive and chronic effects; oxidative stress, mortality.
Fish	Fewer than aquatic	PFOA, PFOS, PFNA,	Lower acute toxicity compared to aquatic invertebrates. Varies with chain length and

Biota	Data availability	PFAAs	Types of effect
	invert- ebrates	PFBS, PFHxS	functional group; short chain and PFSAs more toxic than long chain and PFCAs.
			Reproduction, growth/development, mobility, behaviour, survival, body length, locomotor speed, hatching rate, larval morphology, oxidative stress, genotoxicity and neutrotoxicity, endocrine disruption, reprotoxicity, multigenerational effects (mortality, fecundity, gonad development, swimming rate, thyroid endocrine system, lipid pathways and behaviour in offspring).
Amph- ibians and reptiles	Limited	PFOS, PFOA, PFHxS	Lower acute toxicity compared to aquatic invertebrates. Varies with chain length and functional group and species exposed; PFOS more toxic than PFOA.  Amphibians Growth, development, chronic (body condition and development), lipid metabolism, liver damage, endocrine disruption, immunosuppression, hepatotoxicity.  Reptiles Emergence success of hatchlings, body mass, metabolic impacts, and immune function.
Birds	Fewer than aquatic invert-ebrates	PFOS, PFOA, PFHxS, PFHxA, PFUnDA	C <sub>8</sub> chain and PFSAs more toxic than shorter chain and PFCAs.  Physiological effects on nestlings, immunotoxicity, genoxoticity, hatching success, toxicogenomic effects, body weight, liver weight, endocrine disruption, metabolism disruption, hatching success, oxidative stress.
Plants	Limited	PFOS, PFOA, PFBS	Cell morphology, photosynthetic pigments/activity and plant phenotype, root cell ultrastructure, growth rate, fresh weight, overgeneration of reactive oxygen species,

Biota	Data availability	PFAAs	Types of effect
			gene expression, photosynthesis, energy metabolism, phytotoxicity, immunotoxicity.

<sup>\*</sup>Mammalian wildlife was also covered in the review by Higgins and Luthy (2006), but has not been included here as the human health section covers this.

# Annex E.9 Detection of PFAS in GB close to known firefighting foam sources – Case Studies

# Annex E.9.1 Formulation site - Angus Fire Ltd

The site formulated FFF concentrates since the 1970s, initially using C8 PFOS-based substances before moving to unspecified C6 PFAS by 2009, when PFOS was included in the POPs Regulation. In early 2024, Angus Fire stopped formulation and supply of all fluorinated foams. The site operates under an Environmental Permit EPR/XP3832NV/V003 for the production of allophanate and protein solution for formulation into firefighting foam concentrates. The activities included in the installation boundary are two boilers, materials storage for the protein plant and waste lagoons. The formulation of FFF using the protein solution and PFAS based surfactants is not a listed activity under the permit but took place within the same building as the protein liquor production.

There is a fire testing area on site where new foams under development are tested. Originally the testing took place in a recessed shallow basin on a concreted area, before switching to dedicated steel pans in the same area. The wastewater from the fire testing area and some other parts of the site discharged through an oil/water interceptor and then into two butyl lined wastewater lagoons, prior to discharge to sewer for treatment at the municipal sewage treatment works. The water collected in the lagoons may have contained PFAS from historic spills or contamination of the soil or drainage system on site (Ramboll, 2018). The lagoons have a total capacity of 182 m³ (Environment Agency, 2007c).

The decision document for the original Environmental Permit (number BU5593IL), made on 31/8/06, noted that no integrity testing had been done on the lagoons and that they posed a potential for fugitive releases. An improvement condition was imposed at that time. The effluent in the lagoons was pumped to foul sewer under a trade effluent discharge consent from the water company (Environment Agency, 2007a, 2007b). A survey in 2018 for the site protection and monitoring programme (SPMP) indicated that the lining of lagoons had lifted from the bases and that therefore there may have been leakage into the underlying soil (Waterman, 2018).

### **Monitoring data**

Monitoring at or near the site has been undertaken by both the Environment Agency and on behalf of Angus Fire as part of the requirements of their Environmental Permit.

# **Environment Agency monitoring**

There is a borehole within the site boundary known as the Angus Fire Armour Borehole, which is part of the Environment Agency's groundwater quality monitoring network. Analysis for a number of different PFAS was undertaken in 2021 and 2022 (Environment Agency, 2024c). These data are publicly available as part of the Water Quality Archive.

The substances identified as present in all 4 of the samples taken in 2021/22 were PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFBS, PFPeS, PFHxS (branched and linear), PFHpS, PFOS (branched and linear), 4:2 FTS, 6:2 FTS, 5:2 FTA, FBSA and

FHxSA. The analytical method used was a semi-quantitative method using liquid chromatography mass spectrometry (LC-MS). This method provides an estimate of the concentrations of the PFAS monitored for. However, it is not validated for accuracy and precision in the same manner as a fully quantitative accredited analytical method would be.

The data show that all of the PFAS that have been identified as being in Angus Fire fluorinated foams (Wood, 2020) have been detected in the groundwater on site.

### **Angus Fire SPMP reports**

Angus Fire contracted Ramboll to undertake groundwater monitoring every 5 years and soil monitoring every 10 years, as a systematic appraisal of the risk of contamination (Ramboll, 2018). These monitoring surveys included a number of PFAS. However, Angus Fire determined that "No on-going soil monitoring will occur at the installation during the life of the permit. Soils within the area requiring reference data to be collected are considered to have been sufficiently characterized, based upon current site usage" and therefore there were no soil data submitted in the reports.

Angus Fire commissioned a SPMP for groundwater and water from the lagoon in 2018. Samples were taken from a number of existing boreholes on site and results were submitted to the Environment Agency with comparisons with previous monitoring data from 2008 and 2010 (Ramboll, 2018) provided in Tables E.19 and E.20. The Agency has no information on the method used for the analysis.

Table E.19: Groundwater monitoring data from boreholes on Angus Fire site (Ramboll, 2018).

	Maximum concentration (μg/L)				
	2008	2010	2018		
PFHxA	25.8	10.9	8.8		
PFHpA		6	3.5		
PFOA	18.1	1.3	2.5		
PFNA	0.9	1	0.2		
PFUnDA		0.9			
PFBS	1.2	0.1	0.6		
PFPS	1.2	0.1	0.7		
PFHxS	25.5	1.6	12.7		

	Maximum concentration (μg/L)				
	2008	2010	2018		
PFHpS	1.9	4	0.6		
PFOS	36.1	2.7	10.7		
6:2 FTS	245	29.4	23.1		
FATAS-586	2.8	0.5			
FATAS-686			0.1		

Note: substances are only included where any of the results are above the LOD

Table E.20: Lagoon monitoring data from Angus Fire site (Ramboll, 2018).

	Concentration (µg/L)				
	2008	2010	2018		
PFHxA	8.4	0.3	1.7		
PFHpA		0.1	0.4		
PFOA	9.3	0.2	0.4		
PFHxS		0.3	0.4		
PFOS	2.8	0.6	1.6		
6:2 FTS	146	8.8	28.4		
FATAS-586	825	21.7	13.2		
FATAS-686	5				

Note: substances are only included where any of the results are above the LOD

# Conclusion

The main releases at the Angus Fire site were likely from the testing of the foams and the on-site lagoons, rather than the formulation stage. The monitoring data from both the

Environment Agency and Ramboll (2018) show that the use of PFAS on site has led to contamination of the water in the lagoons and the groundwater beneath the site. PFOS, the use of which had stopped at the site by 2009, continues to be detected in groundwater, thereby demonstrating the persistence of PFOS.

# **Annex E.9.2 Use at Airports**

Airports are considered to account for a significant source of PFAS from firefighting foams into the environment as discussed in section (aviation above). The fire training area has been identified as a major source (Ahrens *et al.*, 2015) as airports have regulatory requirements for regular training of their fire and rescue staff (CAA, 2022). As discussed in section (aviation above) airports are also used for either external training or testing of new foams by formulators.

The Environment Agency commissioned a project to sample water courses upstream and downstream of eight UK airports in 2023: Birmingham, Bournemouth, East Midlands, Gatwick, Leeds Bradford, Manchester, Newcastle and Stansted. The samples were analysed for 17 different PFAS (including C3, C4 and C6-12 PFCAs, C4-8 and C10 PFSAs, 6:2 FTS and PFOSA). A total of 36 samples were taken, 2 upstream and 2 downstream of each airport on 2 different occasions, with an additional 4 duplicates downstream of 4 airports. PFOS was analysed for using three methods, yielding 19 analytical results per sample, including total PFOS, branched PFOS, and linear PFOS. The sample analysis was undertaken by ALS Laboratories (UK) Ltd, a United Kingdom Accreditation Service (UKAS) accredited laboratory using a fully quantitative method. The analytical results were then used as the basis of a Strathclyde University MSc dissertation (Mellor, 2023) whereby conceptual site models were derived for the airports. The maximum values from the analysis are shown in Table 3.3.

