



Poly- and perfluoroalkyl substances (PFAS): sources, pathways and environmental data

Chief Scientist's Group report

August 2021

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Professor Doug Wilson Chief Scientist

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Executive Summary

Poly- and perfluoroalkyl substances (PFAS) are a large group of synthetic organofluorine chemicals that have been widely used since the 1940s. By definition, all PFAS have at least one fully fluorinated methyl ($-CF_3$) or methylene ($-CF_2-$) group. The carbon-fluorine bond (C–F) is very strong. Consequently PFAS can resist chemical attack and withstand high temperatures and are sometimes referred to as 'forever chemicals'.

PFAS have oil and water repellent properties, having been developed for use as surfactants and stain repellents. They have a very wide range of consumer and industrial applications including use in aqueous film forming foams and as fire suppressants, metal finishing and plating, hydraulic fluids, fluoropolymer production, paper products and packaging, semiconductor manufacturing, and textiles and leather including carpets and furniture.

With such a wide range of uses, PFAS can readily enter the environment during manufacture or formulation, use of the substances themselves or products containing them and through disposal. Their stability and resistance to degradation results in almost indefinite environmental contamination, leading to long-term continuous exposure of people and wildlife.

Even if sources of PFAS to the environment are stopped, environmental concentrations will decline very slowly. The long history of use of some PFAS means that there is a legacy of environmental contamination that is challenging to remediate.

Approximately 100 individual PFAS are potentially supplied to the UK in amounts of 1 tonne per year or more, based on European information. We have limited knowledge about their use, the quantities actually on the UK market or their presence in imported goods. There are gaps in our understanding of the potential for release during their life cycle (for example, leaching of residual amounts of PFAS additives and processing aids from polymer products), including recycling and waste disposal.

The evaluation of sources and pathways of PFAS exposure for risk management is complicated by the large number of individual substances and their widespread use over many decades.

Few PFAS have been subject to extensive testing so information about their hazardous properties is also sparse. Our knowledge of environmental fate, behaviour and impacts is based largely on data for a limited number of substances, predominantly perfluoroalkylated acids (PFAAs) that have been subject to risk assessment under regulatory regimes.

Some PFAAs can accumulate in the food chain and others are very mobile in soil and water, travelling a long way from their origin and gradually accumulating in groundwater. In human epidemiological studies some PFAS have been reported to be associated with a range of human health effects, such as increased cholesterol levels, reduced immune response and reproductive effects.

The combination of persistence, bioaccumulation, toxicity and potential for long-range transport of a handful of PFAAs have led to the restriction of these substances and their

derivatives at both European and global levels under the REACH Regulation and the United Nations Stockholm Convention on Persistent Organic Pollutants (POPs). To begin to address the knowledge gaps we have used available data and information to build a picture of the use of PFAS in the UK, sources and pathways to the environment and the extent of environmental presence in English waters.

Working with the 2 major UK-based manufacturing companies, we are evaluating the hazard and risk of 12 individual PFAS used or produced at these sites. We are also evaluating an additional substance that could be used as an alternative to a specific PFAS that is already restricted. The completed evaluations will be used to identify the need for any further monitoring investigations or other regulatory activities.

Despite undertaking UK-based trade-sector surveys, there remains a significant evidence gap regarding current use of PFAS across several trade sectors, including cosmetics, textiles and food packaging in the UK.

In 2019, we commenced a multi-phase project to enhance our understanding of PFAS occurrence in relation to UK sources and to understand the level of risk from source sites. The project looked initially at legacy sources, particularly land contamination associated with historic PFAS use. Civilian airfields, military airfields and bases, fire-fighting training sites and fire stations, wastewater treatment works, and landfills are identified as having the highest potential risk as a source of PFAS. Several manufacturing industry sources including textile and leather, carpets and paper and cardboard manufacture were also identified as requiring investigation as potential high risk sources, as were chrome plating sites.

A multi-criteria geographical information system (GIS) based risk tool has been developed to help identify potential PFAS source areas and enable in-depth local assessments of specific areas and sites that present a potential risk to health and the wider environment. Targeted water quality sampling at highlighted sites will form a key component of the evidence base into 2022/23 to validate the model with real data.

We have sampled rivers, groundwaters, estuaries, and coastal waters for a range of PFAS from 2014 to 2019. To date, our monitoring has focused on the terminal degradation PFAS also known as 'arrowhead' perfluoroalkyl acids (PFAA), with emphasis on regulated PFAS such as perfluorooctane sulfonate (PFOS) - a priority hazardous substance in the Water Framework Directive Regulations. Our data suggests it is likely that some PFAS are widely present in environmental waters. The shorter chain PFAAs are detected most often in both groundwater, fresh and saline water samples.

Our monitoring also shows the widespread presence of PFOS in both freshwater and marine fish from English waters. Whilst we have analysed for perfluorooctanoic acid (PFOA) in the same fish samples, we have not found any at levels above the limit of detection.

Even if sources of PFAS to the environment are stopped, environmental concentrations will decline very slowly. The long history of use of some PFAS means that there is a legacy of environmental contamination that is very hard to remediate.

Interpretation of environmental monitoring data for PFAS requires acceptable limits - derived using toxicological data - against which we can assess potential risk to humans

and the environment. The limited data for the majority of PFAS poses a significant challenge and a potential barrier to effective risk management.

Introduction

Poly- and perfluoroalkyl substances (PFAS) are a class of synthetic organofluorine chemicals that were discovered in the 1930s and went into large-scale production during the 1940s (<u>Buck et al., 2011</u>; <u>OECD, 2018</u>; <u>ITRC, 2020</u>).

The Organisation for Economic Co-operation and Development (OECD)/United Nations Environment Program (UNEP) Global Perfluorinated Chemicals (PFC) Group have proposed an update to their previous (2018) definition of PFAS (UNEP/OECD, 2018) to include all substances having at least one fully fluorinated methyl (–CF₃) or methylene (– CF₂–) group, or one carbon chain that is fully or 'per' fluorinated . Thousands of chemicals are captured by the term "PFAS" (<u>OECD, 2018</u>; <u>Washington et al., 2018</u>; <u>Henry et al.,</u> <u>2018</u>; <u>US EPA, 2021</u>), although the number of commercially important substances is thought to be in the low hundreds (pers comm). An overview of the substances and their groupings is given in Appendix 1 to illustrate the scale and nature of the issue.

The carbon-fluorine bond (C–F) is very strong. Consequently PFAS can resist chemical attack and withstand high temperatures. They are typically oil and water repellent, having been developed for use as surfactants and stain repellents. These properties make them useful in a broad range of processes and products, as illustrated in Table 1.1.

PFAS are costly to produce and typically used where other substances cannot deliver the required performance, or where PFAS can be used in significantly smaller quantities and deliver the same performance as a non-fluorinated substance (<u>Glüge et al., 2020</u>).

The 3 main applications are:

- in protective treatments for example paper, packaging and textiles such as oiland waterproof clothing and carpets;
- in polymer manufacturing; and
- as surfactants including aqueous film fire-fighting foams (AFFFs) and use as mist suppressants in chrome plating.

Environmental concentrations of PFAS may arise from a variety of uses and sources including PFAS manufacturing sites, areas of land where AFFFs have been used such as military or civil aviation and landfill sites.

Some PFAS - such as some polyfluorinated alkyl substances - can partially degrade or transform in the environment. The end degradation products are typically perfluoroalkylated acids (PFAAs), most commonly perfluoroalkylated sulfonic acids (PFSAs) and perfluoroalkylated carboxylic acids (PFCAs) which are highly resistant to further degradation. PFAAs can persist in the environment for decades or longer and are sometimes referred to as 'forever chemicals' or 'arrowheads'.

The term 'arrowheads' refers to a grouping approach commonly adopted for risk assessment and risk management of PFAS. The PFAA is managed together with it salts and precursor substances that would transform or degrade to the PFAA 'arrowhead'. For example, the United Nations Stockholm Convention on Persistent Organic Pollutants (POPs) applies risk management restrictions to perfluorooctane sulfonic acid (PFOS) as 'PFOS, its salts and PFOS-related substances'. Examples of arrowhead substances subject to risk management in the UK are listed in Table 1.1 below.

PFAAs are typically referred to as either short chain or long chain, dependent on the length of the perfluoroalkyl chain. PFCAs with an 8-carbon alkyl chain or longer – including perfluorooctanoic acid (PFOA) – are termed long-chain PFCAs. For PFSAs, a

perfluoroalkyl chain of 6 carbons or longer – including PFOS – is considered to be long chain.

The length of the fluorinated carbon chain can result in different physicochemical properties that influence the substance's behaviour in the environment and in organisms, and its bioaccumulation and (eco)toxicity. Long-chain PFAAs are typically more bioaccumulative and toxic than short-chain homologues. Short-chain PFAAs tend to be more mobile in the environment with a greater tendency to reach groundwater.

Standard wastewater treatment processes that rely on biodegradation or sorption to sewage sludge are often not able to remove PFAS from wastewater. This means that PFAS can readily enter the environment and remain there almost indefinitely, leading to long-term continuous exposure of people and wildlife.

Even if a source of PFAS to the environment is stopped, PFAS concentrations will decline very slowly. The long history of use of some PFAS means that there is a legacy of presence in the environment that is very hard to remediate.

Some types of PFAS, such as perfluorocarbons, appear to be biologically inert, although they can have a significant potential to cause global warming.

For the majority of PFAS there are little or no data on uses and hazardous properties. Our knowledge of environmental fate, behaviour and impacts is based largely on data for a limited number of substances, especially PFAAs that have been subject to risk assessment and restriction under regulatory regimes. A recent review of PFAS toxicity and impacts on human health by <u>Fenton et al. (2020)</u> summarises the current state of knowledge and reports an association, demonstrated through epidemiological studies, between some PFAS and a variety of health impacts including altered immune and thyroid function, liver disease and adverse reproductive and development outcomes.

There is growing concern that some types of effect cannot currently be detected in standard laboratory studies. Some PFAS can also remain in mammalian tissues for a long time. Field studies have established that this can lead to increasing concentrations of these PFAS up the food chain.

Many PFAS, especially those with shorter perfluoroalkyl chains, are also highly mobile in water, so can travel a long way from the original source and gradually accumulate in groundwater. In addition, uptake into plant tissues can be significant, which can lead to contamination of crops (<u>Ritscher et al., 2018</u>; <u>OECD, 2018</u>).

The persistence and mobility of PFAS, combined with decades of widespread use, have resulted in their presence in most environmental media at trace levels across the globe (Danish EPA, 2013; De Silva et al., 2020; Pan et al., 2018; Xiao, 2017).

These properties of persistence, bioaccumulation, toxicity and potential for long-range transport have led to the restriction of some PFAS at both European and global levels under the REACH Regulation and the United Nations Stockholm Convention on Persistent Organic Pollutants (POPs). The UK was the first European country to propose the restriction of a PFAS following a national assessment of the environmental risks from using perfluorooctane sulfonic acid (PFOS) and its derivatives (Environment Agency, 2004). The number of PFAS subject to controls has since increased, although removal of individual substances typically results in their replacement by other types of PFAS.

Despite widespread restrictions on a few PFAS we have little information about the hazards, use and amounts of many other PFAS on the UK market or their presence in imported goods. There are gaps in our understanding of the potential for release during their life cycle, including recycling and waste disposal for the vast majority of PFAS.