Table E.21: Maximum values from monitoring PFAS upstream and downstream of GB airports

			Upstream		Downstream	
Analytical Parameter	Limit of detection ng/L	Chain length	Max ng/L	Location	Max ng/L	Location
PFBA (375-22-4)	<2	C4	5.39	London Gatwick Airport	45.5	East Midlands Airport
PFPeA (2706-90-3)	<1	C5	8.22	London Gatwick Airport	133	East Midlands Airport
PFHxA (307-24-4)	<1	C6	6.24	Bournemouth Airport	97.8	East Midlands Airport
PFHpA (375-85-9)	<1	C7	4.2	London Gatwick Airport	86.4	East Midlands Airport

			Upstream		Downstream	
Analytical	Limit of detection ng/L	Chain length	Max	Location	Max	Location
Parameter			ng/L		ng/L	
PFOA (335-67-1)	<0.65	C8	18.2	Leeds Bradford Airport	48.5	Stanstead Airport
PFNA (375-95-1)	<1	C9	<1	n/a	5.7	Leeds Bradford Airport
PFDA (335-76-2)	<1	C10	<1	n/a	2.08	Stanstead Airport
PFUnDA (2058-94- 8)	<1	C11	<1	n/a	<1	n/a
PFDoDA (307-55-1)	<1	C12	<1	n/a	<1	n/a
PFBS (375-73-5)	<1	C4	3.42	Manchester Airport	3.93	Stanstead Airport
PFPeS (2706-91-4)	<1	C5	2.56	Leeds Bradford Airport	2.96	Birmingham Airport
PFHxS (355-46-4)	<1	C6	6.33	Leeds Bradford Airport	39.2	Birmingham Airport
PFHpS (375-92-8)	<1	C7	1.17	Leeds Bradford Airport	1.58	Leeds Bradford Airport
Branched PFOS	<0.65	C8	24.1	Leeds Bradford Airport	29	Leeds Bradford Airport
Linear PFOS (1763- 23-1)	<0.65	C8	4.31	London Gatwick Airport	43.1	Birmingham Airport
Total PFOS	<0.65	C8	27.1	Leeds Bradford Airport	70	Birmingham Airport
PFDS (335-77-3)	<1	C10	<1	n/a	<1	n/a
6:2 FTS (27619-97- 2)	<1	C6	2.9	London Gatwick Airport	180	East Midlands Airport
PFOSA (754-91-6)	<2	C8	<2	n/a	<2	n/a

The monitoring data show that PFAS commonly used in firefighting foams, historically PFOS and PFOA and more recently 6:2 FTS, have been found at greater concentration in surface water samples downstream than upstream at 7 of the 8 airports, with the exception

of 1 sampling occasion at Leeds Bradford Airport where the upstream concentration of branched PFOS was 24.1 ng/L and downstream it was 12.3 ng/L.

A similar pattern was observed for the other PFAS monitored for, with increased concentrations downstream of the airport, with the exception of eight samples: both sampling occasions for PFBS, one sampling occasion for PFHxS and PFPeS at Leeds Bradford Airport; PFBA, PFPeA, PFHxA and PFHpA at Manchester Airport; and PFHxA in one sampling occasion at Stansted Airport.

The sum of total PFAS was also reported. East Midlands Airport showed the highest downstream levels with a total PFAS concentration of 575.84 ng/L. East Midlands Airport also showed the highest percentage increase between upstream and downstream of 63,179 % (0.91 ng/L total PFAS upstream).

A limitation of the study was that all the samples were taken from easily accessible locations outside of the airports' boundary, and therefore no on-site samples were taken. Although the data appear to indicate a contribution from sources on/within the airports and other upstream PFAS sources were not identified, further work would be required before definitive pollutant linkages can be proved.

Limited environmental monitoring data for PFAS are available from Scotland, though this was not targeted to potential sources. PFAS monitoring data from 2018 for 22 rural, industrial and urban sites across Scotland have been released under the Environment Information Regulations. The highest level of PFAS at any site was 18.2 ng/L for PFHxA, found in the River Almond near Craigiehall, downstream of Edinburgh Airport (SEPA, 2021).

### Annex E.9.2.1 Heathrow

Heathrow Airport Ltd (HAL) is the largest London airport. It is located 15 miles west of central London and covers an area of 1,227 hectares. It has 2 runways and 4 passenger terminals along with a large infrastructure for cargo (Heathrow Airport, 2024). The site is split into three drainage catchments;

- i. the Western Catchment which covers Terminal 5 and part of the southern runway,
- ii. the Southern Catchment which covers parts of Terminals 1 and 2 and all of Terminal 3, the cargo terminal and part of the southern runway, and
- iii. the Eastern Catchment which covers the remainder of Terminals 1 and 2, most of the northern runway, the eastern stand, engineering hangars and the fire training ground.

The Western and Southern Catchments drain into Clockhouse Lane Pit then via the Feltham Relief Sewer to Portlane Brook. The Eastern Catchment drains into the Eastern Balancing Reservoir (EBR) (Ricardo, 2021).

### **Environment Agency monitoring**

Data from the Environment Agency's routine monitoring programme showed presence of both PFOS and PFOA in the Eastern Lagoons at the outlet weir and the discharge to Clockhouse Lane pit between 2019 and 2024.

# **Heathrow monitoring programme**

Heathrow Airport has undertaken an extensive PFOS monitoring programme since 2019, including 3 rounds of intrusive sampling on the site and the nearby River Crane. Samples were taken in November 2019, December 2020 and March 2021. The Environment Agency has been supplied with a copy of a summary presentation (Ricardo, 2021), but has not seen the report the presentation is based on, or the raw monitoring data.

Samples of the water in the drainage system were taken across the site and clusters of "high" results (defined by Ricardo as above 0.1  $\mu$ g/L) were identified in the following places:

- Terminal 5 stands and local road drainage highest level found: 1.43 μg/L in round 3.
- Eastern end of North Runway highest level found: 0.344 μg/L in round 3.
- Fire Training Ground highest level found: 0.31 μg/L in round 2.
- Grass area 20 (dewatering location) highest level found: 0.13 μg/L in round 1.

The data show that the fire training area is one of the sources of PFOS contamination, but that other areas are also significant sources. The Agency has no information as to any incidents on the Heathrow site where PFAS-containing foam may have been used.

The results for 21 samples from the River Crane found that levels of PFOS increased by 50% on average from upstream to downstream of the discharge from the EBR (0.02 ng/L to 0.03 ng/L on average). This indicates that while the airport is contributing to the PFOS levels, it is not the only source in the River Crane catchment.

### Other sources of PFAS at Heathrow

HAL started a transition to PFAS-free foams in 2012 for all aircraft uses in the areas under their control, including training (Wood, 2020). The transition to PFAS-free foams has been completed (IPEN, 2019). Churches Fire Security confirmed that they maintain a foam system at a hangar at Heathrow and are currently looking at replacement with fluorine-free alternatives (Call for evidence, Fire Security). It is also possible that PFAS-containing foams are still present in other areas such as maintenance hangers operated by airlines or maintenance companies on site.

Some PFAS are also reported to be used in hydraulic fluids on aircraft. A study in the US found that an aviation hydraulic fluid contained 344 ng/g of total PFAA's prior to TOP analysis (Zhu and Kannan, 2020). The use of PFAS in hydraulic fluids is not within the scope of the restriction.

### **Environmental permit**

Heathrow has a number of Environmental Permits covering discharge to surface waters from the site. One of these (permit number CO3033) covers discharge from the EBR. The EBR receives runoff from the Eastern Catchment of the airport which contains rainwater, groundwater (from the shallow water table) and de-icers from periods of adverse weather (Environment Agency, 2024b).

HAL undertook a water quality screening assessment in 2019 as part of a permit variation application for upgrades to the EBR for PFOS using the Environment Agency's H1 impact assessment tool. It found that "the PFOS dataset passes for all Maximum Annual Concentration (MAC) tests but fails Annual Average (AA) tests under both low and high flow scenarios, noting the LOD is substantially higher than the AA EQS. A source review indicates that this is likely to be a legacy pollutant from historic use in firefighting foams used by HAL" (Ricardo, 2019).

In February 2024, an improvement condition was added by the Environment Agency requiring HAL to further assess the sources of PFOS on the site, identify improvements that could be made on site to reduce the concentrations of PFOS and set out an emissions management plan to manage residual risk. The Environment Agency further required monitoring for additional PFAS in areas where PFOS had been found and to produce a monitoring programme for the discharges from the Eastern Catchment. Following this a complete surface water risk screening should be done and then produce a long term PFOS management plan, within 3 years of issue of the permit (Environment Agency, 2024b).

### Conclusion

PFAS-free foams are in use at Heathrow Airport, but there could be residual use in some areas owned by operators other than HAL. The monitoring programme undertaken by HAL shows that there are hotspots of PFOS contamination on the site arising from legacy use, including the northern runway and the fire training area, despite usage stopping over 9 years previously. Monitoring for additional PFAS is on-going.

### Annex E.9.2.2 Duxford

The former RAF Duxford site in Cambridgeshire opened as a Royal Air Force base in 1917 and served as a United States Army Air Force airbase from 1943-45. Military flights ceased in July 1961 (IWM, 2024). In 2008 Cambridgeshire County Council agreed to sell the runways and some of the land around them to the Imperial War Museum (IWM) (Cambridgeshire CC, 2008) and it now houses the IWM's Fighter collection and two private collections of vintage aircraft, as well as operating as a civilian airfield (Duxford Aerodrome), which is licenced by the CAA (DARFFS, 2024).

There is a permanent Rescue and Fire Fighting Service on site as required by the CAA. The service operates 3 vehicles, all with foam capabilities. According to the Rescue and Fire Fighting Service website, fire training for staff takes place on site and the contaminated water is collected for safe disposal. However, there are no details of what disposal method is used (DARFFS, 2024). The site also hosts training for other organisations, including other airfields and the British Antarctic Survey (DARFFS, 2024) and there are other organisations also based on the site. Cambridge Water engaged with the air museum to confirm the type of foams used on site. The use of PFOS based foams stopped in 2008, when an alternative PFAS-containing foam was used, and the airfield transitioned to a PFAS-free foam in March 2022 (DWI, 2022b).

There is a drinking water pumping station within the airfield site boundary, which is fed by two borehole extraction points. The water is pumped to the nearby Sawston Mill works for blending, treatment and onward distribution to consumers in the Cambridge Rural water supply zone. At Sawston Mill, the treatment consists of ultraviolet (UV) disinfection, which

is followed by phosphoric acid dosage for plumbosolvency control and chlorination as an additional disinfection procedure (DWI, 2022b).

Cambridge Water has monitored for PFOS in the Duxford source since 2007. Between 2007 and 2013, 55 samples had PFOS concentrations ranging from <0.1  $\mu$ g/L to 0.422  $\mu$ g/L in the untreated water. Between 2014 and 2015, 33 samples were taken from a range of Cambridge source waters and all sites were determined as low risk, based on the 1.0  $\mu$ g/L upper threshold guidance value issued on 1 June 2007 for treated water by the Drinking Water Inspectorate (DWI) (DWI, 2021). Monitoring was then suspended between 2015 and 2020 as Cambridge Water considered that there was a very low risk of the site exceeding the 1.0  $\mu$ g/L upper threshold guidance level (DWI, 2022a).

In 2020 the DWI requested further PFOS monitoring from Cambridge Water to understand the current concentrations in light of emerging evidence on the potential impacts of this substance on human health. The concentration in the samples ranged from 0.1  $\mu$ g/L to 0.3  $\mu$ g/L in the untreated water (DWI, 2022a).

New threshold guidance levels were published by the DWI for PFOS in 2021, reducing the threshold for wholesomeness to 0.1  $\mu$ g/L in treated water (DWI, 2021). Four samples taken from the untreated Duxford Airfield (S. Mill) borehole in 2021 had levels between 0.254  $\mu$ g/L and 0.394  $\mu$ g/L, up to almost 4 times the revised drinking water threshold. Concentrations above the revised drinking water threshold had also been reported over the period 2007-2020 in the untreated water.

The DWI opened an investigation on 8 February 2022 after receiving notice from Cambridge Water that PFOS was present in drinking water sources in the Cambridge Rural district. According to the DWI's investigation, PFOS was found in the supply as a result of the use of PFOS-containing firefighting foam at Duxford airfield. The raw water used for abstraction became contaminated when the firefighting and training water runoff containing the foam entered the aquifer (DWI, 2022a).

The DWI issued a Regulation 28(4) Notice under the Water Industry Act 1991 and the Water Supply (Water Quality) Regulations 2016 to Cambridge Water on 21 February 2022 requiring a number of actions, including monitoring the source water, plans to mitigate the risks, and implement and conduct continuous review of an audit strategy. It also contained a prohibition section which prevented the company from supplying water from Sawston Mill unless the concentrations of PFAS substances in the source water were controlled and below the precautionary level of 0.1 µg/L (DWI, 2022a).

### **Environment Agency monitoring**

The Environment Agency has a groundwater monitoring point at "Sawston Inv. Springfield Road. Upwelling", which is on the same aquifer as the Duxford abstraction points (Environment Agency, 2024c). Monitoring for a number of PFAS started in 2023. The substances identified as present in 10 samples taken in 2023-24 were PFBA, PFHxA, PFOA, PFBS, PFHxS (linear) and PFOS (branched and linear). The analytical method is a semi-quantitative method using liquid chromatography mass spectrometry (LC-MS). This method provides an estimate of the concentrations of the PFAS monitored for using a method that is not validated for accuracy and precision in the same manner as a fully

quantitative accredited analytical method would be. The Agency is using this monitoring data to report presence or absence of a substance and not its concentration.

#### Conclusion

The DWI concluded that the use of PFOS-containing firefighting foam on the Duxford airfield has contaminated the local aquifer and subsequently impacted drinking water supplies. The analysis conducted by Cambridge Water and the investigation undertaken by the DWI only looked at PFOS (DWI, 2022a). The Environment Agency monitoring data shows that the groundwater also contains PFOA, PFHxA, PFBA, PFBS and PFHxS (linear), all of which are PFAA arrowheads. This analysis has not necessarily identified all of the PFAS that may be present. As the DWI concluded in their investigation that the PFOS originated from the use of firefighting foams on site the Agency considers it likely that the other PFAS present are from the same source.

# Annex E.9.3 Use at Military sites RAF St Athan

A 2010 investigation on a parcel of land which included the former fire training area at RAF St Athan in Barry, South Wales detected a variety of PFAS in soil and groundwater samples (Ramboll, 2022). PFAS were found in eight out of fifteen shallow soil samples, mostly in the fire training area in the south of the site. The maximum levels were 4  $\mu$ g/kg for PFOA and 8  $\mu$ g/kg for PFOS, the report did not state whether the analysis was on dry weight or wet weight. Six groundwater samples and one surface water sample were analysed for 37 different PFAS. At least one PFAS was found in five of the seven samples tested. Ten PFAS were discovered at one sampling location south of the fire training area, with the highest concentrations recorded for each: 1.13  $\mu$ g/L for PFOS, 16.8  $\mu$ g/L for 6:2 FTS, 4.26  $\mu$ g/L for PFPeA, 2.49  $\mu$ g/L for PFHxA, 1.9  $\mu$ g/L for 8:2 FTS, 1.14  $\mu$ g/L for PFOA, 1.02  $\mu$ g/L for PFHpA, 0.81  $\mu$ g/L for PFBA, 0.16  $\mu$ g/L for PFNA and 0.1  $\mu$ g/L for PFHxDA. This shows that PFAS had contaminated the groundwater close to the fire training area, and PFOS was present following its ban under the POP Regulations.

### **United States Airforce sites in GB**

The United States Airforce, known as the United States Visiting Forces (USVF), operates on 6 RAF bases in GB (US DoD, 2025). The Airforce undertakes routine monitoring for PFAS in their public water systems, which are used to supply drinking water on the bases (US EPA, 2025). At RAF Mildenhall, where the USVF occupies part of the site, the drinking water is drawn from an on-base groundwater borehole and is passed through a granulated activated carbon (GAC) filter (US DoD, 2023b). A monitoring programme undertaken in 2023 showed that while no PFAS were detected above the maximum contaminant level (MCL) of 70 ng/L for PFOS and PFOA that is allowed in drinking water in the US at RAF Mildenhall or RAF Lakenheath, a maximum of 6.65 ng/L of PFOS and 2.5 ng/L of PFOA was found at RAF Mildenhall. PFHxA was also found at Mildenhall at a maximum concentration of 11.5 ng/L, PFHxS at a maximum concentration of 14.1 ng/L and PFPeA at 15 ng/L. None of the PFAS substances monitored for in the routine monitoring were detected above the limit of detection at RAF Feltwell (US DoD, 2023b). The main source of the PFAS at Mildenhall was identified as being from AFFF (US DoD, 2023a).

### Conclusion

The use of FFF on military sites has led to PFAS contamination in surface water and groundwater, as demonstrated by the high levels at the fire training area at RAF St Athan and the identification of AFFF as the source of PFAS in the drinking water at RAF Mildenhall.

### Annex E.9.4 Use at Moreton-in-Marsh training centre

The Fire Service College in Gloucester provides training for firefighters, advanced training for senior fire officers and industrial staff. RAF Moreton-in-Marsh was operational during World War Two and despite being closed in the late 1950s was used by the government to train ex-national servicemen in firefighting. This led to the establishment of a Fire Service Technical College in 1966. The college became known as the national Fire Service College in 1981 (FSC, 2024). Extensive fire training on industrial equipment takes place on site, some of it using foams (BFRS, 2022; FSC, 2025).

The college is located on the outskirts of Moreton-in-Marsh village in Gloucester and has a discharge consent to discharge treated effluent to the Fire College Stream. Thames Water operates a WwTP to the south of the site which discharges treated effluent to a tributary of the River Evenlode.

Under the UK Water Industry Research (UKWIR) Chemical Investigation Programme (CIP) samples were taken upstream (south-east of the college) and downstream (south of the college) of the Moreton-in-Marsh WwTP and of the treated effluent from the WwTP. The groundwater is anticipated to run primarily southerly or south-westerly. Between the upstream and downstream sampling points there are only fields. There were 37 sampling events between March 2017 and February 2019 for the upstream sampling point. The average concentrations in these upstream samples were 0.0068 µg/L for PFOS and 0.00099 µg/L for PFOA. There were 20 sampling events between March 2017 and February 2019 for the treated effluent. The average concentrations in these treated effluent samples were 0.0054 µg/L for PFOS and 0.0072 µg/L for PFOA. There were 38 sampling events between March 2017 and Feb 2019 for the downstream sampling point. The average concentrations in these treated effluent samples were 0.43 µg/L for PFOS and 0.022 µg/L for PFOA (UKWIR, 2025). This shows that the significantly higher levels of both PFOS and PFOA in the downstream samples in comparison to the upstream samples is not considered to be from the treated effluent, and therefore there is another source of PFOS and PFOA between these two points which is still releasing both PFOS and PFOA at the time of the sampling.