The intrinsic physical and chemical properties of PFAS also makes them particularly challenging to analyse in environmental media. Analytical methods with sufficiently low detection limits only became widely available in the early 2010s, and most methods focus on the relatively small number of PFAAs. Comprehensive risk assessments and prioritisation of the most important substances and sources are therefore still under development.

| CAS no. | Name | Acronym | Alkyl | Typical uses | Restrictions |
|-----------|-----------------------------|---------|-----------------|---|--|
| | | | chain length | (including derivatives) | (date restricted) |
| 307-24-4 | Perfluorohexanoic acid | PFHxA | C6 | Aqueous film forming foams (AFFFs)s, mist suppressants for metal plating applications, textiles and leather, surfactants, inks, paints, waxes, manufacturing of electronics and semiconductors | Proposed for restriction under EU REACH due to its persistent, mobile and toxic properties (2020) |
| 335-67-1 | Perfluorooctanoic acid | PFOA | C8 | Processing aid for fluoropolymer manufacture, printing inks, coatings, surfactants, water and oil proofing agents for textiles (including outdoor and protective clothing), photolithography, AFFFs | Designated as a persistent organic pollutant (POP) (2020) |
| 375-95-1 | Perfluorononanoic acid | PFNA | C9 | Textiles and leather, surfactants, paper and packaging, inks, paints, waxes, manufacturing of electronics and semiconductors | Substances of Very High Concern (SVHC) under UK REACH based on their persistent, bioaccumulative and toxic properties (2017) Proposed for restriction under EU REACH (2018) |
| 335-76-2 | Perfluorodecanoic acid | PFDA | C10 | Textiles and leather, surfactants, paper and packaging, inks, paints, waxes, manufacturing of electronics and semiconductors | Substances of Very High Concern (SVHC) under UK REACH based on their persistent, bioaccumulative and toxic properties (2017) Proposed for restriction under EU REACH (2018) |
| 2058-94-8 | Perfluoroundecanoic acid | PFUnA | C11 | Textiles and leather, surfactants, paper and packaging, inks, paints, waxes, manufacturing of electronics and semiconductors | Substances of Very High Concern (SVHC) under UK REACH based on their persistent, bioaccumulative and toxic properties (2017) |

Table 1.1 Uses and regulation of some commonly detected PFAS

| CAS no. | Name | Acronym | Alkyl chain | Typical uses (including derivatives) | Restrictions (date restricted) |
|----------------|----------------------------------|---------|----------------|---|--|
| | | | length | | (date restricted) |
| | | | | | Proposed for restriction under EU REACH (2018) |
| 307-55-1 | Perfluorododecanoic acid | PFDoA | C12 | Textiles and leather, surfactants, paper and packaging, inks, paints, waxes, manufacturing of electronics and semiconductors | Substances of Very High Concern (SVHC) under UK REACH based on their persistent, bioaccumulative and toxic properties (2017) Proposed for restriction under EU REACH (2018) |
| 72629-94- 8 | Perfluorotridecanoic acid | PFTrDA | C13 | Textiles and leather, surfactants, paper and packaging, inks, paints, waxes, manufacturing of electronics and semiconductors | Substances of Very High Concern (SVHC) under UK REACH based on their persistent, bioaccumulative and toxic properties (2017) Proposed for restriction under EU REACH (2018) |
| 335-76-2 | Nonadecafluoro- decanoic acid | PFTDA | C10 | Textiles and leather, surfactants, paper and packaging, inks, paints, waxes, manufacturing of electronics and semiconductors | Substances of Very High Concern (SVHC) under UK REACH based on their persistent, bioaccumulative and toxic properties (2017) Proposed for restriction under EU REACH (2018) |
| 375-73-5 | Perfluorobutane sulfonic acid | PFBS | C4 | AFFFs, mist suppressants for metal plating applications, textiles and leather, surfactants, paper and packaging, inks, paints, waxes, the manufacturing of electronics and semiconductors, aviation and automotive hydraulic fluid and oil, fluoropolymers | SVHC under UK REACH based on its persistent, mobile and toxic properties (2020) |
| 355-46-4 | Perfluorohexane sulfonic acid | PFHxS | C6 | AFFFs, mist suppressants for metal plating applications, textiles and leather, polishing and cleaning/washing agents, coatings including for impregnation/damp- proofing, the manufacturing of electronics and semiconductors | SVHC under UK REACH based on its persistent and bioaccumulative properties (2017) Proposed for restriction under EU REACH (2020) Nominated as a POP (2020) |

| CAS no. | Name | Acronym | Alkyl chain length | Typical uses (including derivatives) | Restrictions (date restricted) |
|----------------|--|---------|--------------------------|--|--|
| 1763-23-1 | Perfluorooctane sulfonic acid | PFOS | C8 | AFFFs, textiles (including carpets) and leather goods, paper/packaging – including food contact materials, general coatings, mist suppressants for metal plating applications | POP (2009) |
| 62037-80- 3 | Propanoic acid, 2,3,3,3-tetrafluoro-2- (1,1,2,2,3,3,3- heptafluoropropoxy)-, ammonium salt | HFPO-DA | C3-O- C3 | Processing aid for fluoropolymer manufacture | SVHC under UK REACH on the basis of its persistent, mobile and toxic properties (2019) |

This narrative presents the evidence we have on levels of PFAS in the aquatic environment in England, together with information on sources and uses of PFAS in a UK context. We are using this evidence to inform the discussion on development of future UK policy on PFAS to ensure they are used safely, and to identify critical evidence gaps for further work.

In this report, we summarise our data on the current uses of PFAS and identify, as far as possible, UK relevant sources and pathways of environmental exposure. Our environmental monitoring data for PFAS in rivers, estuaries, coastal waters, and groundwater and in marine and freshwater fish are summarised in Chapter 3. We also signpost environmental data collected by other UK organisations.

Uses and sources of PFAS

The evaluation of sources and pathways of PFAS exposure in the environment is complicated. This is because of the large number of individual substances and their widespread use over many decades. Some PFAS can accumulate in the food chain and others are very mobile in soil and water. Many will eventually degrade to highly persistent final degradation products –PFAA or "arrowheads", as described in Chapter 1.

To help prioritise risk management we have gathered information on uses and sources of those PFAS which can potentially be used in the UK. Information sources have included:

- regulatory registration databases,
- discussions with UK manufacturers of PFAS
- information from UK trade sector surveys
- wider scientific literature and published reports (particularly from the OECD)

There are a number of limitations in the data, but the summary below represents the first step towards a possible UK based 'inventory' or list of UK relevant PFAS and emissions and highlights evidence gaps.

1.1. Uses of PFAS

<u>Glüge et al. (2020)</u> provide a comprehensive summary of the major historical and current uses of PFAS in Europe and North America, with additional information on uses elsewhere such as China. Two hundred use categories and subcategories were identified for more than 1,400 individual substances. Based on this paper and an OECD database on PFAS (<u>OECD, 2018</u>), PFAS are used globally in a wide range of industries which include:

- Fire-fighting (AFFFs and as fire suppressants)
- chemical manufacturing
- building and construction
- cabling and wiring
- metal finishing and plating
- hydraulic fluids
- fluoropolymer production
- paper products and packaging
- semiconductor manufacturing
- textiles, leather and apparel (including carpets and furniture)
- cleaning products (including industrial surfactants)
- refrigeration

Further information can also be found in <u>Meegoda et al. (2020)</u>, <u>Stoiber et al. (2020)</u> and the curated website of the Interstate Technology and Research Council (<u>ITRC, 2020</u>).

The use of PFAS is governed by different legislation depending on use pattern. Further regulatory information about PFAS on the UK market is provided in the following sections.

1.2. PFAS regulated under REACH

The majority of PFAS are industrial and consumer chemicals that are regulated under the Registration, Evaluation, Authorisation and restriction of Chemicals (REACH) Regulation ($\underline{EC}, 2006$).

Until 1st January 2021, REACH registration allowed an EU-based manufacturer or importer to supply their substance to the European Economic Area (EEA) including the UK. The UK has retained REACH in national legislation (<u>REACH Regulations 2019</u>) following withdrawal from the EU, but it will take several years for UK registration to be completed. For the time being, the European Chemicals Agency (<u>ECHA</u>) public registration database (ECHA, 2021b) is the only readily accessible source of information about potential production and use of chemicals in the UK.

We searched the ECHA database using the CAS numbers of PFAS included in the OECD database (<u>OECD, 2018</u>) in November 2018, and identified 114 individual substances potentially supplied to the UK market above 1 tonne per year. Table 2.1 provides a summary of the uses of these substances in each tonnage band and the number of substances registered. Full details are provided in Appendix 2. For 57 substances the tonnage and use were either not declared or confidential, so these have not been included in our table. Most substances are not supplied in large quantities. Only 36 individual PFAS are supplied in quantities greater than 10 tonnes per year.

| Tonnage band | No. of PFAS | Declared uses | | | |
|--------------|-------------|--|--|--|--|
| ≥ 10,000 | 1 | Chemical intermediate or monomer for polymer manufacture | | | |
| | | Refrigerant gas | | | |
| 1,000 to | 1 | Cover gas | | | |
| 10,000 | | Functional fluid in a closed system | | | |
| | | "Mixture formulation" | | | |
| 100 to 1,000 | 12 | Calibration of analytical equipment | | | |
| | | Chemical intermediate or monomer for polymer manufacture | | | |
| | | Cleaning and etching | | | |
| | | Consumer portable fire extinguishers | | | |
| | | Coolant and detector fluid | | | |
| | | Electronic component manufacture | | | |
| | | Industrial use in inks and films | | | |
| | | Insulation foam | | | |
| | | "Mixture formulation" | | | |
| | | Polymerisation solvent / processing aid | | | |
| | | Professional fire-fighting foams | | | |
| | | Refrigerant | | | |
| 10 to 100 | 22 | Calibration of analysis equipment | | | |
| | | Chemical intermediate or monomer for polymer manufacture | | | |
| | | Electronic component manufacture | | | |
| | | Industrial heat transfer fluid | | | |

Table 2.1 Overview of declared uses of PFAS identified in the ECHA public registration database

| No. of PFAS | Declared uses |
|-------------|--|
| | Industrial paint |
| | Laboratory chemical |
| | "Mixture formulation" |
| | Non-metal surface treatment agent |
| | Polymerisation solvent / processing aid |
| | Preparation/pre-treatment solutions |
| | Professional fire-fighting foams |
| 21 | Catalyst |
| | Chemical intermediate or monomer for polymer manufacture |
| | Coatings and paints, thinners, paint removers |
| | Industrial solvent |
| | Heat transfer fluid |
| | Fabricated metal products |
| | Fire-fighting foams/gaseous fire suppression |
| | Fragrance and cosmetics |
| | Functional fluid in motor vehicles or industrial sites (e.g. insulator for manufacture of computer, electronic and optical products, electrical equipment) |
| | Manufacture of bulk, large scale chemicals (including petroleum products) |
| | Metal surface treatment chemical |
| | Non-reactive processing aid at industrial site |
| | Processing aid in the manufacture of pharmaceuticals, fine chemicals and laboratory chemicals |
| | Production of rubber products for the automotive industry |
| | Semiconductors |
| | Washing and cleaning product |
| | |

The ECHA registration database cannot provide a complete picture because it does not include PFAS manufactured or imported by individual companies below 1 tonne per year. Neither does it identify any UK companies that may be importing from EU-based suppliers, although this information will eventually become available in UK REACH registrations. It is also likely that PFAS are present in small quantities in semi-finished or finished goods imported from outside the EU, but suppliers may be unaware of their presence and therefore unaware of any obligation to register them.

There is no registration requirement for polymers under REACH either. This is an important information gap because polymers containing residual PFAS additives or processing aids are a source of PFAS in the environment due to degradation and/or weathering over time. It is not currently possible to estimate the contribution of such polymers to the environmental burden of PFAS.

1.3. UK REACH Registrants

In 2018, we identified 2 UK-based manufacturers and six importers of one or more PFAS from the ECHA registration database. Three of the importers were inactive so their substances are presumably no longer commercially relevant. The other three are consultancy firms with legal responsibilities for their registrations, but they are unlikely to process any substance themselves.

Both manufacturers have sites in Lancashire with environmental permits under the Environmental Permitting (England and Wales) Regulations, 2016.

The environmental permit of the first company indicates that it produces fluoropolymers such as polytetrafluoroethylene (PTFE) and ethylene-tetrafluoroethylene (ETFE) with a capacity of a few thousand tonnes per year. The company had EU REACH registrations for 12 PFAS.

The second company produces a range of liquid and gaseous perfluorocarbon substances with a capacity of around 400 tonnes per year. The company had EU REACH registrations for 10 PFAS.

Following further dialogue with both manufacturing companies we have a programme of work to evaluate the hazard and risk of 12 individual substances used or produced at these manufacturing sites. These PFAS are listed in Table 2.2. The completed evaluations will be used to identify the need for any further monitoring investigations. The evaluation reports are subject to independent peer review and will be complete by the end of 2021.

| Substance | CAS number | UK use |
|--------------------------------------|------------------|---|
| Perfluoropropane | 76-19-7 | Electronics industry |
| Hexafluoropropene | 116-15-4 | Intermediate |
| Perfluoroperhydrophenanthrene | 306-91-2 | Electronics industry |
| Perfluorodecalin | 306-94-5 | Medical applications |
| | | Cosmetics |
| Perfluorooctane | 307-34-6 | Tracing and tagging applications (oil and gas industry) |
| Perfluoroisohexane | 355-04-4 | Electronics industry |
| | | Rigid foam blowing agent |
| | | Tracing and tagging applications (oil and gas industry) |
| Perfluoro-1,3-dimethylcyclohexane | 335-27-3 | Electronics industry |
| | | Low-temperature cure resin systems |
| | | Energy transfer applications |
| Polyfluorinated polymerisation media | N/D ¹ | Polymerisation processing aid |
| Perfluorinated monomer | N/D | Co-monomer for fluoropolymers |

Table 2.2 EU REACH-registered PFAS currently under evaluation by the Environment Agency

¹ N/D – Not disclosed at request of company.

| Substance | CAS number | UK use |
|---|-------------|-------------------------------|
| Perfluoro(4-methyl-2-pentene) | 3709-71-5 | Intermediate |
| Perfluorinated monomer | N/D | Co-monomer for fluoropolymers |
| Ammonium difluoro[1,1,2,2- tetrafluoro-2-(pentafluoroethoxy)- ethoxy]acetate [EEA-NH ₄] | 908020-52-0 | Polymerisation processing aid |

1.4. PFAS regulated under other legislation

<u>Glüge et al. (2020)</u> identified that PFAS were used as plant protection products, biocides, veterinary medicines, human pharmaceuticals and in food contact materials, all of which have different legislative requirements.