### Conclusion

Samples taken downstream of the Moreton-in-Marsh WwTP had significantly higher concentrations of PFOS and PFOA than samples taken upstream or from the WwTP effluent. This indicates that there is an additional source of these PFAS. Due to the location of and activities undertaken at the Fire Service College the Agency considers it likely that the PFAS detected are from this source.

### Annex E.9.5 Industrial site incident - Buncefield

The Buncefield site is a large oil storage depot in Hemel Hempstead, Hertfordshire, receiving aviation fuels, petrol and diesel through a system of 3 pipelines from oil refineries in Humberside, Merseyside and the Thames. Fuels leave the site either by tanker or, in the case of aviation fuels, by pipeline to the West London pipeline system which supplies Gatwick and Heathrow Airports amongst others. In 2003, the site had consent to hold up to 194,000 tonnes of fuels (BMIIB, 2008).

In December 2005 there were a number of explosions at the site, which led to a catastrophic fire. The fire burned for 3 days and destroyed a substantial portion of the site. During the operation to extinguish the fire approximately 786,000 litres of firefighting foam, of which at least some contained PFOS, and 68 million litres of water were used (BMIIB, 2008).

About 33 million litres of contaminated firewater were contained and recovered after the fire, but the rest was released into the local environment (Nicholas and Whitfield, 2013). The contained firewater was transported to a number of sites around the country for storage prior to treatment and discharge, including approximately 12 million litres at Maple Lodge Sewage Treatment works near Rickmansworth and 4 million litres at Blackbirds Treatment works near Radlett, two Thames Water sites. This firewater contained a combination of firefighting foam, oils, unburnt fuel, and water (BMIIB, 2008).

Of the contaminated water that was released locally, some drained onto local land during the incident, as the firewater moved around the site drainage system and in one case overtopped onto a local road adjoining the site. The site sits above a major aquifer, which is considered to be the primary water resource receptor associated with the site (Arcadis, 2018a; BMIIB, 2008). Despite being capped by a low permeability layer of clay, the drainage areas around the site and the neighbouring road contain pathways into this aquifer.

The remaining uncontained water drained into local culverts and ultimately into the River Ver and River Colne, a tributary of the River Ver (BMIIB, 2008).

The depot is located within the catchment for a drinking water abstraction point. This abstraction point was closed after the fire and remained so as of 2013. During this time polluted groundwater was being pumped out of a number of boreholes and treated to remove fuel and PFOS. This work was costing approximately £1 m a year and was expected to continue for many years (Nicholas and Whitfield, 2013).

There has been significant remediation work done on site and the depot has since been rebuilt. In the waste management plan all soil containing >0.5 mg/kg PFOS was to be disposed of via incineration (BPA, 2012), although there is no information on how much was disposed of via this method (Arcadis, 2012). This work was completed in 2013 (IEMA, 2013). There were also significant additional contaminated waste streams produced during the remediation work, including water and concrete / building debris.

The environmental consultancy Arcadis have undertaken a number of monitoring programmes and risk assessments across the site since the fire on behalf of the site operators. The monitoring on the site (Arcadis, 2014, 2018a, 2018b) has only analysed for PFOS, which was used as a suitable indicator compound for the assessment of PFAS-

containing firefighting foam used during the incident, and PFOA. This monitoring did not include any of the other PFAS which may have been present in the firefighting foam.

A detailed quantitative risk assessment was done by Arcadis in 2014 following the completion of the remediation. An intrusive investigation was undertaken which included the analysis of soil in 27 boreholes. PFOS and PFOA were detected above the laboratory method detection limit (MDL). PFOS was detected in 3 of the 64 samples taken, with concentrations ranging from 0.02 mg/kg to 0.31 mg/kg and PFOA was detected in 7 of the 64 samples, with concentrations ranging from 0.01 mg/kg to 0.08 mg/kg (report does not state if dry weight or wet weight) (Arcadis, 2018a, 2018b). Groundwater samples were also taken in the northern area of the site, where PFOS and PFOA concentrations ranged from 0.05  $\mu$ g/L to 0.46  $\mu$ g/L, and 0.04  $\mu$ g/L to 0.55  $\mu$ g/L, respectively (Arcadis, 2014). The conclusion of the consultants was that following the significant remediation effort the concentrations of PFOS and PFOA in the soils had dropped in the areas where intrusive monitoring had taken place (the initial monitored values were not reported).

#### Conclusion

The monitoring done on the site shows that the firefighting efforts during the incident led to significant PFAS contamination that took a number of years to remediate. It also led to the closure of a drinking water abstraction point. PFOS and PFOA were still found in local soils and groundwater beneath the site in 2014, following the remediation. However, the monitoring did not include many of the substances now known to be in PFAS-containing firefighting foams.

The initial contamination of the site following the fire shows that the use of large quantities of firefighting foams can lead to significant environmental contamination which can be very costly to remediate and produce a significant quantity of contaminated waste streams, including the firewater and contaminated soils and concrete during the remediation phase. Due to the use of PFAS containing foam the contamination is *particularly long-lasting* being detected at mg/kg levels 9+ years later.

### Conclusion on known source releases

The case studies described above show that FFF formulation (at least if testing takes place on site), use at airfields and during a large incident result in emissions of PFAS to the environment that remain measurable for many years after the event. For example, PFOS has been banned for over a decade but is still being found in monitoring around GB airports. The Agency considers that use of PFAS-containing FFF in other sectors would result in similar emission pathways and long-term environmental exposure.

Of particular concern is the potential for PFAS emitted from use in FFF to contaminate drinking water sources, whether that be groundwater or surface water. The case studies from Duxford airfield and Buncefield show that PFAS contamination from use in FFF can result in drinking water abstraction points being closed in order to prevent human exposure via this route.

# **Annex E.10 Standards**

EN 1568 Parts 1-4 tests extinguishment and burnback of foams in sea and potable water. The different standards refer to different foam expansions, water-immiscible liquids and water-miscible liquids.

The International Maritime Organization (IMO) has two testing standards, IMO MSC.1/Circ.1312 and MSC Circ.670, which ensure foam used at sea is fit for purpose and considers performance with sea water induction and temperature conditioning. These standards are required by many maritime administrations and classification bodies for foam concentrates used on board ships in international waters, as part of the implementation of the SOLAS Convention (Safety of Life at Sea). IMO MSC.1/Circ.1312 sets testing protocols and acceptance criteria for Low Expansion foam concentrates, while IMO MSC Circ.670 sets testing protocols and acceptance criteria for High Expansion foam concentrates.

LASTFIRE, an international collaborative project, reviews fire hazards associated with large diameter, open top floating roof tanks. The test protocol is designed with tank fire-specific considerations, including forceful foam impact, hot tank walls, and distorted tank shells and test foams in both seawater and potable water (LASTFIRE, 2015). Foams are scored against numerous performance gradings, including time-critical aspects like fire extinguishment and vapor suppression. GESIP, a French testing facility, offers performance testing of foams in dedicated tanks, with some foams in manufacturers' portfolios gaining accreditation relevant to the oil sector. Test methods used by the petrochemical industry, such as LASTFIRE and GESIP were developed to take into consideration potential longer pre-burn times and larger fuel depths than other flammable fuel fires (NFPA, 2022). They also were developed with more focus on the formation of a robust blanket which helps reduce the potential for reignition near the tank walls and surfaces as well as preventing the release of flammable gases (Wood, 2020). This is achieved by a reduction in extinguishment times compared to some other areas of class B firefighting. (NFPA, 2022).

In the aviation sector, the Civil Aviation Authority (CAA) requires the test standards for foam concentrates to meet International Civil Aviation Organization (ICAO) Level A, B, or C using potable (fresh) water. The different standards relate to varying sizes of fires (2.8 – 7.3 m²) to be extinguished with different application rates (4.1 to 1.75 L/min/m²) of firefighting foam. Offshore helidecks must meet CAP 437 regulations and standards (CAA, 2023), which specify that foams compatible with seawater need to meet ICAO Level B or ICAO Level C performance tests.

In the US, the Federal Aviation Administration (FAA) Reauthorization Act of 2018 stated that the FAA could not require the use of PFAS containing AFFF after Oct 2021. Prior to this, the US FAA required that all Certificated Part 139 airports use MIL-PRF-24385 qualified AFFF for firefighting operations. Additionally, the '2020 National Defense

Authorization Act' required the US Department of Defence (DoD) to phase out PFAS-containing AFFF by October 2023, with an exemption for "ocean-going vessels" (Miller, 2024; US Congress, 2020). In October 2021, the FAA released a statement confirming that fluorinated AFFFs were no longer required but the foams must still meet the performance requirements of the military specification (MILSPEC) (Back et al., 2022). Consequently, the FAA and the DoD collaborated in a research project to test F3s and in January 2023, the DoD published a MILSPEC for F3 for firefighting operations (FAA, 2023; US DoD, 2023c). Foam agents must meet the requirements of the MILSPEC in order to be listed and used for military applications. MIL-PRF-32725 or "Fire Extinguishing Agent, Fluorine-Free Foam (F3) Liquid Concentrate, for Land-Based, Fresh Water Applications" is the title of the new performance specification for F3 (US DoD, 2023c).

The Underwriters Laboratory (UL) 162, an internationally recognised test method conducted by the Underwriters Laboratory (UL), an independent not-for-profit organisation. It requires a 50 sq ft heptane fire to be extinguished using freeze-protected foam with potable and sea water. The test is pass or fail, and UL listed products undergo conformance testing every three months. This ensures the foam being supplied matches the original tested formulation, unlike any other test standard that requires this monitoring.

NFPA 11 is a US standard introduced by the National Fire Protection Agency (NFPA) for low-, medium-, and high-expansion firefighting foam systems. It covers the design, installation, operation, testing, and maintenance of these systems for fire protection. The current revision, NFPA 11: 2021, stipulates that both foam concentrates and foam proportioning systems should be tested at least annually. The foam concentrate induction rate of a proportioner must be within 0 % to 30 % of the manufacturer's listed concentrations.

BS EN 13565-1 and BS EN 13565-2 are internationally recognised European Standards for Fixed Firefighting Foam Systems. BS EN 13565 Part 1: 2019 was introduced in 1998 and is the current revision. It covers the requirements and test methods for components of fixed firefighting systems using foam concentrates. Section 5 of the standard outlines the accuracy of the foam system's proportioning components, stating that produced foam should be not less than the rated concentration and not more than 30% above the rated concentration or 1 percentage point above the rated concentration. BS EN 13565-2: 2018 was introduced in 2004 and covers the design, construction, and maintenance of fixed firefighting systems using foam concentrates. Section 11 requires annual inspections of foam systems, including tests of the proportioner and associated fittings, and annual checks of stored foam concentrates by competent and trained foam laboratory personnel.

# **Annex E.11 Decontamination and Waste**

# Annex E.11.1 Decontamination of equipment previously used to hold PFAS-containing FFF concentrate

Firefighting equipment and systems (i.e. tenders, monitors, tanks, pipework, hoses, nozzles, etc) can continue to be a source of PFAS even after they have been emptied and cleaned. This is because amphiphilic PFAS molecules in PFAS-containing FFF can form surface-bound liquid crystal supramolecular assemblies over time. Fluoro-surfactants move to an interface, reach a critical concentration and then self-assemble. The perfluoroalkyl chains provide a driving force for self-association, and their amphiphilic nature results in stable vesicles, fibres or tubules. PFAS tend to produce numerous layers and microtube structures, with some approximately 50  $\mu$ m in size having been observed. Surface-associated PFAS layers with a surface density of approximately 10  $\mu$ g/cm² have been demonstrated on internal pipe surfaces following decades of exposure to PFAS-containing FFF (Lang and Divine, 2024; Lang *et al.*, 2022).

These layers are water-resistant and are therefore difficult to remove by water flushing alone. As a result, there has been observed "rebound" of PFAS into replacement F3, originating from prolonged contact within firefighting equipment that has previously used PFAS-containing FFF even after flushing out with water (Lang *et al.*, 2022; Oshaughnessy and Calveley, 2024; Ross, 2023; Ross and Storch, 2020). Additionally, the level of desorption from these layers can vary over time, so that following reduction to an apparent minimum following cleaning of firefighting equipment, concentrations of PFAS may still be detected a long time afterwards. For example, Ross and Storch (2020) found that 20 months after transition to F3 following dual water flushing of an aircraft hangar foam supply and delivery system (i.e., foam monitor, hose reel, valve room and pump room), PFAS concentrations in the replacement foam varied from  $60 \mu g/L$  (60 ppb) to  $1,600,000 \mu g/L$  (1,600,000 ppb).

PFAS rebound may also potentially lead to ongoing exposure to firefighters via aerosol inhalation and ingestion where breathing apparatus is not used, typically during prolonged periods of training (stakeholder meeting, Ross, Aug 2024; IPEN, 2019).

This makes rebound a potentially significant issue for regulation and enforcement depending upon which restriction limits/standards are set for PFAS. For example, rebounding PFAS concentrations may result in 'fluorine-free' foam stock breaching regulatory limits, which may also lead to significant costs at the point of disposal (Ross, 2024).

Currently, there are no regulatory limits for surface bound PFAS concentrations (per cm<sup>2</sup>) for decontamination of equipment that has previously held PFAS, and it is unlikely that it would be possible to set meaningful limits. However, UK and EU regulatory PFAS

concentration limits as unintentional trace contaminants (UTCs) under the Persistent Organic Pollutants (POPs) Regulations are:

- PFOA <25 ppb and PFOA derivatives <1,000 ppb where they are present in substances, mixtures or articles (European Commission, 2020)
- PFOS and derivatives 10 ppm where they are present in substances or mixtures (European Commission, 2019)
- PFHxS and derivatives 100 ppb in firefighting foam mixtures that are to be used or are used in the production of other firefighting foam mixtures (European Commission, 2023).

Additionally, EU REACH regulatory PFAS concentration limits (for foams) are (European Commission, 2023): C9-C14 PFCA <25 ppb and C9-C14 PFCA derivatives <260 ppb where they are present as or in substances, mixtures or articles (European Commission, 2021).

Evaluation undertaken by the US Department of Transport suggests that mixing of FFF concentrates containing equal quantities of AFFF and F3 would not be detrimental to fire extinguishing performance, stating "the performance of mixtures between AFFF and F3s tended to be close to the performance of AFFF alone or between the performance of the individual foams" (Trazzi and Casey, 2023). Therefore, the Agency considers that the quantities of PFAS likely to rebound are unlikely to have a negative impact on the performance of the F3 foam. The SEA consultation report undertaken on behalf of the Environment Agency has used an average concentration value of 2.5 % PFAS in firefighting foams, based on a concentration range of between 2 and 3 % estimated from the annual tonnage of fluorosurfactants used in the EU (Wood, 2020; WSP, 2023). Information from Eurofeu suggested that the minimum PFAS concentration that would deliver functionality was 0.1 % (Wood, 2020). It should be noted that the maximum recorded rebound concentration of 0.16 % (1,600,000  $\mu$ g/L) described above exceeds this (Ross and Storch, 2020).

In the absence of any universally adopted official guideline detailing the cleaning/decontamination procedures and acceptable remaining PFAS levels allowed for any transition from PFAS-containing FFF to F3, individual entities (including states, companies, airlines and fire brigades) have developed their own protocols (ECHA, 2023c). As examples from stakeholders of decontamination procedures, nine separate cleaning scenarios are provided in the ECHA Appendices to the Annex XV Restriction Report (ECHA, 2023c) including:

- Non-cleaning no specific cleaning steps. Stakeholders found that contamination of the replacement F3 subsequently occurred requiring development of cleaning strategies.
- BIOEX hot water flushing and scrubbing.

- Arcadis flushing and soaking with the proprietary 'V171' cleaning agent, followed by high-pressure washing.
- Cornelsen's PerfluorAd Technology emptying of equipment and flushing with Perfluorad™ followed by water flush.
- Bavarian State Ministry for the Environment and Consumer Protection rinsing and flushing with hot water.
- Fire Rescue Victoria 32-stage decontamination and verification process involving water flushing, agitation and pressure washing with water.
- Fire Protection Association Australia flush with hot or cold water.
- Australian Department of Defence water flushing and soaking of different components.
- German Industrial Plants Fire Brigades Association (Werkfeuerwehrverband Deutschland) – repeated flushing with hot water.

It is noteworthy that the US FAA have not required decontamination or set limits as a regulatory measure as part of transition to F3 and have left it for relevant environmental authorities at the state level (FAA, 2023). Similarly, a guidance 'Memorandum on Rinsing Aircraft Rescue Firefighting (ARFF) Vehicles Transitioning from Aqueous Film Forming Foam (AFFF) to Fluorine-Free Foam (F3)' from the US Department of Defence (DoD) released in August 2024 (FAA, 2024) stipulates that for mobile systems that previously utilized AFFF and will be reused with fluorine-free firefighting agents, the DoD Components will:

- "Completely drain the system of AFFF.
- Conduct a single water rinse of the entire system from the AFFF tank through all components and piping to all discharge nozzles, including external equipment (e.g., hoses, nozzles, fittings) that previously contained AFFF.
- Empty rinsate from the system and reconfigure it for the selected fluorine-free alternative agent in accordance with the agent manufacturer's recommendations.
- Ensure appropriate spill prevention measures and containment are incorporated into the process to minimize any releases or impacts."