1.4.1. Biologically active substances

<u>Ogawa et al. (2020)</u> investigated the 18th Edition of the Pesticide Manual (<u>Turner, 2018</u>) and found that 202 of 1,261 (16%) agrochemical pesticides contain a per- or polyfluorinated alkyl group. At least some of these are likely to meet the OECD PFAS definition (<u>OECD, 2018</u>).

The Health and Safety Executive (HSE) is the regulator for pesticide and biocide authorisations.

Fluorine is increasingly used in drug design due to its influence on the metabolic potential of an active ingredient and reduced synthesis costs (<u>Zhou et al., 2016</u>; <u>Johnson et al.,</u> <u>2020</u>). <u>Inoue et al. (2020</u>) estimated that organofluorine compounds could contribute up to 20% of commercial pharmaceutical products.

The Veterinary Medicines Directorate (VMD) are responsible for the regulation of veterinary medicines.

The Medicines and Healthcare Products Regulatory Agency regulate pharmaceuticals.

We do not have access to information about the number of pharmaceuticals registered or licensed in the UK that contain a per- or polyfluorinated alkyl group.

1.4.2. Food contact materials

PFAS coatings provide grease or water resistance in food packaging and non-stick surfaces in cookware. The OECD have recently published a report identifying which PFAS are used in food contact materials. Although this study does not present a definitive list of PFAS used in food packaging/wrapping, it does highlight that Europe and the USA have phased out PFOA and other longer chain PFAAs, which have typically been replaced by shorter chain (C6) PFAS. Some non-fluorinated alternatives are also on the market.

FIDRA, an environmental charity, carried out a study to explore the extent of PFAS use in food packaging in the UK. They noted widespread use of PFAS across the UK food sector in food contact materials. Supermarket bakery bags, microwave popcorn packaging, pizza boxes and takeaway packaging were highlighted as items very likely to contain PFAS (FIDRA, 2020). Once used, the disposal of this packaging as waste is a potential secondary source of PFAS to the environment.

1.5. Sector-specific information

To improve our understanding of the emissions and risks of PFAS in the UK, further information from specific industrial sectors is needed to identify the range and amounts of PFAS used and understand potential pathways for release to environment.

In 2020, we commissioned surveys of 5 UK-based trade sectors to try to obtain additional information on PFAS use in the UK. The trade sectors were identified as potentially significant users of PFAS using information from REACH registrations. The response was entirely voluntary and unfortunately, the surveys did not provide much additional information about the current use of PFAS in these sectors in the UK. This is now being followed up by the Environment Agency as part of the development of a Risk Management Options Analysis. The data obtained is commercially confidential, but a brief summary is presented below.

1.5.1. Cosmetic and personal care products

The Cosmetics, Toiletry and Perfumery Association (CTPA) circulated our questionnaire to raw material suppliers and other appropriate companies and provided a consolidated response. We do not know how many businesses were contacted or how many responded. CTPA reported the use of 9 individual PFAS in this sector.

1.5.2. Textiles

Thirteen trade associations were contacted, but no survey responses were received.

In 2018, the <u>EU MIDWOR-LIFE</u> project explored the environmental impact of current durable water and oil repellents (DWOR) and alternatives. They recommended replacing current DWOR based on long-chain fluorocarbon chemistry with alternatives that are considered less harmful (<u>MIDWOR-LIFE, 2018</u>).

1.5.3. Paper and board

Eleven trade associations were contacted, of which 7 replied. The Confederation of Paper Industries (CPI) stated that the vast majority of their members' product range is PFAS-free, but 2 companies were known to use PFAS in small quantities in food packaging and medical non-packaging products as grease and detergent proof barriers.

Another company reported that some of their products contain PFAS in quantities and purposes that were not described. One further company reported using very small quantities of PFAS as a water and grease barrier for food packaging bags and takeaway food containers.

The <u>OECD (2020)</u> reports the use of up to 28 fluorinated substances in paper and board for food packaging purposes in the United States. We do not have any information to indicate if a comparable range of substances are used in products on the UK market.

1.5.4. Cleaning products

Seven trade associations were contacted and 4 companies responded. One PFAS was reported to be used in 4 floor polish products as a wetting and levelling agent. The concentration of PFAS in these products ranged from 0.015 to 1.448%. This represents use of up to a total of 10 tonnes per year of the substance.

1.5.5. Paint and coatings

Six trade associations were contacted of which 3 participated. The British Coatings Federation (BCF) represent 95% of the UK sales of coatings, inks and wall coverings. They reported that one member company is supplied with raw materials containing PFAS, but no further information was available.

1.5.6. Chrome plating

PFAS are used as mist suppressants in some processes to reduce worker exposure to toxic chromium(VI) ions.

There is an industrial site in Birmingham that formulates chromium(VI) plating solutions and mist suppressants using PFAS, which has an environmental permit under the <u>Environmental Permitting (England and Wales) Regulation 2016</u>.

This is a derogated use of PFOS under Commission Regulation (EU) 2019/1021 and will expire in June 2025. We hold records on PFOS for this use and are aware of 13 sites in England that held stockpiles totalling approximately 56.8 kg of neat PFOS in 2018, although no quantities of PFOS were reported in 2020.

There are approximately 100 metal treatment sites in the UK currently using chromium(VI) compounds for chrome plating (personal communication with the Surface Engineering Association, December 2018). Around 90% of companies must therefore be using PFAS other than PFOS. A large number of the Surface Engineering Association's members have switched to 6:2 fluorotelomer sulfonate (6:2) FTSA or 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanesulfonic acid (CAS no. 27619-97-2), which is registered under REACH in the 10 to 100 tonnes per year band (personal communication with the Surface Engineering Association, December 2018).

Another PFOS alternative reportedly used in China for chrome plating is F-53B (CAS no. 73606-19-6) (Wang et al., 2013). Although it has not been registered under REACH, it has been detected at low concentrations in the River Thames (Pan et al., 2018) and is also found in otters from the UK (<u>O'Rourke et al., 2020</u>). This suggests that there may be low level use possibly involving mist suppressants in the UK. Based on its structural similarities to PFOS, we are performing an evaluation under the assumption that it may be imported below one tonne per year by individual companies for use in chrome plating. A report will be published later in 2021. F-53B has also been added to our list of PFAS for inclusion in our targeted analytical methods (see Chapter 4).

All UK users of chromium(VI) compounds for chrome plating are (or will be) subject to authorisation decisions under the REACH Regulation. We will explore how further information about the fate of any PFAS-containing effluents and wastes can be obtained through further dialogue with the metal treatment industry.

1.5.7. Aqueous film-forming foam (AFFF)

There is an industrial site in North Yorkshire that produces synthetic AFFF concentrates containing fluorochemical surface active agents for fire-fighting applications. It has an environmental permit under the <u>Environmental Permitting (England and Wales)</u> <u>Regulations 2016</u>.

AFFF products are widely used to tackle fires that involve flammable or combustible liquids, particularly in oil, gas and chemical production. This includes petroleum tankers, bulk storage and production platforms, the aviation sector and ship engine rooms (<u>Darwin, 2004</u>; <u>Darwin, 2011</u>; <u>OECD, 2021</u>). Fire-fighting training facilities and military sites are also

potentially significant users (<u>Darwin, 2004</u>). The foams are typically stored over long periods of time and may be released in large quantities when used.

This use pattern is known to have caused soil pollution and associated groundwater, surface water and drinking water contamination near to some fire training areas, airports and sites of major incidents in various parts of the world (<u>Kwadijk et al., 2014</u>; <u>Jersey</u> <u>Airport, 2017</u>; <u>ATSDR, 2018</u>). In the UK, an example was the major incident at the Buncefield Oil Storage Depot in 2005, where a large proportion of the national inventory of PFOS-related fire-fighting foam was used up in a single event tackling an explosion and fire (internal Environment Agency data).

In 2003, we reviewed the environmental impact of AFFF products (<u>Environment Agency</u>, <u>2003</u>), but since then concerns around PFAS have extended to include their mobility. In 2020, we commissioned a desk study (<u>Environment Agency</u>, <u>2020b</u>) to identify and prioritise sources and create site risk profiles for high risk sites associated with PFAS use, including those that use AFFFs (see Section 2.7).

The Department for the Environment, Food and Rural Affairs (Defra) also undertook a research project to investigate AFFF use in the UK, with a focus on PFOA and related substances (<u>Defra, 2019</u>). PFOA-containing foams replaced PFOS-containing foams, and are now in turn due to be phased out and replaced with AFFFs containing PFAS with perfluorinated carbon chain lengths of 6 atoms and fluorine-free foam (F3) products.

In 2019, the UK stockpile of PFOA-containing foam was estimated to be in the range 1.5 million to 1.8 million litres (Defra, 2019). The Environment Agency (2004) estimated that around 2.4 million litres of PFOS-related foams were stockpiled in the UK at the time (equivalent to 114 kg per year of PFOS-related substances), which indicates the overall potential market for this type of product. Additional reviews of the use of PFAS (and fluorine-free alternatives) in – and emissions from – fire-fighting foams have been published by ECHA (2020) and OECD (2021).

We work closely with the Fire Service to manage the impact of firefighting foam whenever it is used. Fluorine-free foams are now available for all fire classes. We have worked with the UK Fire and Rescue Service to review the use of available product using environmental scoring criteria to identify the least polluting foams for each class of fire. As a consequence, the UK Fire and Rescue Service has revised its National Foam Procurement Process. Fluorinated foams are only recommended for the highest performance situations such as oil refinery fires, where full containment of foam would be part of risk management measures (UKFRS, 2020).

1.5.8. Other users

We are aware of a few UK suppliers of PFAS in small quantities for research and development purposes. Other companies may supply, formulate, distribute or use mixtures that contain PFAS. These companies either supply or use quantities below the REACH registration threshold of one tonne per year, or obtain their substances from other companies. If their suppliers are based in the EU, there are new obligations to register under UK REACH from 2021 onwards.

Downstream users of PFAS supplied by the 2 UK manufacturers, for example companies in the electronics industry, do not have any REACH registration obligations. Our hazard and risk evaluations of PFAS manufactured in the UK (see Section 2.3) consider the life cycle of the substances. If the evaluations indicate that downstream uses will be a significant source of exposure for these PFAS, these will be investigated further.

1.6. Sources and pathways

Globally, the major sources of PFAS to the environment are recognised as (<u>CLAIRE</u>, <u>2019</u>; <u>ITRC</u>, <u>2020</u>):

- Industrial facilities that produce PFAS or process PFAS, or facilities that use PFAS chemicals or products in manufacturing or other activities.
- Areas where fluorine-containing fire-fighting materials are or have been stored, used, or released.
- Waste management facilities such as landfills.
- Wastewater treatment residuals and areas of bio-solids production and application, with more significant impacts associated with industrial wastewater discharges.

Diffuse sources will also contribute to the overall environmental load. Examples include use in consumer products and subsequent release through washing and general wear and tear of textiles (<u>Commission for Environmental Cooperation, 2017</u>), and coatings such as anti-graffiti paints (<u>Scheeder et al., 2005</u>).

Historic use that has led to legacy contamination also contributes to the environmental burden because of the lifespan of the products containing them as well as their own intrinsic persistence. Those PFAS which have had historic use and are now subject to restrictions have been summarised previously in Table 1.1, Chapter 1.

Figure 2.1 provides an overview of sources of PFAS and pathways for environmental exposure.



Figure 2.1 Sources of PFAS and pathways for environmental exposure.

The following sections focus on waste management at the end of the life cycle for PFAScontaining products. Disposal to waste-to-energy installations (incinerators) is the only way to ensure that PFAS are destroyed. The most-difficult fluorinated organic compound to decompose is tetrafluoromethane (CF₄), requiring temperatures over 1,400°C (<u>Tsang et al., 1998</u>; <u>US EPA, 2020</u>). Incineration must therefore be at very high temperatures to destroy PFAS.

1.6.1. Landfill

Disposal to landfill is often the end of the life cycle for consumer products containing PFAS (Eggen et al., 2010). One example is discarded textiles including carpets and clothing that are not suitable for recycling (Lang et al., 2016).

Industrial waste can also be a significant source of PFAS in landfills (ITRC, 2021). Landfill leachate can be transferred to WWTWs directly or via a tanker system; consequently, PFAS may be transferred from landfill leachate via WWTWs to sewage sludge, groundwater or surface water.