There is a growing industry advancing decontamination of PFAS-impacted equipment and offering proprietary technologies. Studies suggest that simply undertaking multiple water flushes will be insufficient for effective decontamination (Lang *et al.*, 2022; Oshaughnessy and Calveley, 2024). Difficulties in achieving effective decontamination were demonstrated by comparing rebound following water flushing, hot methanol flushing, hot methanol with sonication/brushing, glycol, and proprietary products. A variety of alternative cleaning agents have been investigated, e.g. butyl carbitol (diethylene glycol monobutyl ether (DEGBE); 2-(2-butoxyethoxy) ethanol; CAS: 112-34-5) at 70°C with pressure washing / abrasion appears to be an effective method. Butyl carbitol is used as a solvent for PFAS in

PFAS-containing foam concentrates (stakeholder meeting, Ross, Aug 2024). The Arcadis proprietary Fluoro Fighter™ cleaning agent showing higher PFAS removal per surface area of pipe than methanol or water extraction (Lang, 2023; Lang and Divine, 2024). Improved removal of 6:2 FTS and 8:2 FTS was demonstrated with a reagent comprising propylene glycol (30 %), ethanol (10 %), citric acid (2 %) and water (58 %) when compared to water or methanol (Bellona, 2023).

Certain equipment is easier to decontaminate than others, e.g., tanks versus hose or nozzles. It has been suggested that decontamination is more difficult in rough / abraded surfaces, e.g., rusty pipes versus smooth stainless steel (stakeholder meeting, Ross, Aug 2024).

A sampling and analysis methodology with multiple lines of evidence is essential to demonstrate successful decontamination. Ross (2023) indicates surface testing with swabs is required using total oxidizable precursor (TOP) / Adsorbable Organic Fluorine (AOF) assays to demonstrate decontamination of equipment. TOP assay is problematic for analysis of rebound PFAS concentrations in replacement F3 foam, which instead requires AOF/Extractable Organic Fluorine (EOF) analysis (stakeholder meeting, Ross, Aug 2024). False negatives will be derived if only the rinsate water is sampled for verification, as PFAS will remain bound to the interior surfaces (Oshaughnessy and Calveley, 2024).

As part of a proposed foam transition strategy, Ross (2024) suggests operators should:

- "Perform a cost benefit analysis to compare replacement of specific components vs. decontamination.
- Implementing decontamination with verification of progress and success done via assessment of total PFAS within the cleaning agent and on the surfaces of fire suppression system components.
- Manage waste firefighting foams and PFAS saturated cleaning agents via multiple disposal routes."

Any waste PFAS-containing cleaning liquids will need to be contained and disposed of appropriately (Lang *et al.*, 2022; Oshaughnessy and Calveley, 2024; Ross and Storch, 2020). For onshore scenarios (e.g., aviation, fire emergency services, etc.), the potential volumes of waste washings generated using a 20 % volume glycol solution to pressure wash and recirculate might be 2,000 L for an 800 L tank and 6,000 L for a 3,000 L tank (stakeholder meeting, Ross, Aug 2024). It is therefore evident that large volumes of PFAS-containing rinsate would be generated as part of any decontamination procedure. Methods of concentrating the PFAS out of solution to allow reuse of reagent and reduce disposal costs and volumes have been investigated, including foam fractionation and GAC (Lang, 2023; Lang and Divine, 2024) and a variety of closed-circuit high-pressure nanofiltration/reverse osmosis (CCNF/RO) systems (Bellona, 2023).

In marine / maritime and offshore scenarios, effective decontamination is likely to be more complex and expensive than for onshore scenarios, as access to components of dedicated

systems may be very difficult, and replacement very costly. For maritime vessels it would potentially require work to be undertaken while docked, so there would be a cost associated with taking the vessel out of commercial use for the duration. There may be implications for defence for naval vessels if they must be pulled from duty to undertake decontamination unless it can be incorporated as part of wider scheduled shore maintenance.

Similarly, there will be significant costs associated with downtime of offshore sector installations, many times the cost of the actual decontamination. A preliminary internet search suggests that costs for unplanned downtime could be in the region of \$1 to 2 million/day (GE, 2016; JPT, 2022). However, ECHA queries whether additional downtime of production beyond that already programmed could be avoided if decontamination and transition could be coordinated with other planned maintenance activities (ECHA, 2023b). Such costs / constraints would depend on whether regulatory standards are set and what the thresholds are for PFAS concentrations of F3s post-restriction and transition (ECHA, 2023d).

Fuels Industry UK highlighted the lack of an agreed protocol and specifications for the cleaning of existing tanks and distribution systems, meaning that industry / contractors were left to best endeavours (Call for evidence, Fuels Industry UK). Similarly, the CIA questioned whether companies would be required to test FFF storage tanks following replacement with a non-PFAS alternative for residual PFAS concentrations. The CIA was concerned that under the UK POP Regulations the UTC limit for PFOA has been set at 25 ppb and any equipment that has been inadequately decontaminated, i.e. exceeding the UTC limit, may "likely trigger the need to remove the new foam resulting in repeat of the costs to businesses." The CIA queried whether the same UTC limit would apply for replacing all PFAS-containing FFFs, requested more guidance on best techniques to decontaminate equipment and sharing of any available learning experiences from organisations that had already undertaken the transition (Call for evidence, CIA). The Agency considers that relevant POPs Regulations would need to be complied with regardless, so if a PFAS substance is restricted under POPs, sufficient decontamination would need to be undertaken to ensure that the replacement F3 does not contain POPs at levels greater than the relevant UTC.

In relation to decontamination, RAC and SEAC made the following recommendations in their final opinion (ECHA, 2023d):

- RAC suggested the following amendments to the Dossier Submitter's restriction proposal:
  - o Column 2, Paragraph 4d: "Ensure that the collected PFAS-containing waste resulting from cleaning of firefighting equipment, where the concentration of total PFAS is greater than 1 mg/L shall be handled for adequate treatment."
  - o Column 2, Paragraph 6: "From six months after entry into force, containers of PFAS-waste in relation to cleaning of firefighting foam equipment where

concentration of total PFAS is greater than 1 mg/L shall all be labelled indicating the presence of PFAS above this threshold with the following wording: "WARNING: Contains per- and polyfluoroalkyl substances (PFAS)."

- SEAC suggested the following amendment to the Dossier Submitter's restriction proposal:
  - o Column 2, Paragraph 4d: "Ensure that the collected PFAS-containing waste resulting from cleaning of firefighting equipment shall be handled for adequate treatment where the concentration of total PFAS is greater than 50 mg/L for the offshore oil and gas industry and 1 mg/L in all other uses/sectors."

ECHA calculate that a minimum reduction in PFAS concentrations of 99.99 % would be achievable with a limit of 1 ppm (1 mg/L), whereas a threshold of 50 ppm (50 mg/L) would represent a reduction of 99.80 % (ECHA, 2023d).

It should be noted that the RAC/SEAC opinion states "considering the high cost of eliminating the last units of contamination and the relatively low impact on emissions, SEAC supports to set the limit value at 50 mg/L for already contaminated systems in the offshore sector. SEAC highlights that the higher limit is solely intended to help avoid the high costs of cleaning and underlines that the foam concentrates used should comply to the limit value of 1 mg/L when placed on the market or used" (ECHA, 2023d). SEAC has also recommended an extended transition period of 10 years in line with corresponding onshore Seveso directive activities. SEAC highlighted that respondents to the EU Public Consultation commented that there would be high financial costs to reach the level of 1 mg/L for decontamination and that sections of the fire protection systems would require replacement to maintain a PFAS residual below a level of 1 mg/L (ECHA, 2023d). From the ECHA RAC/SEAC opinion, stakeholders did not raise concerns about setting the limit value at 1 mg/L for placing firefighting foams on the market; however, stakeholders requested that the decontamination limit value should be higher (ECHA, 2023d). SEAC states "a specific alternative level for the limit value was, however, not proposed and justified. In the absence of further information SEAC cannot propose any specific higher limit value" (ECHA, 2023d).

RAC further recommended that "guidance is provided on analytical methods and on PFAS-containing firefighting foam management plans and cleaning of equipment including handling of resulting waste" (ECHA, 2023d). However, uncertainty remains whether decontamination technologies would be effective in preventing rebound to the EU limits in F3 of 1 mg/L or 50 mg/L (for the offshore sector) suggested in the RAC/SEAC opinion. It is also suggested that it would be very difficult if not impossible to set a regulatory limit for decontamination (stakeholder meeting, Ross, Aug 2024).

In Australia, the Queensland Department of Environment and Science Operational Policy for the Environmental Management of Firefighting Foam (Queensland Gov, 2021) states that after one-month's residence time in an existing system, contamination of new F3 by residual PFAS or PFAS from another source must not exceed the following limits:

- 10 mg/kg for perfluoroalkyl sulfonates and ≥C4 to C12 precursors, the sum of the compounds (PFBS + PFPeS + PFHxS + PFHpS + PFOS + PFDS + PFDS + PFDoS + precursors)
- **50 mg/kg (as fluorine)** for ≥C4 perfluoroalkyl carboxylates and higher homologues as the sum of the TOP-A analyses results for C4 to C14 compounds (TOP-A C4-C14)

Where it is not practical to clean out or replace equipment, "calculations should be made of the probable contamination, or contribution to contamination, based on known, or reasonably inferred quantities and concentrations of PFAS residues in the system" to meet limit values equal to half or less than half of the above limits (Queensland Gov, 2021). Alternatively, the guidance also allows total organic fluorine (TOF - combustion ion chromatography) analysis with a limit value of ≤6.4 mg/kg (as fluorine), derived from the above limits (Queensland Gov, 2021).