We hold details of historic landfill sites and those operated under Environmental Permitting regulations (<u>Environment Agency, 2020a; 2020c</u>). Although PFAS are not commonly measured at UK landfill sites, various studies of the PFAS composition of landfill leachate have been carried out in other countries.

A critical review of existing publications on the fate and transport of PFAS in landfills was carried out by <u>Hamid et al. (2018)</u>. PFOA and short-chain PFCAs (C4 to C7) and their precursors such as fluorotelomer carboxylic acids were frequently reported in landfill leachate across numerous studies. PFBS, PFHxS and PFOS were also reported (<u>Harrad et al., 2020</u>). The exact nature of PFAS reported varied between individual studies and landfill sites. For example, PFOA and PFHxS were the most commonly detected PFAS in leachate samples from northern Spain (<u>Fuertes et al., 2017</u>), whereas PFHxA was found to be the major contaminant in Australian landfill leachate (<u>Gallen et al., 2017</u>).

Analysis of leachate for PFAS from a number of landfill sites is being undertaken in 2021 and this is part of a wider Defra-funded research project on POPs in different operational and closed landfills that took a range of waste (hazardous, non-hazardous and inert) over a wide date range from the 1960s through to present. The findings will be used to develop our understanding of the fate of PFAS emissions and exposure routes in the wider environment.

1.6.2. Recycling facilities

UK industrial/commercial recycling facilities have waste acceptance criteria and work under the Environmental Protection (Duty of Care) Regulations 1991. Waste that is suspected or known to contain regulated PFAS should be disposed of appropriately. However, this only covers PFOS and PFOA as they are identified under the POPs Regulations. Household recycling is a known area where PFAS such as PFOS and PFOA may be disposed of incorrectly and therefore become a barrier to a more circular economy and also potential environmental sources.

1.6.3. Waste water treatment

PFAS are commonly detected in influents, effluents and sludges from Waste Water treatment Works (WWTW) around the world. PFOS and PFOA have been included in monitoring at UK WWTW as part of the UK water industry's Chemicals Investigations Programme (CIP) (see Section 3.1.4) The third phase of the CIP is being expanded to include sampling for additional PFAS in effluent, sewage sludge and groundwater.

Concentrations of PFAS in WWTW effluents are likely to be variable and dependent on the type of treatment involved and partitioning to sludge during secondary and tertiary treatment (Earnshaw et al., 2014). Some types of PFAS are very difficult to remove from the water using conventional wastewater treatment processes. This is due to their resistance to degradation as well as low sorption to solids - the same properties also make the remediation of contaminated sites difficult (Ross et al., 2018).

There is some evidence that terminal PFAAs such as PFOS and PFOA can be formed in WWTW through the transformation of precursor compounds. Higher concentrations of PFOS and PFOA have been reported in the effluents from some WWTW compared to incoming waste water (<u>Posner and Jarnberg, 2004</u>; <u>Schultz et al., 2006</u>; <u>Becker et al., 2008</u>; <u>Arvanii and Stasinakis, 2015</u>). This usually occurs during secondary treatment by activated sludge, where PFOS levels can significantly increase (<u>Schultz et al., 2006</u>; <u>Sinclair and Kannan, 2006</u>; <u>Earnshaw et al., 2014</u>). For example, <u>Becker et al. (2008</u>) reports a threefold increases in mass flow of PFOS during wastewater processing and a 20-fold increase of PFOA from influent to effluent. There is little information available on concentrations of precursor compounds or conditions for transformation during waste water treatment and currently no UK-specific data.

Sampling and measurement of PFAS in sewage sludge from UK WWTW is planned under the third phase of the water industry's Chemicals Investigation Programme (CIP3), which commenced in September 2020.

1.6.4. Spreading of materials on land

The spreading of materials to land is regulated through the <u>Environmental Permitting</u> <u>Regulations (England and Wales) 2016</u>; the Environment Agency is the key regulatory body in England. Some materials are not included in this regulation such as the spreading of sewage sludge to land.

There has been a significant increase in the volume of material spread on land for agricultural benefit in recent decades. This is in response to the desire of successive governments for the UK to adopt a more sustainable approach to waste management. However, there is concern that spreading materials on land could be a growing source of PFAS contamination, particularly in groundwater.

An example of PFAS contamination arising from the spreading of waste materials to land comes from Rastatt in Baden-Wuerttemberg, Germany (<u>Brendel et al., 2018</u>). A large area of arable land has been affected following a long period of application of compost mixed with sludge from paper production. The paper sludge was contaminated with various PFAS that degraded to short-chain PFAS in the soil, which were subsequently detected in groundwater at significant concentrations. This led to the closure of some abstraction points for drinking water, as well as the loss of crop growing potential as plants were found to exceed recommended maximum concentrations.

The spreading of materials to land is regulated through the <u>Environmental Permitting</u> <u>Regulations (England and Wales) 2016</u>; the Environment Agency is the key regulatory body in England. The Environment Agency introduced soil screening values (SSVs) for PFOS and PFOA to help operators assess the potential ecotoxicological impacts from PFAS in waste being spread to land (<u>Environment Agency, 2017</u>). Further work is underway to better understand and substantiate the risks to the water environment from land spreading.

Identification of the PFAS used or present in paper products in the UK and confirmation of controls on site effluents and use of paper waste, including animal bedding made from paper sludge, are currently an evidence gap as identified in our wider PFAS action plan.

1.7. PFAS source and risk evaluation at UK sites

In 2019, we commenced a multi-phase project to enhance our understanding of PFAS occurrence in relation to UK sources and to understand the level of risk from source sites. The project looked initially at legacy sources, particularly land contamination associated with historic PFAS use. A multi-criteria GIS-based risk tool is being developed to help us identify potential PFAS source areas, the key chemicals of concern and the risk to the wider environment across England.

In the first phase of this work (<u>Environment Agency, 2020b</u>), a wide ranging literature review was carried out on PFAS usage, occurrence, fate, and transport to create source profiles for a range of industries and sites with the potential to release PFAS to the environment. The source profiles created assessed the likelihood and severity of PFAS emissions. Where possible they included details of the most likely PFAS to have been used and in which areas of a site release was most likely. Developing site profiles will help us to understand the type of sites and activities where PFAS release is likely to have occurred or may be ongoing.

Civilian airfields, military airfields and bases, fire-fighting training sites and fire stations, wastewater treatment works, and landfills were identified as having the highest potential risk as a source of PFAS. Several manufacturing industry sources including textile and leather, carpets and paper and cardboard manufacture were also identified, as were chrome plating sites. Site profiles have been developed for the highest risk source site types first. As part of future work, these profiles will be refined and extended to include further sources.

Information on site type has been used in conjunction with environmental setting (hydrogeological information) and water quality monitoring data to generate a set of data layers including heat-maps and site scores.

Phase 2 of the project (2020/21) is currently underway and aims to test the initial GIS model through environmental sampling and the use of additional source information including site visits.

The project output will facilitate in-depth local assessments of specific areas and sites that present a potential risk to health and the wider environment. Targeted water quality sampling at highlighted sites will form a key component of the evidence base into 2022/23 to validate the model with real data.

Monitoring data

This chapter provides an overview of our environmental data for PFAS collected between 2014 and 2019) and briefly describes planned monitoring for PFAS for 2021 and beyond. The chapter also includes data from other national scale environmental surveillance monitoring programmes.

Between 2014 and 2019, we have sampled groundwater, surface water (fresh, estuarine and coastal waters), freshwater fish (roach, chubb, trout) and marine fish (dab, flounder), for a range of 16 perfluoroalkyl carboxylic acids and perfluoroalkyl sulfonic acids. In 2020, Defra funded an estuarine sediment sampling programme, undertaken in collaboration between the Environment Agency and CEFAS (Centre for Environment, Fisheries and Aquaculture).

A list of the PFAS our National Laboratory Service can measure in environmental water samples is provided in Appendix 1. Further method development to increase the range of PFAS is on-going by our National Laboratory Service (NLS) and described further in Chapter 4. Cefas routinely analyse environmental samples including marine fish, sediment and water for a broad range of PFAS, also listed in Appendix 3.

Figure 3.1 below provides an overview of our sampling programmes between 2014 and 2019 and illustrates the relative size of each programme. PFOS is a priority hazardous substance under the Water Framework Directive Classification Directions (2015). The majority of our monitoring has been focussed on regulated substances such as PFOS.

Figure 3.1 Overview of Environment Agency sampling for PFAS 2014 – 2019. Relative size of sampling programme is represented by circle size.



1.8. Water monitoring

Main conclusions

- Our monitoring data in rivers, lakes, groundwaters, estuaries and coastal waters between 2014 and 2019 suggests that PFAS is likely to be widely present in English surface waters and groundwaters.
- Short-chain, more-mobile PFAS (PFBS, PFHxS, PFHxA, PFPeA) are detected at the highest percentage of sites across both groundwater, fresh and saline water sites sampled.
- Longer perfluoroalkyl chain, less-mobile PFAS such as PFUnDA and PFDoDA are very rarely detected in water samples.
- Data for PFOA and PFOS collected at wastewater treatment works (WWTW) through the Chemicals Investigation programme (CIP2) show concentrations are highly variable between works. The CIP data corroborates our own data, demonstrating that PFOS and PFOA are widespread contaminants in surface waters.
- Measurements of PFOS and PFOA at sites upstream of CIP2 works, in the effluent and downstream of the discharge indicate that whilst WWTWs add to the PFAS load, further investigation of sources of PFAS within catchments are required.

Since 2016, we have sampled approximately 470 freshwater sites and approximately 55 estuarine and coastal locations in England for PFOS and PFOA as part of our routine surveillance monitoring programme. The majority of fresh surface water sites are rivers but canals and lakes are also sampled. This programme samples a wide range of water quality parameters to support our water body classification decisions. To the end of 2019 water samples were collected monthly and PFOS and PFOA determined using a fully quantitative analytical method. In March 2020, our routine sampling was paused as a consequence of the Covid-19 pandemic and associated difficulties with both sample collection and laboratory analysis.

Additional surface water sampling has been conducted across fresh, estuarine and coastal water sites as part of our emerging substances contaminant monitoring between 2014 and 2019. The emerging contaminant programme is designed to cover a range of pressures on the aquatic environment including those arising from agriculture, urban and industry and is not targeted specifically to PFAS.

We have sampled groundwater at a sub-set of sites (322) across our groundwater quality monitoring network (GWQMN) as part of our on-going monitoring programme to investigate levels of organic contaminants in groundwater using the same targeted screening approach.

Water samples were analysed using a semi-quantitative screening approach targeted to a broad range of micro-organic contaminants of interest. Using this screening approach we can scan for thousands of chemicals in our groundwater and surface water surveillance programmes which helps us to detect emerging issues.

Analytes determined using this targeted screen include 16 PFAS. They are terminal or arrowhead substances – either perfluoroalkyl carboxylic acids or perfluoroalkyl sulfonic acids. The full list is provided in Appendix 3.

The semi-quantitative method provides an estimate of the concentrations of analytes using a method that is not validated for accuracy and precision in the same manner as a fully quantitative accredited analytical method would be. Concentrations are considered estimates and not treated as absolute values. In this chapter, we have presented our screening data qualitatively – to report presence or absence of a substance only. From 2021 onwards we will be measuring a broader range of PFAS in groundwater samples, using a quantitative method which will allow us to report environmental concentrations.

A summary of the data we have collected to date is described below in Sections 3.1.1 and 3.1.2 for groundwater and surface waters, respectively.

1.8.1. PFAS in groundwater

Routine groundwater monitoring data collected between 2014 and 2019 show widespread presence of some PFAS in groundwater. These data have been collected from sites across our GWQMN. GWQMN sites have been assessed by local groundwater staff as being representative of local aquifer water quality. Sites are sampled on a three year rolling basis as part of ongoing investigations into levels of organic contaminants in groundwater.

Analysis of PFAS in groundwater and surface waters using this screening approach commenced in 2014. In 2018 and 2019 a further three PFAS (PFPeS, PFHxS and PFBA) were added. Data for different PFAS and in different years should therefore be compared with caution.

To date, our groundwater monitoring for PFAS has been restricted to a relatively small number of sites and in most cases only a single sample has been taken from each site. However, future monitoring from 2021 onwards will include a broader range of PFAS substances and use a recently developed quantitative analytical method.

Table 3.1 below presents an overview of the PFAS data collected to date using the scan method. All samples have been aggregated to produce national level summary statistics. Our targeted scan only reports data where there is a positive detection. We have estimated the total number of samples analysed for PFAS in Table 3.1 so that we can report a detection frequency.

Our emerging contaminants screening method is a semi-quantitative method so results reported should be treated as indicative and data used with caution. For this reason, we have not reported concentrations in this report.

Data are organised in the table such that the most frequently detected PFAS are at the top of the table. However, care should be taken to compare data for individual PFAS directly with each other as some PFAS were only added in to the analytical suite in 2019 and so the total number of samples analysed is much lower.

Samples associated with obvious point sources of pollution such as waste or effluent have been excluded from this analysis, along with pollution incident monitoring data.

Not all sites in the GWQMN have been sampled. Further monitoring is planned for 2021.

The perfluoroalkyl sulfonic acids PFBS (4 carbons), and PFHxS (6 carbons) are detected most frequently in groundwater samples.

PFOS and PFOA (both 8 carbons), the most frequently reported PFAS in the wider scientific literature have been detected at 26% and 29% of sites sampled respectively.

The short chain perfluroralkyl carboxylic acids PFHxA (6 carbons), PFPeA (5 carbons) are also detected at 23 % and 22 % of sites respectively.

Longer carbon chain, less mobile PFAS such as PFUnDA (11 carbons) and PFDoDA (12 carbons) are rarely detected.

| Compound ² | No. of samples | No. of detections (%) | No. of sites sampled | No of sites detected (% detection) |
|-----------------------|----------------|--------------------------|-------------------------|--|
| PFBS | 756 | 324 (43%) | 547 | 214 (39%) |
| <u>PFHxS</u> | 756 | 297 (39%) | 547 | 192 (35%) |
| <u>PFOA</u> | 1076 | 303 (28%) | 655 | 196 (29%) |
| PFOS | 1076 | 309 (29%) | 655 | 175 (26%) |
| <u>PFPeA</u> | 1076 | 233 (22%) | 655 | 152 (23%) |
| <u>PFHxA</u> | 1076 | 235 (22%) | 655 | 145 (22%) |
| <u>PFHpA</u> | 1076 | 195 (18%) | 655 | 123 (19%) |
| PFPeS ³ | 336 | 74 (22%) | 116 | 36 (31%) |
| <u>PFNA</u> | 1076 | 38 (3%) | 655 | 28 (4%) |
| <u>PFBA</u> | 570 | 17 (3%) | 547 | 16 (3% |
| <u>PFDA</u> | 1074 | 3 (0.3%) | 655 | 2 (0.3%) |
| <u>PFOSA</u> | 1046 | 2 (0.2%) | 655 | 2 (0.3%) |
| <u>PFTDA</u> | 1046 | 2 (0.2%) | 655 | 1 (0.2%) |
| <u>PFUnDA</u> | 873 | 1 (0.1%) | 655 | 1 (0.2%) |
| <u>PFDoDA</u> | 1071 | 1 (0.1%) | 655 | 1 (0.2%) |

| Table 3.1 Frequency of detection of PEAS | in groundwator quality notwork sites (GWOMN) |
|--|--|
| Table 3.1 Frequency of detection of FFAS | in groundwater quality network sites (GWQMN) |

Neither PFHxS, PFBS nor PFPeS have current registered uses under REACH. Their presence in the environment may be caused by historic use of PFHxS or precursors that degrade to PFHxS or imported products containing PFHxS. For example, PFHxS has been reported to be used as a replacement for PFOS in fire-fighting foams.

In the past PFHxS was used in a number of applications in the EU and elsewhere, and was also present as an impurity in PFOS formulations. The major uses identified in the REACH Annex XV dossier proposing restrictions on PFHxS include apparel and leather (20%), carpets (60%), fabric and upholstery (15%), coatings (0.4%) and fire-fighting foams (5%).(ECHA, 2020) As a result of these uses PFHxS may also be present in landfill leachate, waste water and bio solids (Environment Agency, 2020b).

Wood (2020) summarised information on the presence of different PFAS in various AFFF formulations and reported PFHxS present in AFFF formulations from multiple producers in the 1980s, 1990s and early 2000s.

² Compound name in full and CAS number given in Appendix 1

³ Data for 2019 only

PFPeS is likely to be present as an impurity in historically used PFAS formulations (Environment Agency, 2020b).

A report by the Norwegian Environment Agency (Lassen & Brinch, 2017) into sources of PFBS to the environment identified use of PFBS related substances in the treatment of leather, textiles, carpets and hard surfaces as the main application. Minor uses included surfactants for inks, paints and waxes; as a mist suppressant for metal electroplating and as surfactants in the electronics industry (Lassen & Brinch, 2017).

Short chain PFAS were introduced by industry as replacement substances in products and formulations in response to restrictions on longer chain PFAS such as PFOS. They are typically considered to be less likely to bioaccumulate and less harmful. However short chain PFAS are more mobile than their long chain homologues and we are now their widespread presence in the environment as a consequence of this substitution of one PFAS for another.

Under the OECD definition only PFBS and PFPeS can be considered short-chain PFAS, although we also observe high levels of PFHxS and PFOS in water samples, indicating their high mobility despite being considered long chain PFAS within the OECD definition.

The shorter chain perfluoroalkyl carboxylic acids (PFCAs) - PFPeA and PFHxA are found in water in greater concentrations than the longer alkyl chain carboxylic homologues. These PFCAs, are much more mobile than their longer carbon chain homologues. Their presence in groundwater and surface waters at elevated levels is therefore unsurprising.

Environmental levels of PFAS will be highest in the vicinity of sites impacted by known sources and uses of PFAS. Airports, fire training grounds, manufacturing and formulation sites and major incident sites are typically identified as high risk with significant potential for environmental contamination by PFAS (Environment Agency, 2020b). Earlier monitoring carried out in 2006 sampled surface water and groundwater at sites associated with known uses of PFOS and other PFAS and reported the widespread presence of these substances at the sites sampled (Environment Agency, 2007).

It is difficult to directly compare this earlier data from 2007 with our more recent monitoring data since there are a number of differences. The locations are not the same - the earlier study was targeted to industrial and urban sites likely to be contaminated by PFAS, whereas this was not always the case in the more recent emerging contaminant scan data sampling.

We are evaluating our recent monitoring data to identify and understand likely sources of PFAS at sites with significant environmental contamination. We continue to build our evidence base with further targeted quantitative sampling to determine environmental concentrations and source and site risk mapping to develop tools for management of land contamination and associated water quality issues (Environment Agency, 2020).

Comparison of our data with groundwater sampling from other European countries shows a similar but not identical pattern in PFAS detection in groundwater. This is likely due to different sampling and monitoring regimes across those countries and may also reflect slightly different use profiles.

A report by <u>WFD CIS Voluntary Groundwater watch list group (2020)</u> bringing together groundwater data from 11 European countries in order to identify PFAS for inclusion on a future European groundwater Watch list, reported the greatest number of detections for the short chain substances PFBA (46.4% of sites) and PFHxS (37.5% of sites) followed by PFPA (28.6%) and PFBS (26.1%). Of these substances, the perfluoroalkyl carboxylic acids PFBA and PFPA were present most frequently in the highest concentrations with 14% and 12% of European sites sampled having concentrations greater than 0.1µg/l.

The European data are broadly similar to data reported here for English groundwaters and surface waters.

1.8.2. PFOS and PFOA in surface water, fully quantitative analysis

A summary of our water column data for PFOS and PFOA, analysed using a fully quantitative analytical method is provided in Table 3.2. River samples were collected monthly through our routine surveillance monitoring programme between 2016 and 2019 and. Values are reported here as the mean of the most recent three years of data - a metric routinely used for assessment of water body chemical status.

The fully quantitative data for estuarine and coastal waters consists of data from two national investigations (i) the key estuary project which looked at monthly water samples over 12 months in the Severn, Humber, Mersey, Tees, Thames and Southampton water (39 sites) and (ii) water samples over 12 months at 15 blue mussel sampling sites around the coast. The majority of sampling occurred between 2016 and 2018.

The data illustrates a wide range of concentrations of both PFOS and PFOA in English waters. Sampling locations (470 freshwater sites and 54 estuarine and coastal sites) and mean measured concentrations of PFOS and PFOA are mapped in Figure 3.4 and Figure 3.5 respectively.

Detectable levels of PFOS are found at over 99% of surface water sites sampled and detectable levels of PFOA at over 99% of freshwater sites and over 96% of estuarine and coastal sites sampled. The data show significant spatial variation in concentrations measured.

Mean measured concentrations of PFOS in fresh surface waters range from less than the minimum reporting value (MRV) to $0.61\mu g/l$. Mean measured concentrations of PFOA in fresh surface waters range from less than the MRV up to $0.073\mu g/l$. MRV values are provided in Table 3.2.

Lower concentrations of PFOS were observed in estuarine and coastal waters than in freshwaters, with reported mean values ranging from 0.00004µg/l to 0.0095µg/l. Mean measured concentrations of PFOA in estuarine and coastal waters ranged from less than the MRV up to 0.0076µg/l.

| | minimum reporting value μg/l (MRV) | mean site values (µg/l) |
|--|---------------------------------------|----------------------------------|
| Freshwater | | |
| (2017 to 2019) | | |
| PFOS | 0.00005 | <mrv 0.61<="" td="" –=""></mrv> |
| PFOA | 0.0002 | <mrv 0.073<="" td="" –=""></mrv> |
| Estuarine & coastal waters (2016 to 2018) | | |
| PFOS | 0.00002 | 0.00004 to 0.0095 |
| PFOA | 0.0001 | <mrv- 0.0076<="" td=""></mrv-> |

Table 3.2 Summary of PFOS and PFOA water column data. Mean values are calculated using the most recent three years of data

PFOS is a priority hazardous substance under the Water Environment (Water Framework Directive) (England and Wales) Regulations 2017. It is listed as a ubiquitous, persistent, bioaccumulative and toxic (uPBT) substance and as such, has a biota based environmental quality standard (EQS) set to protect both human health and the environment. This biota-based EQS should be used for assessment of chemical status and water body classification (UK Government, 2015).

An annual average (AA) EQS in water is derived by back calculation from the biota EQS. The AA EQS for PFOS is $6.5 \times 10^{-4} \mu g/l$ for freshwaters and $1.3 \times 10^{4} \mu g/l$ for estuarine and coastal waters. We have not compared our water column data against the AA EQS in this report, since this value has not been used in our assessment of chemical status for water body classification.

The regulation also sets out a maximum allowable concentration (MAC) for PFOS of $36\mu g/l$ for inland surface waters and $7.2\mu g/l$ for other surface waters. The MAC is a threshold intended to protect the aquatic environment from short-term toxic effects. The MAC EQS should be applied where the biota EQS are applied or where emissions or environmental concentrations indicate potential short-term risk.

All measured concentrations in freshwaters, estuaries and coastal waters are below the MAC EQS indicating that short term exposure risk to aquatic organism is likely to be low.

Figure 3.4 Sampling locations and mean measured PFOS concentrations from Environment Agency surveillance monitoring programme



Figure 3.5 Sampling locations and mean measured PFOA concentrations from Environment Agency monitoring in England, 2016 to 2018



Concentrations of PFOS and a number of other PFAS were measured in both groundwaters and in untreated surface waters at drinking water abstraction sites as part of an earlier monitoring study in 2006 to investigate the occurrence of PFOS and related compounds in the environment (Environment Agency, 2007). Sampling was targeted to areas associated with release of PFAS and a less sensitive analytical method was used. Measured concentrations of PFOS ranged from less than the limit of detection (0.1µg/l) up to a maximum of concentration of 33µg/l. This upper value being an extreme value. Most detections of PFOS were in the range 0.1µg/l up to 3µg/l. For PFOA, a range of concentrations between 0.1µg/l up to a maximum of 0.34µg/l was reported. This earlier study also looked and reported the presence of other perfluoroalkyl carboxylic acids. PFPeA, PFHxA and PFHpA were reported in some samples at concentrations above the limit of detection of 0.1µg/l (Environment Agency, 2007).

It is not possible to directly compare our recent water column monitoring with these older data because of differences in sampling locations and analytical methods.

In addition to PFOS and PFOA, a broader range of PFAS have been analysed for in surface water samples using the targeted screening method described in Section 3.1.

The substances observed in surface waters follow a very similar pattern to those reported in groundwater in Section 3.1.1. Between 2014 and 2019, approximately 100 surface water locations have been sampled for PFAS and analysed using the targeted screen.

A summary of substances detected in surface water using the targeted screen is provided below in Table 3.3. Fewer sites have been sampled compared with GW, but there are a greater number of samples per site.

Some PFAS are very frequently detected in surface water samples. PFBS is detected at 97 % of sites. PFOA and PFOS at 96 % of sites sampled. PFHxA and PFHxS are also detected at a high proportion of sites – 94 % and 90% respectively.

Overall PFAS are detected at a much higher percentage of sites sampled in surface water compared with groundwater locations.

PFAS have also been measured in some estuarine and coastal waters using our targeted scan. The data are summarised in Table 3.4. These data have not been generated as part of a national surveillance programme and have been generated through locally targeted monitoring programmes and a relatively small number of sites have been sampled.