### Summary

Due to their properties, there is the potential for equipment that has used PFAS-containing FFF concentrate to have become coated with a layer of PFAS. This layer is hard to remove using water flushing alone and may consequently act as an ongoing source of PFAS contamination in replacement F3s (so-called 'rebound'). There is no clear agreement on the most appropriate or most effective decontamination techniques (e.g., single or multiple cold/hot water flushing, scrubbing or use of proprietary solvents), and decontamination can be costly and result in downtime of operations.

There are few confirmed regulatory limits for PFAS decontamination although ECHA has proposed 1 mg/L and 50 mg/L (for offshore) and the Queensland Government in Australia has set limits of between ≤5 mg/kg and 50 mg/kg depending on substance and assay.

There does not appear to be any reduced effectiveness of F3s if rebound occurs. Therefore, the issue is around the potential continued emissions of PFAS even after transition to F3 has occurred. Section 6.4.2.1.11 outlines potential PFAS emissions resulting from rebound and estimates that under conservative assumptions there may be a few tonnes of PFAS emission expected over a two-year period (after which it is assumed that rebound ceases due to the stock of residual PFAS in equipment being exhausted). This is contrasted with the estimated ~1,120t (across 30 years) of avoided PFAS releases associated with a restriction where stringent decontamination is not undertaken. Further detail is explored in Section 6.4.2.11.

# Annex E.11.2 Waste Disposal Methods

### **Cement Rotary Kilns**

The Environment Agency scoping review of PFAS remediation (Environment Agency, 2024a) highlights that cement kilns are a viable option for the destruction of PFAS and "use existing facilities without requiring modifications. This method is cost-effective, energy-efficient, and produces no additional CO<sub>2</sub>, making it environmentally sustainable. It can handle substantial amounts of both liquid and solid wastes and offers higher safety margins for temperatures and residence times compared to standard commercial incinerators. Cement kiln incineration achieves destruction efficiencies of approximately 99.999% for PFAS by operating at very high temperatures (1,200 to 1,400°C) and ensuring long residence times, which are crucial for thorough decomposition. Emissions in the flue gas, including HF, dioxins, and sulphur oxides, are kept well below regulatory levels, with no detectable residual PFAS remaining post incineration".

Future use would be reliant on compliance with waste legislation and permit conditions, requiring permit variation. It would also require demonstration by the Operators of the technical feasibility and efficacy of destruction.

Interim guidance published by the US EPA in April 2024, also suggests conditions in cement kilns (e.g., ≥1,650°C, long gas phase residence time (4 to ≤16 seconds in long kilns) may effectively treat PFAS waste (US EPA, 2024c). Research suggests that available or added calcium in the form of calcium oxide, calcium hydroxide or calcium carbonate is able to capture free radical fluorine generated during the high temperature destruction to form stable calcium fluoride, reducing/eliminating emissions of fluorinated species (Klein, 2022; Patterson and Dastgheib, 2020; Ross and Storch, 2020; Spinney, 2022; Wang et al., 2015; Wang et al., 2011a). The US EPA 2024 interim guidance reports that studies indicate the potential benefit of treating PFAS wastes in cement kilns where available calcium can react with fluorine to form calcium fluoride. Laboratory studies indicate that calcium species promote mineralization of PFAS waste at relatively low temperatures (400-800°C). "However, the currently available lab-scale data are insufficient to determine with confidence the effectiveness of treating PFAS waste in commercial cement kiln operations" (US EPA, 2024c). Australia undertook proof-of-concept trials using cement kilns in 2016-17 and successfully demonstrated destruction (with destruction efficiencies of 99.999%) of both liquid and solid PFAS-containing waste (Klein, 2022). Since 2018, Cement Australia (Geocycle) has undertaken destruction of AFFF under licence (rate of 5 kg-F/hr of PFAS) at its cement kiln in Queensland (Klein, 2022; Spinney, 2022).

There are 10 cement kilns in the UK. Currently cement kilns are not utilised as a method of disposal of PFAS-containing wastes in GB. Future use would be reliant on compliance with waste legislation and permit conditions, requiring permit variation. It would also require demonstration by the Operators of the technical feasibility and efficacy of destruction.

Furthermore, there may be other potential barriers, such as the willingness of the kiln operators to take the material (given the cost and permitting implications), public perception of a cement kiln burning PFAS, the implications for the cement product and the opinion of their customers. Notwithstanding these points, cement kilns appear to be an effective technical option for PFAS waste disposal.

#### **Other Disposal Methods**

Both the US EPA interim guidance (US EPA, 2024c) and the Environment Agency scoping review (Environment Agency, 2024a) describe other commercially available disposal methods for managing PFAS waste:

- Underground Injection in the USA, disposal of Class I non-hazardous industrial or hazardous waste via deep underground injection wells is permitted. The wells are confined, preventing contamination of groundwater aquifers. Capacity and transportation logistics may significantly limit their use.
- Landfills in GB, the Landfill Directive (1999/31/EC), which was transposed into UK domestic legislation by the Landfill (England and Wales) Regulations 2002 (then superseded by the Environmental Permitting (England and Wales) Regulations 2007), and in Scotland with The Landfill (Scotland) Regulations 2003, prohibits any landfills from accepting liquid / foam wastes. Therefore PFAS-containing firefighting foam concentrates or liquids must first be pre-treated / transformed to allow them to be disposed of to landfill.

A variety of solidification / stabilisation methods exist, e.g. cement, fly ash, hydraulic lime or hydrated lime (ECHA, 2023c). PFAS is expected to remain encapsulated in the solidified waste matrix and any leaching is expected to be minor, although "leaching from the solidified product cannot be excluded" (ECHA, 2023c). The encapsulated waste will need to be assessed after the solidification / stabilisation process to decide its waste classification and whether it needs to go to a hazardous or non-hazardous waste receiving landfill. Furthermore, if POPs such as PFOS, PFOA, PFHxS are present then the POP Regulations will apply. As solidification / stabilisation does not destroy or irreversibly transform the POPs, it is not a suitable treatment process and so landfill disposal would not be applicable (ECHA, 2023c).

Current GB legislation and guidance do not prevent a landfill operator from accepting PFAS wastes, subject to the application of the Hazardous Waste guidance (WM3) and Waste Acceptance Criteria (hazardous landfills). However, the Environment Agency recommendation is that if an operator wants to accept such wastes, the waste producer / landfill operator would need to provide evidence to show that PFAS-containing solidified / stabilised wastes will not degrade over the longer-term and release PFAS (personal communication, Environment Agency Waste Regulation Jan 2025). Long-term environmental liabilities associated with PFAS presence in landfills must be considered, as they can potentially become significant sources of contamination (Environment Agency, 2021, 2024a; Ross et

al., 2018; Song et al., 2018b). Furthermore, landfill operators are becoming more aware of the PFAS issue in landfill leachates and may decide not to accept such wastes (personal communication, Environment Agency Waste Regulation Jan 2025). In summary, for GB the Agency position is that whilst it is currently legal for non-POPs, non-hazardous PFAS-containing waste to be accepted at any classification of landfill it would not be the preferred option and high temperature destruction / full mineralisation of PFAS remains the preference. Furthermore, the waste producer/landfill operator would have to provide robust evidence that PFAS-containing solidified / stabilised wastes will not release PFAS over the longer-term to the satisfaction of the Environment Agency / SEPA / NRW. Additionally, there would be a potential long-term environmental liability with the acceptance of such waste, with associated business risks to the operator.

- In Europe, solidification / stabilisation of PFAS-containing FFF concentrates or liquids and their disposal to an appropriate landfill can be a viable alternative to incineration, but would need to be assessed before disposal as it would not be applicable to every PFAS product (ECHA, 2023c).
- In the USA, an allowed disposal route for PFAS is to permitted hazardous waste landfills with protective landfill engineering controls and practices (Subtitle C landfills). "However, for all landfill types, new information demonstrates landfilling could have higher PFAS releases to the environment than previously thought in 2020" (US EPA, 2024c).

#### Sequestration

As part of the disposal/treatment process there may be potential to use technologies to separate and concentrate PFAS from large volume liquids, which may assist in capacity management and cost reduction (Environment Agency, 2024a; US EPA, 2024c). These include:

- Granular activated carbon (GAC) is effective for removing long-chain PFAS such as PFOS and PFOA from water, but less effective for short-chain PFAS like PFBS and PFBA. Variables such as pH, surface charge, ionic strength, and temperature will impact removal efficiency.
- Ion exchange (IX) resins use adsorption and electrostatic attractions to remove PFAS and are more effective than GAC for removal of short-chain PFAS.
   Combining both GAC with IX resins in sequence may optimise PFAS removal, by first removing larger PFAS to GAC.
- Reverse osmosis (RO) selectively allows water molecules to pass through membranes, retaining larger PFAS molecules. Solute concentration, pressure, water flux rate and temperature all impact membrane efficiency.
- Foam fractionation (FF) involves bubbling gas through PFAS-containing liquid to separate the PFAS based on their surfactant properties, which causes PFAS

molecules to accumulate at air-water surface interfaces. FF is only effective at PFAS concentrations ≥0.5 µg/L and is less effective for shorter-chain PFAS. Ultimately, any PFAS concentrated and / or removed from solution will need to be disposed of appropriately, whilst minimising emissions. It may be possible to utilise GAC and IX resin technologies to concentrate PFAS from large volume liquids and destroy these using HWI or cement kilns with the GAC/resin acting as a fuel supplement (Bellona, 2023; Klein, 2022; Lang, 2023; Lang and Divine, 2024). However, as previously discussed in the Cement Rotary Kilns section, there are a number of obstacles to the application of cement kilns as a destruction method that would first need to be overcome. Therefore, it should not be expected that their use would be an immediate option.