The shorter chain PFAS and PFOS and PFOA are detected most frequently across sites. The relative rank order of substances is different in saline waters, with PFPeA and PFOS being reported most frequently at sites sampled (88% and 81% of sites respectively), followed by PFHxA (79% of sites); PFBS (70% sites), PFHxS (68%) and PFOA (61%).

| Substance | Number of samples | Number of detections | Number of sites sampled | Number of sites detected (% detection) |
|-----------|-------------------|----------------------|----------------------------|--|
| PFBS | 1169 | 1076 (92%) | 98 | 95 (97%) |
| PFOA | 2742 | 2482 (90%) | 101 | 96 (95%) |
| PFOS | 2742 | 2296 (84%) | 101 | 96 (95%) |
| PFHxA | 2742 | 2340 (85%) | 101 | 95 (94%) |
| PFHxS | 1169 | 1070 (92%) | 98 | 88 (90%) |
| PFHpA | 2742 | 2066 (75%) | 101 | 89 (88%) |
| PFPeA | 2742 | 2166 (79%) | 101 | 85 (84%) |
| PFPeS | 505 | 241(48%) | 98 | 69 (70%) |
| PFNA | 2733 | 907(33%) | 101 | 64 (63%) |
| PFDA | 2728 | 324 (12%) | 101 | 34 (34%) |
| PFBA | 777 | 14 (1.8%) | 98 | 6 (6%) |
| PFUnDA | 2690 | 7 (0.2%) | 101 | 7 (7%) |
| PFDoDA | 2690 | 5 (0.2%) | 101 | 4 (4%) |

Table 3.3 Frequency of detection of PFAS in fresh surface water sites

Table 3.4 Frequency of detection of PFAS in estuarine and coastal sites 2014 to 2019 (targeted screening method)

| Substance | Number of samples | Number of detections | Number of sites sampled | Number of sites detected (% detection) |
|-----------|-------------------|----------------------|-------------------------|--|
| PFPeA | 277 | 180 (65%) | 44 | 36 (88%) |
| PFOS | 277 | 178 (64%) | 44 | 36 (81%) |
| PFHxA | 277 | 156 (56%) | 44 | 35 (79%) |
| PFBS | 217 | 137 (63%) | 44 | 31 (70%) |
| PFHxS | 217 | 139 (64%) | 44 | 30 (68%) |
| PFOA | 277 | 134 (48%) | 44 | 27 (61%) |
| PFHpA | 277 | 118 (43%) | 44 | 27 (61%) |
| PFNA | 277 | 50 (18%) | 44 | 14 (32%) |
| PFPeS | 64 | 6 (9%) | 44 | 6 (14%) |
| PFDA | 277 | 7 (3%) | 44 | 6 (14%) |
| PFBA | 125 | 1 (0.8%) | 44 | 1 (2%) |

1.8.3. Is there a risk to public drinking water supplies from PFAS?

The <u>Water Supply (Water Quality) Regulations 2016 (as amended)</u> require that, in order to be considered 'wholesome', drinking water must not contain any substance at a level which would constitute a potential danger to human health.

There is a very high standard of drinking water quality in England which is enforced by the Drinking Water Inspectorate (DWI). We have compared our data against the DWI's <u>updated guidance on PFOS and PFOA</u> which sets the levels of PFOS and PFOA that water companies should act upon in if exceeded in drinking water, in order to fulfil their statutory obligations to ensure the safety of drinking water. The guidance requires water companies to consider these chemicals in their risk assessments and consider initiating monitoring for them at any of their works where appropriate.

Water companies are required to sample the drinking water supply for any element, organism or substance that they believe may cause the supply not to be wholesome. This includes the detection of PFAS, other than PFOS and PFOA. They are required to notify the Inspectorate of any event, which has or might affect the quality of the water supplied.

At the point of writing there have been no notifications of an event associated with elevated levels of PFOS or PFOA (or any PFAS) which could impact drinking water quality, in England since the Buncefield fire in 2005.

We have compared our fully quantitative PFOS and PFOA data from surface water sites located in drinking water protected areas (DrWPA) to the DWI 2020 Guidance Tier 2 'sampling: further provision' and Tier 3 'wholesomeness' values. Table 3.5 summarises the results. Our data has been shared with water companies and the DWI.

Table 3.5 Percentage of sites with exceedances of DWI 2020 guidance values in surface water monitoring data in DrWPAs 2017 to 2019 (fully-quantitative analysis)

| | PFOS | PFOA |
|---|------|------|
| Tier 3: wholesomeness (0.1µg/l) | 0% | 0% |
| Tier 2: sampling: further provisions (0.01µg/l) | 13% | 0.5% |

We have not compared groundwater data collected between 2014 and 2019 to the tier 2 and tier 3 thresholds since the concentration data collected using our targeted screening method are approximate. From 2021 we will be sampling groundwater using a quantitative method which will allow us to report measured concentration of a range of PFAS in groundwater.

1.8.4. Chemical Investigation Programme (CIP)

Monitoring carried out under phase 2 of the Chemical Investigation Programme (CIP2) for PFOS and PFOA between 2015 and 2020 is summarised below in Tables 3.6 and 3.7 respectively.

The programme is a collaboration between water companies in England and Wales, the Environment Agency and Natural Resources Wales (NRW). Its purpose is to gain a better understanding of the occurrence, behaviour and management of trace contaminants in the wastewater treatment process and in effluents. Because of the size of the work programme, it is divided into four 'tranches'. Effluent from of 609 WWTWs has been sampled between 2015 and 2020, together with associated upstream and downstream river samples.
The CIP2 has focused on sites with low dilution in the receiving waters and so at greatest risk of causing noncompliance with EQSs downstream. WWTW sampled have ranged in size from 250-1.6 million population equivalents (PE), although most are between 5,000-50,000 PE.

Upstream and downstream environmental sites have also been sampled, providing a detailed picture of chemical loads and discharges at these sites.

A summary of measured PFOS concentrations in the WWTW effluents, sites sampled upstream of the WWTW, and the downstream sites collected between 2015 and 2020 in CIP 2 are presented in Table 3.6.

The mean concentration of PFOS in effluent across all WWTW sampled is $0.0053\mu g/l$, with a standard deviation of $0.0044\mu g/l$. The mean PFOS concentration measured at sites upstream of the CIP2 WWTWs was $0.0047\mu g/l$ and downstream of the discharge a mean value of $0.0052\mu g/l$ was reported.

Mean concentrations of PFOS and PFOA measured through CIP show a similar pattern of widespread, variable levels of presence across English waters. The data reported by CIP reports a lower range of concentrations compared to our own surface monitoring data for which a range of concentrations more than an order of magnitude higher for both PFOS and PFOA have been reported. Our data includes a number of high concentration sites – some over an order of magnitude than other sites. Extremely high values may have been excluded as outliers from the CIP data set. In addition, whilst some sampling locations may be similar for CIP and our surveillance programme, sampling times are not the same and this may, in part, explain the observed difference.

Table 3.6 Summary of PFOS concentrations in WWTW effluent, upstream samples and downstream of discharges measured as part of CIP2 tranche 3 (UKWIR, 2020).

| Sample | units | mean | Standard deviation (between WwTWs) | median | 25 %ile | 75 %ile | 95 %ile |
|------------|-------|--------|---|--------|---------|---------|---------|
| Effluent | µg/l | 0.0053 | 0.0044 | 0.0018 | 0.0039 | 0.0063 | 0.0147 |
| Upstream | µg/l | 0.0047 | 0.0063 | 0.0005 | 0.0026 | 0.0061 | 0.0159 |
| Downstream | µg/l | 0.0052 | 0.0060 | 0.0009 | 0.0032 | 0.0064 | 0.0164 |

Table 3. Summary of PFOA concentrations in WWTW effluent, upstream samples and downstream of discharges measured as part of CIP2 tranche 3 (UKWIR, 2020).

| Sample | units | mean | Standard deviation (between WwTWs) | median | 25 %ile | 75 %ile | 95 %ile |
|------------|-------|--------|---|--------|---------|---------|---------|
| Effluent | µg/l | 0.0053 | 0.0026 | 0.0026 | 0.0047 | 0.0065 | 0.0107 |
| Upstream | µg/l | 0.0037 | 0.0040 | 0.0006 | 0.0026 | 0.0061 | 0.0159 |
| Downstream | µg/l | 0.0040 | 0.0028 | 0.0013 | 0.0034 | 0.0052 | 0.0095 |

A large variability in concentration between individual WWTW is observed for both PFOS and PFOA. As an indication of potential risk, the CIP have compared concentration data against the water column EQS for PFOS (0.00065µg/l for freshwater) There is currently no EQS for PFOA.

At over 80% of the 609 WWTW sampled in CIP2, the concentration of PFOS downstream of the WWTW discharge is above the water column EQS (<u>UKWIR, 2020</u>). Comparing measured data for PFOA against the PFOS EQS showed a similar level of exceedance of the threshold. This level of exceedance of the EQS is considerably greater than that reported for many of the other substances monitored as part of the CIP2 where exceedance is typically less than 10% of sites.

The concentration of PFOS was close to, or above, the EQS in samples collected upstream of many WWTW (UKWIR, 2020) as well as downstream, suggesting that local WWTW discharges may not be the only source.

Concentrations of PFOS and PFOA upstream of WWTW discharges already exceed the PFOS EQS by a large margin. On average, the concentration of PFOS is 19% higher downstream of WWTW compared with upstream samples and for PFOA, downstream concentrations are 35 % higher (<u>Comber et al. (2021)</u>).

Sources of trace substances such as PFOS and PFOA within a catchment are not yet fully understood. In addition to domestic sources, industrial sites and waste may also be significant sources.

As noted in Chapter 2, there may be high PFAS content in some landfill leachate or industrial waste which has subsequently been managed through WWTW. It would be beneficial to examine the influence and significance of this pathway further.

A third phase of the Chemicals Investigation Programme (CIP3) is now underway and sampling commenced in September 2020. CIP3 seeks to build further knowledge and understanding of PFAS in WWTW. Effluent sampling for PFOA and PFOS is continuing, to provide data for trend analysis. WWTW influent and effluent will be screened for a broader range of PFAS (PFBS, PFHXA, PFHxS, PFPA, PFHpA, GEN-X, 6:2 FTSA). Other components of CIP3 include measurement of PFAS in sludge, estuarine and saline waters and groundwater samples, studies to understand mechanism of removal and removal rates, and sewer and river catchment studies to further explore sources.

1.9. Biota monitoring

Key conclusions

- Our monitoring data show the widespread presence of PFOS in both freshwater and marine fish from English waters. Concentrations range from below the limit of quantification to significantly above the EQS (9.1µg/kg).
- PFOA has not been detected above the limit of quantification (1µg/kg) in any fish sampled in our monitoring programme. However, the presence of PFOA is widely reported in aquatic mammals and other aquatic biota, including some reports of PFOA in marine fish in sampling carried out by other organisations.
- We do not currently analyse for any other PFAS in fish, although method development is on-going by our labs.
- A range of PFAS have been measured in otter livers from English sites. The longer alkyl chain PFAS - PFOS, PFOA, PFNA and PFDcA were reported at the highest concentrations. This is consistent with other reports of PFAS in aquatic biota where PFOS and the long chain perfluoroalkyl carboxylic acids PFNA, PFUnA and PFDcA are often reported as the dominant PFAS, as well as the PFOS precursor compound PFOSA.

1.9.1. Freshwater and marine fish data

Between 2015 and 2019 we sampled a total of 78 freshwater sites for fish (roach 'Rutilus', brown trout 'Salmo trutta' and chubb 'Squalius cephalus'). Sampling location has varied between years – a smaller subset of these sites have data for three or more years.

Concentrations of PFOS and PFOA were determined in whole fish, (limit of dection1µg/kg). Results, reported by year, are summarised below Table 3.11.

PFOS was found in measureable concentrations in fish at all locations sampled. In freshwater fish, the annual mean measured concentration of PFOS range from the limit of detection to 60.5µg/kg wet weight.

PFOA was not detected above the limit of detection $(1\mu g/kg)$ in any samples. Detectable levels of PFOA in whole fish from UK marine waters have been reported previously (Fernandes et al., 2015)

Concentrations of PFOS reported are those measured in whole fish. Values are reported as wet weight for comparison with the EQS_{biota} but have been normalised to a standard dry weight. Normalisation of measured concentrations is a useful approach, allowing for comparison of concentrations in samples from different locations. It is described in detail in the <u>Technical Guidance Document on biota monitoring (EC, 2014</u>).

A whole fish sampling programme for PFOS and PFOA in estuarine and coastal waters was instigated in 2018, collecting fish – dab ('Limanda limanda') and flounder ('Platichthys flesus') from sites around England. All sampled fish had detectable levels of PFOS.

Mean concentrations of PFOS in whole marine fish (2018 to 2019) ranged from $1\mu g/kg$ to 19.7 $\mu g/kg$. PFOS concentrations were highest in fish sampled from the Humber and Thames estuaries.

Sampling locations and mean measured PFOS concentrations in freshwater and marine fish, as assessed against the EQS_{biota}, are shown in Figure 3.2. For ubiquitous persistent,

Figure 3.6. Mean measured whole fish concentrations of PFOS (wet weight, normalised) in freshwater and saline fish assessed against biota EQS.



bioaccumulative and toxic (uPBT) substances such as PFOS, the EQS_{biota} is set to protect both wildlife and people. The EQS_{biota} is 9.1µg/kg.

The biota EQS for PFOS was set to protect both wildlife and people and is based on human health endpoints as these are the most sensitive. There are currently no regulatory limits for PFAS in in food, including fish, although this situation is under review by the Committee on Toxicology (COT) following the publication of the European Food Safety Authority opinion on safe limits in food.

The fish sampled in our monitoring programmes are typically smaller than those likely to be consumed by humans. Data can be transformed to estimate the concentrations that would occur in larger fish representing a higher trophic level (\underline{EC} , 2014). This transformation of the data allows comparison of data observed across a broad spatial area in the different types and sizes of fish, and is commonly used to compare levels across the EU but is subject to uncertainty because of variations in possible trophic magnification factors.

Reporting concentrations in the fish sampled, as we do here, and not adjusting concentrations to larger higher trophic level fish, may better represent the prey fish likely to be present in a location but it is possible that concentrations of chemicals that bio magnify in fish at a higher trophic status may be underestimated.

Analysis of levels of PFAS and other emerging contaminants in a range of fish from UK and other nearby marine waters by <u>Fernandes et al (2015)</u> for the Food Standards Agency reported the presence of PFAS in all fish sampled with PFOS concentrations were significantly higher than other PFAS followed by PFOSA and the long chain PFCAs PFUnA and PFDoDA and PFOA. Sum of the nine PFAS measured ranged from 0.64μ g/kg to15.3 μ g/kg (<u>Fernandes et al., 2015</u>).

| Sample type | Year | Number of sites | No. of sites above EQS | Mean annual concentration range (µg/kg) |
|-----------------|------|--------------------|---------------------------|--|
| Freshwater fish | 2015 | 7 | 3 (42%) | 4.0 – 21.6 |
| | 2016 | 22 | 13 (59%) | 3.9 – 36.7 |
| | 2017 | 20 | 11 (55%) | 1.3 – 32.9 |
| | 2018 | 43 | 14 (32%) | 0.9 – 47.0 |
| | 2019 | 28 | 12 (43%) | 1.1 – 60.5 |
| Saline fish | 2018 | 9 | 2 (22%) | 1.0 – 11.7 |
| | 2019 | 20 | 3 (15%) | 1.0 – 16.4 |

Table 3.11. Summary of assessment of the annual mean measured whole fish concentration of PFOS reported as wet weight, normalised.

PFOS analysis in mussels 'Mytilus edulis' was included as part of our saline waters sampling programme at 15 sites from 2016 to 2018. However, PFOS was not detected in any mussel samples collected. There is evidence to suggest that mussels are not a suitable substrate for analysis of PFOS as they have an internal detoxification process that limits bioaccumulation of PFOS (Fernández-Sanjuan et al, 2010).

1.10. Water body classifications

PFOS is listed as a priority hazardous substance (PHS) under the Water Environment (Water Framework Directive) (England and Wales) Regulations 2017.

To assess good chemical status against the biota environmental quality standard (EQS) we have used a series of data sources in a hierarchy to increase our spatial coverage. As biota shows the direct risk of exposure, concentrations of PFOS in biota have been used as a priority, then water monitoring data using an equivalent EQS and finally modelled surface water concentrations. Water body classifications are available online in our catchment data explorer tool.

Using this approach the 2019 classification show that in surface waters in England 25% of all water bodies fail for PFOS.

1.11. PFAS in otters

<u>Cardiff University</u> run a long term environmental surveillance scheme using otters found dead to investigate contaminants, disease and population biology across the UK. As part of their work, Eurasian otter (Lutra lutra) liver tissue samples taken from carcasses collected at sites across England have been analysed to determine the pollutant profile of 33 PFAS compounds, including perfluoroalkyl carboxylic acids, perfluoroalkyl sulfonic acids, perfluoroalkane sulfonamides, fluorotelomer sulfonates and 'other' PFAS compounds. Appendix 2 lists the PFAS analysed for in this study. At the time of writing, the study is ongoing, however interim results have been shared with us (<u>O'Rourke, E. et al., 2020</u>).

Otter carcasses found at locations close to Environment Agency fish sampling sites have been analysed, in order to provide an opportunity to explore bio magnification through the food chain. A further 20 otters collected in at locations along a transect away from a factory producing fluoropolymers in the north west of England have also been analysed.

Figure 3.7 provides an overview of the data reported to date. <u>O'Rourke et al., (2020)</u> reported 14 of the PFAS analysed were present in all liver samples tested; three compounds (Gen-X, 4:2 FTS and ADONA) were not detected in any samples. The longer chain PFCAs and PFSAs – PFOS, PFOA, PFNA and PFDA – were reported at the highest maxima and mean concentrations.

Figure 3.7. Concentrations of compounds with detection frequency above 80%. Reproduced with permission from <u>O'Rourke, E. et al., (2020)</u>

Concentrations are μ g/kg wet weight. Compounds are shown in order of decreasing median concentration. Concentrations are presented as a boxplot; the thick black line indicates the median concentration, the lower and upper extent of the box indicate the 25th (Q1) and 75th (Q3) percentiles of the data distribution, whiskers show the lowest and highest values excluding outliers, and circles indicate outliers (1.5x the interquartile range).



1.12. PFAS in estuarine sediments

Sediment samples from 15 estuaries around England were sampled in 2020 and analysed for a suite of 31 PFAS which included PFCAs, PFSA, perfluoroalkane sulfonamides, fluorotelomer sulfonates and a number of other PFAS compounds. The project was a joint CEFAS – Environment Agency project (<u>Barber et al., 2021</u>).

In 85 out 103 sediment samples collected, PFAS were detected above the limit of quantification. PFOS and PFOA were detected most frequently in 50% of samples and 32% of sediment samples respectively. PFOS was often present in samples in the highest concentration. The authors note that only 5 out of 103 stations exceeded a recently derived advisory limit in sediment that is protective of 99% of benthic species in the marine environment (60µg/kg dry weight, normalised to 1 % total organic carbon; Simpson et al., 2021) for PFOS in sediment and none for PFOA.

A range of other PFAS were reported – the number and nature of which varied between locations. The largest number of PFAS detected in a single estuary was 18 in the Thames, followed by 13 in the Severn, 11 in the Tyne and 10 in the Orwell. Sediment collected from the Dart estuary had only 3 PFAS (Barber et al., 2021).

In contrast to results reported for surface water and groundwater samples, PFBS and PFPeS were infrequently detected in sediment – their presence reported in three samples or less.

Other notable PFAS with fairly high frequencies of detection were PFBA, PFHxA, PFDcA, PFHpA and PFHxS. Full results and data presented by site location in estuary are available in <u>Barber et al., (2021)</u>.

1.13. Atmospheric levels

We do not sample for atmospheric levels of PFAS.

PFAS are known to be released to air from a variety of sources and may travel significant distances in air, depending on the physico-chemical properties of the substance. The presence of PFAS in remote locations such as the Arctic demonstrates their potential for long-range atmospheric transport.

Surface deposition of atmospheric PFAA emissions followed by leaching of PFAS to groundwater has been demonstrated at sites in the vicinity of industrial emissions of PFAS (<u>de Silva et al., 2021</u> and references cited therein).

1.14. PFAS in soil

We do not routinely monitor for PFAS in UK soils.

The application of materials to land as an exposure pathway for PFAS is discussed in Chapter 2. The significance of this exposure pathway in the UK as a route for PFAS contamination of soil, plants, animals and groundwater is an evidence gap. Work has commenced through CIP3 to measure levels of PFAS in WWTW sludge and characterise exposure via this route. The significance of atmospheric transport and subsequent deposition to UK soils is another exposure pathway identified as an evidence gap.

We have collated available data on human health endpoints and physico-chemical properties and during 2021 will be deriving indicative soil guideline values for PFAS for use in the early stage management of land contamination.

1.15. Trends in environmental levels of PFAS

A systematic review covering 186 articles and 26 grey literature reports of the effect of restrictions on PFAS, including PFOS, on global concentrations was published by <u>Land et al (2018)</u>. Overall the review of evidence suggested that for PFOS in environmental samples there are no clear patterns of declining trends yet. Insignificant and decreasing trends were equally predominant in studies reporting times series concentrations of PFOS in fish, mussels and loggerhead sea turtles.

Trends in environmental levels of PFOS are discussed in more detail in a separate report (<u>Environment Agency, 2019</u>) and also summarised below.

The pattern of PFOS contamination in wildlife varies greatly among species and geographical locations. PFOS tends to be one of the dominant perfluoroalkylated compounds but other PFAS compounds are also reported. (<u>Huber et al., 2012</u>; <u>Kratzer et al., 2011</u>; <u>Ahrens et al., 2009</u>).

Trend data for PFAS in biota collected through UK-based environmental surveillance schemes are summarised below.

1.15.1. Predatory bird monitoring scheme

Long term trends in concentrations of PFCAs and PFSAs in eggs from two UK colonies of the Northern Gannet (Morus bassanus) have recently been reported by Pereira et al (2021), through analysis carried out under the Predatory Bird Monitoring Scheme (PBMS). The study provides data over a significant time period (37 years) that covers a use period before and after the partial ban on PFOS.

These authors report that over time the total sum of PFSAs measured in eggs first rose and then fell from the late 1990s, whilst the total sum of PFCAs remained unchanged and then rose from the late 1980s.

PFOS dominated the PFAS profile in eggs from both colonies. PFOS and PFOA concentrations increased in early years but are now declining. However, long-chain PFCA concentrations in eggs are still increasing, demonstrating their potential to bioaccumulate. In contrast, the shorter chain PFCAs and PFSAs such as PFHxS, with much lower bioaccumulation potential, are reported to be present in very low concentrations.

The rise in PFCAs is attributed to the rise in manufacture of fluorotelomer-based fluorinated compounds (Gebbink et al, 2011, cited by <u>Pereira et al, 2021</u>). Whilst PFUnA and PFTrDA dominate the profile of PFCAs observed, the authors note that these compounds were not intentionally produced. Their presence is attributed to their presence as impurities in PFOA and PFNA (<u>Pereira et al., 2021</u>).

1.15.2. Cetacean sampling

The Centre for Environment Fisheries and Aquaculture Science (CEFAS) measured levels of various PFAS in harbour porpoises stranded or by-caught in the UK during 2012-2014 (<u>Barber et al., 2016</u>). Livers from 51 animals were analysed. PFOS was found in all samples. Comparison of the data from 2012 to 2014 with an earlier study also carried out by CEFAS (<u>Law et al., 2008</u>) shows that the mean concentration of PFOS in UK harbour porpoises had decreased by approximately one third since 2001. The mean PFOS

concentration reported in UK harbour porpoises in 2012 to 2014 was 178ng/g wet weight compared with 600ng/g wet weight in 2001. A similar study of harbour porpoises in Northern Europe between 1991 and 2008 showed comparable decreasing concentrations of PFOS on a wider scale (<u>Huber et al., 2012</u>).

1.16. Planned environmental monitoring for PFAS – 2021 and beyond

To date our environmental monitoring for PFAS has had greatest emphasis on understanding the scale and extent of PFAS in water.

The inclusion of PFOS as a priority hazardous substance has resulted in a large, fully quantitative dataset on PFOS and PFOA in English surface waters, groundwater and estuarine and coastal waters, as well as measurements in both freshwater and marine fish.

The emerging contaminant targeted screen, although providing only semi-quantitative estimates of environmental concentrations, has yielded a valuable dataset on the broader range of terminal PFAS present in English waters. To the best of our knowledge our data represents the largest set of data on PFAS in UK waters published to date.

Monitoring data for PFAS in otters and the eggs of seabirds, collected as part of the Cardiff University otter surveillance programme and the Predatory Bird Monitoring Scheme (PBMS) respectively, together with data published in the scientific literature highlight a broad range of PFAS present in the UK environment including precursor compounds – and shorter chain PFAS introduced as replacements following restriction of PFOS and PFOA.