#### Alternative and emerging technologies

Alternative technologies are actively being investigated but all will require further research and development before they can be applied in real-world scenarios. Technologies described in the US EPA interim guidance (US EPA, 2024c) and the Environment Agency scoping review (Environment Agency, 2024a) include:

- **Supercritical water oxidation (SCWO)**: under supercritical conditions PFAS contaminants are degraded through thermal oxidation.
- Plasma-based water treatment technologies: a gas is introduced through diffusers to form a foam layer that concentrates PFAS at the liquid surface, where electric discharges generate reactive species which degrade PFAS.
- **Bioremediation**: microorganisms, such as bacteria and fungi, may be used to metabolise PFAS.
- Chemical oxidation and reduction or electrochemical oxidation: these may have the potential to break the C-F bonds in PFAS molecules under ambient conditions.
- **Ozonation**: generates aggressive radicals capable of degrading PFAS at high pH levels, and may be combined with photolysis or foam fractionation or with oxidants like hydrogen peroxide and persulfate.
- **Photolysis and photocatalytic degradation**: this technique uses radiation and photochemical catalysts to generate oxidising species that degrade PFAS.
- Catalysed hydrogen peroxide propagation (CHP): hydrogen peroxide and catalysts are used to generate hydroxyl radicals to attack alkyl groups in PFCAs and PFSAs, transforming their precursors into related PFCAs.
- Alkaline hydrothermal treatment (HALT): high-pressure, high-temperature, and high-pH conditions may degrade PFAS to produce carbonate and fluoride salts.
- **High-energy electron beam (eBeam)**: this technology uses electron accelerators to generate ionising irradiation to de-fluorinate PFAS.
- Precipitation, coagulation (including electrocoagulation), and flocculation: these methods would physically remove PFAS as a sediment from solution.

- **Ball milling**: involves colliding PFAS with metal balls (particularly boron nitride, a piezoelectric material) at high speeds. The collisions create solid-state reactions that break the C-F bonds in PFAS.
- **Pyrolysis**: this process decomposes dried biosolids at moderately elevated temperatures (610 °C) in an oxygen-free environment to produce biochar.
- **Sonication**: ultrasound can mineralise PFAS to form fluoride and carbon dioxide at temperatures around 30 °C (Cao *et al.*, 2020; Ross, 2020).

# Annex F Analysis of existing regulatory measures

PFAS within FFF are potentially regulated to a certain extent within GB at various points in their life cycle, covered by a mixture of regulations.

#### Workplace

Risks to human health from the use of chemicals in the workplace are covered by the Control of Substances Hazardous to Health (COSHH) Regulations. Duty holders are required to prevent, or, where this is not reasonably practicable, control exposure to hazardous substances to protect the health of people affected by their work activities.

Under COSHH, for substances that are classified as Carcinogens or Mutagens, Regulation 7(7) imposes a duty on employers to reduce exposure to a level as low as reasonably practicable (ALARP). Most PFAS that have a Mandatory Classification and Labelling (MCL) under GB Classification, Labelling and Packaging Regulations (GB CLP) are carcinogenic meaning that exposure to those substance will need to be kept to ALARP. COSHH can also impose a Workplace Exposure Limit (WEL). There are no WELs for PFAS substances; for this to be considered more information on use, exposure and hazard would be needed.

COSHH is also supported by other health and safety legislation such as the Management of Health and Safety at Work Regulations, and even more broadly the Health and Safety at Work Act. This legislation also requires that dutyholders take responsibility for assessing and controlling the hazards created by their work.

#### **Product Safety**

The General Product Safety Regulations (GPRS) impose requirements concerning the safety of products intended for consumers, or which are likely to be used by consumers. The regulations contain a general requirement that producers are obliged to place only safe products on the market.

The broad definition of "product" means that PFAS-containing products that are available for use by consumers, including those with FFF (e.g. hand-held extinguishers), are in scope. The lack of information on FFF composition, hazard data and possibly a MCL for many of the groups mean that it is difficult to deem which, if any, products could be regarded as unsafe. Additionally, the issue of concern in this proposal is to control the potential to cause harm at a population level, over long timeframes. GPRS does not explicitly or implicitly cover these aspects.

#### **Drinking water**

For drinking water, standards for certain substances can be set, there are currently no statutory drinking water limits for any PFAS in England and Wales. However, in England and Wales there is some additional guidance on PFAS in water, which was revised in 2024 (DWI\_PFAS-Guidance\_Aug-2024\_FINAL-2.pdf). This guidance includes the expectation from the Drinking Water Inspectorate (DWI) that it is reasonably practicable to achieve a concentration of individual PFAS in drinking water below 0.1 µg/L and that sites exceeding this should put in place emergency contingency measures to reduce the PFAS concentration (these actions vary but can include the blending of water sources to reduce the concentration, use of granular activated carbon or the shutdown or procurement of water from alternative sites). The PFAS chemicals of interest which sites should be monitoring for are detailed within the DWI parameter code list Annex C - Parameter Code List - Drinking Water Inspectorate. This includes 48 PFAS, some of which are PFAAs present in FFF. However, repeated releases and those of a direct nature/magnitude of PFAS FFF, could result in the need for continuous treatment and the possibility of the need for provision of alternative supplies of water. This may impact on what is reasonably practicable action (meaning weighing the risk against the time and money needed to control this) in order to continue the use of certain water sources.

In Scotland, the Public Water Supplies (Scotland) Amendment Regulations 2022 reflect the requirements of the recast EU Drinking Water Directive These regulations introduce a "sum of PFAS" standard, i.e., level that drinking water in Scotland must not contain above 0.1  $\mu$ g/L at consumers' taps. This standard encompasses 20 PFAS and sampling for all of these substances is required if the risk assessment of drinking water shows that there is a risk of PFAS being present in raw or final water supplies. Where a risk assessment, or review, establishes a risk of supplying water that may contain levels above standards set for PFAS, Scottish Ministers may then give notice to Scottish Water requiring it to take specified actions

#### **Water Framework Directive**

Water protection legislation is implemented in the UK by a series of related regulations (such as Water Environment and Water Services (Scotland) Act 2003 and The Water Environment (Water Framework Directive) (England and Wales) Regulations 2017). The overall aims include the achievement of good chemical status for all surface water bodies by 2027. Chemical status in surface waters depends on compliance with Environmental Quality Standards (EQS) for priority substances (including priority hazardous substances, for which the aim is the elimination of emissions). PFOS is the only PFAS that currently has an Environmental Quality Standard as a priority substance.

The Water Environment (Water Framework Directive) England and Wales Regulations 2017 also require 'good' chemical status in groundwater bodies by 2027. There are two additional quality objectives that apply to all groundwater: to prevent or limit the inputs of pollutants into groundwater; and to implement measures necessary to reverse any

significant and sustained upward trend in pollutant concentrations in groundwater. Priority substances are included in this list.

#### **Environmental Permitting**

In England and Wales, The Environmental Permitting (England and Wales) Regulations 2016 (as amended), are used to regulate emissions from installations that come within scope of the Industrial Emissions Directive (2010/75/EU). In Scotland, implementation is through The Pollution Prevention and Control (Scotland) Regulations 2012.

The regulations require operators of industrial installations to obtain a permit from the national authorities to continue operating. All installations covered by Annex 1 of the Directive must obtain a permit from the national authorities to continue operating.

Permits place a requirement for the use of Best Available Techniques (BAT) to reduce emissions and the impact on the environment as a whole and must include emission limit values for pollutants (e.g., EQS). In particular, those listed in Annex 2 to the Directive likely to be emitted from the installation concerned in significant quantities. For example, regulated installations will be required to implement accident prevention and management plans, which covers fires. The plan must include measures to minimise the impact of a fire, which would include the release of fire water.

#### **UK REACH**

For UK REACH, there are some existing regulatory measures in place, with some PFAS in scope of this Annex 15 dossier already identified as Substances of Very High Concern (SVHCs) but none have yet been placed on the Authorisation List (Annex 14).

Restriction is a risk management tool that can consider future releases of chemicals for which a risk that is not adequately controlled has been identified. As such, restriction cannot address the risks from existing (legacy) environmental contamination nor consider remediation of the tonnage already emitted. UK REACH restrictions are in place for two PFAS substances, PFOA and its salts and perfluorinated silane.

#### **Persistent Organic Pollutants (POPs) regulations:**

The POPs regulations, which implement the UN Stockholm Convention, restrict the use of PFOS and eliminate the use of PFOA and its salts. The UK is a signatory to the convention and implements these measures.

Recently PFHxS, its salts and PFHxS related compounds have been added as a POP for elimination via a POPs restriction. A recommendation for long-chain (C9-C21) PFCAs to be listed as a POP will be tabled for agreement in April/May 2025.

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