The distribution of individual PFAS between environmental compartments varies with the physicochemical properties of each substance. Short chain perfluoroalkylated substances are more mobile and are more likely to be present in water, having greatest potential to reach groundwater. Longer perfluoroalkylated chain substances have a greater potential to bioaccumulate, as evidenced by their presence in otters, cetaceans and birds. Some compounds such as PFHxS, PFOS and PFOA are both mobile and bioaccumulate.

A number of additional monitoring programmes and projects have commenced in 2021 to expand our existing evidence base. This will include further analysis of PFAS in:

- groundwater
- surface water (fresh and saline)
- fresh water fish (PFOA and PFOS only)
- marine fish
- landfill leachate
- WWTW effluent and sludge (Chemical Investigation Programme (CIP), phase 3)

A future monitoring strategy for PFAS

Management of the risk to humans and the environment from PFAS is a complex challenge that requires a co-ordinated approach between UK regulators, industry and users across the full life cycle from manufacture through to disposal. For evidence-based policy development and to measure the success of risk management options we need to:

- (i) understand the different sources of PFAS in the UK, both legacy and current and identify the those that pose the greatest risk
- (ii) identify key environmental exposure pathways
- (iii) characterise the PFAS load in different environmental compartments to understand the scale of the challenge and the identify the most relevant substances
- (iv) Ensure we have appropriate analytical methods to measure PFAS in environmental samples.

Analytical methods for PFAS are rapidly developing and our understanding of the most appropriate techniques for analysis of exposure in wildlife and the environment are evolving.

There are a number of resources on analytical methods for PFAS that provide a forum for discussion amongst regulators, industry and researchers. These include the <u>OECD portal</u> on per- and polyfluoroalkylated substances, <u>US EPA analytical methods development and</u> research on PFAS and the <u>ITRC (Interstate Technology and Regulatory Council) resource</u> on PFAS. Collaborative research networks such as <u>NORMAN</u> – a network of reference laboratories, research centres and related organisation for monitoring of emerging environmental substances also provide valuable information sharing and knowledge exchange on emerging contaminants including PFAS.

A recent synthesis of the current understanding of PFAS exposure, including review of methods to measure exposure in humans and wildlife by <u>de Silva et al., (2021)</u> provides a useful overview of analytical techniques for measuring PFAS.

A UK-based cross-regulator analytical working group is being established in 2021 to work collectively to develop and enhance analytical capability for PFAS and forms an important element of our PFAS UK evidence action plan. In addition, we have recently established a PFAS analytical exchange network amongst members of the <u>NORMAN</u> network.

The future direction of UK policy on PFAS and approach to risk management and regulation will be significant in informing our future strategic monitoring needs.

Defra are leading work to inform and develop the UK approach. A risk management and options appraisal (RMOA) for PFAS is underway and will be completed in 2022.

1.17. Determining which PFAS are present

Analytical methods for PFAS can usefully be grouped into three broad categories:

- (i) fluorine mass balance measurement of the total PFAS burden
- (ii) targeted PFAS analysis
- (iii) suspect screening and non-target analysis

There are a number of recent reviews providing a useful overview of the approaches including <u>Ross and Hurst, (2019), Koch et al., 2020, Cousins et al., 2020, de Silva et al., (2021)</u> and references therein.

A brief summary is provided in the sections below.

1.17.1. Measuring the total PFAS burden

To date our monitoring for PFAS has focused on individual perfluoroalkyl acids (PFAAs) or arrowheads, in water (see chapter 3). They are substances in their own right but may also be formed from different precursor substances over time. Some of these arrowhead PFAS are constituents of widely used substances that have been, or will shortly be, extensively banned, but are still in the environment from historical sources. Their extreme persistence means that they will be present in the environment as legacy contaminants for many years.

With so many individual PFAS substances and precursor substances, quantifying the scale and nature of environmental contamination by PFAS is challenging. Targeted methods for measuring individual PFAS are not able to keep pace with the introduction of new PFAS.

The diverse and complex chemistry in this group of substances, the sheer number of precursor PFAS and transformation products, a lack of identity of many of these substances, the difficulty in sourcing analytical standards and the lack of analytical methods means that measurement of individual PFAS through a targeted screening method, is likely to significantly underestimate the magnitude of the environmental burden of PFAS.

Several strategies have been developed for estimating total PFAS in environmental samples and these are described briefly below. Table 4.1a summarises two approaches to estimating the total PFAS burden; the total organofluorine (TOF) and total oxidisable precursor (TOP) assay. Table 4.1b sets out pros and cons for each.

Further work is need to explore the applicability of each approach for generating environmental data for regulatory risk management and how such data could be used in conjunction with targeted analysis for assessment against regulatory risk thresholds.

Organofluorine compounds are very rare in nature and almost always man-made in origin. Measurement of total organofluorine in a sample can act as a useful proxy for measurement of total PFAS.

A number of strategies have been developed in recent years to measure total organofluorine (TOF). Techniques to measure either extractable organofluorine (EOF) or adsorbable organofluorine (AOF), combined with targeted analysis for 'known' individual PFAS enables a mass balance type approach for PFAS analysis of samples and allows better characterisation of the total PFAS burden.

It should be noted that a number of pharmaceutical compounds are also organofluorine compounds and this may cause some interference, although it may be possible to adapt methods to avoid co-extraction of non-PFAS organofluorine (see Miaz et al., 2020).

Table 4.1a comparison of total organic fluorine (TOF) and total organic precursors (TOP) as methods to measure the total PFAS burden in environmental samples

| Total Organic Fluorine (TOF) | Total Organic Precursors (TOP) assay |
|--|--|
| Non-targeted method | Targeted to PFAAs |
| Total Fluorine (TF) measured. Fraction of TF then extracted using a sorbent (absorbable organofluorine (AOF)) or organic solvent (extractable organofluorine (EOF). | Oxidative sample pre-treatment method converting PFA precursors to stable target perfluoroalkyl acids (PFAAs) |
| EOF or AOF assumed to be total organofluorine (TOF) | |
| Determine Σ 'known PFAS' through targeted screen (LC-MS/MS) | Separation and detection via LC- MS/MS |
| TOF – Σ 'known PFAS' = unknown PFAS burden | |

Table 4.1b pros and cons of total organic fluorine (TOF) and total organic precursors (TOP) as methods to measure the total PFAS burden in environmental samples

| Total Organic Fluorine PROS | Total Organic Fluorine CONS | Total Organic Precursors (TOP) assay PROS | Total Organic Precursors (TOP) assay CONS |
|---|--|--|--|
| Generates ΣPFAS value | non-targeted – interpretation of results is unclear | estimates total load of known PFAS from PFAA precursors | interpretation of results is unclear |
| Relatively low cost compared to LC- MS/MS | interference from 'non- PFAS' such as pharmaceuticals and pesticides | can provide indicative data on PFA chain length which may aid source identification | does not account for non PFAA precursors and novel/next generation PFAS such as Gen-X |
| Good screening approach | Lack of standardised methods leads to variable results between labs. (potential bias from sample extraction) | Sensitive (0.1 – 1ng/l) | aqueous samples |
| | uncertain if it its sufficiently sensitive (0.1 – 0.5µg/l) | | non- representative end-products |
| | EOF – all matrices | | Variable recoveries/ |

| Total Organic Fluorine PROS | Total Organic Fluorine CONS | Total Organic Precursors (TOP) assay PROS | Total Organic Precursors (TOP) assay CONS |
|--------------------------------|--------------------------------|--|--|
| | AOF – aqueous samples only | | potential bias from sample extraction |

In general, studies on TOF and EOF/AOF indicate that a significant portion of organofluorine in biota and the environment is not captured by monitoring of the typical suite of PFAA congeners (de Silva et al., 2020). The 'known' or identified PFAS within a sample may range from as low as 2% to 60% depending on sample type and the nature of the analysis (Kemi 2021 and references therein).

For example, using targeted PFAS analysis in combination with EOF, Koch et al. (2019) demonstrated that up to 55 % of the EOF measured in water samples could be accounted for by the specific PFAS, leaving 45% 'hidden' or unidentified.

Kärrman et al., (2019) demonstrated that PFAS in wastewater sludge was dominated by PFAAs precursors and showed that 90% of the EOF in sludge samples analysed was unknown.

Cousins et al. (2020) advocate the potential for total fluorine (TF) measurement combined with EOF/AOF as a screening approach for estimating drinking water exposure to total PFAS instead of targeted analysis for groups of PFAS. The advantage, for a screening methodology, is that all PFAS can be captured in a single relatively inexpensive measurement, which can if required, then undergo further targeted analysis.

An alternative approach to EOF/AOF is the total oxidizable precursor (TOP) assay. This method provides an estimation of the perfluoroalkyl acid (PFAA) precursors or polyfluorinated compounds that can be converted to PFAAs within a sample and has mainly been applied to aqueous samples. Using this approach, Houtz et al., (2013) demonstrated precursors in AFFF had significantly contributed to PFCA and PFSA in groundwater from a firefighting training area (Houtz et al. 2013).

Samples are subjected to oxidation to transform PFAA precursors to their terminal products (Houtz et al. 2013, 2016). The oxidized and oxidised extracts are analysed by LC-MS/MS for PFAS to quantify the concentrations of oxidizable precursors.

Neither the TOF (EOF/AOF) approach nor the TOP assay have validated, standardised methods yet.

1.17.2. Targeted analysis for PFAS

In chapter 3 we reported concentrations and presence/absence of individual PFAS measured in environmental samples by targeted PFAS analysis using LC-MS/MS.

Most studies in the scientific literature report concentrations measured analysis targeted to individual substances. It is possible to measure individual PFAS accurately and at low levels using this approach. However the approach is limited to a finite number of substances as analysis is dependent upon availability of suitable analytical standards and knowledge of which PFAS are of most relevance to target.

To date, we have used a targeted screening approach (see Section 3.1) to identify the presence of a range of PFAS in environmental waters.

To expand the range of PFAS we measure and to move to a reliable and precise quantitative targeted LC-MS/MS method we have identified PFAS that are most likely to be relevant in UK environmental monitoring programmes. Water samples collected from 2021 onwards will be analysed using our 'new' PFAS targeted analytical method.

The list of PFAS is based on existing available information and is not exhaustive. We will continue to amend and update our informal PFAS 'surveillance list' as new information becomes available.

The current list of substances identified for inclusion in our targeted LC-MS/MS analysis is provided in full in Appendix 4.

Criteria for inclusion included:

- (i) highlighted as having hazardous properties and restricted or under consideration for restriction or monitoring under regulatory regimes
- (ii) currently registered for UK use under REACH with high tonnage (> 10 t/y)
- (iii) identified as a potential contaminant of concern through hazard and risk assessment (Environment Agency, 2021)
- (iv) potential for significant environmental exposure through UK source assessment and risk evaluation work
- (v) associated with UK manufacturing sites with potential for environmental exposure
- (vi) commonly reported as a significant contaminant in environmental samples in other studies in the scientific literature, especially those with close geographic proximity to UK.

1.17.3. Non-target screening for PFAS

Non-target screening for PFAS using high-resolution mass spectrometry allows discovery of non-target PFAS using chemical databases that contains details on molecular structures of thousands of PFAS. Such techniques are typically qualitative, because of the lack of available analytical standards but allow discovery of previously unidentified emerging contaminants, including anionic, cationic and zwiterionic and neutral PFAS in a variety of sample matrices (de Silva et al., 2021 and references cited therein).

1.17.4. Characterising the extent of any adverse impacts on the environment and human health – evidence gaps

Interpretation of environmental monitoring data for PFAS requires risk thresholds – or safe limits - against which we can assess potential risk to humans and the environment.

Typically risk thresholds, such as environmental quality standards, soil screening values and safe limits in food and drinking water are derived using toxicological data. The lack of toxicological data for all but a few legacy PFAS is a significant challenge to effective risk management.

Generating intrinsic hazard data for individual PFAS is too resource intensive. <u>Cousins et</u> <u>al., (2020)</u> discuss a number of different grouping strategies that could be used for the future assessment and management of PFAS.

A number of different approaches to measuring and estimating toxicity have been proposed. It is beyond the scope of this report to go into further detail here. A recent

review (<u>Fenton et al., 2020</u>) describes the current state of knowledge regarding toxicological effects of PFAS and discusses strategies for informing further research.

Conclusions

We have used available data and information to build a picture of the use of PFAS in the UK. Information on sources and pathways to the environment and the extent of environmental presence in English waters is also reported.

Approximately 100 individual PFAS are potentially supplied to the UK market in amounts greater than 1 tonne per year, according to the ECHA database. Only 36 PFAS are supplied to the European market in quantities greater than 10 tonnes per year. The UK market is likely to be smaller.

This does not represent a complete picture because it does not include PFAS manufactured or imported by individual companies below 1 tonne per year. This includes goods imported from outside the EU. The identity of UK companies that may be importing from EU-based suppliers will become apparent over the next few years once the registration requirements of UK REACH have been fulfilled.

There are two major UK-based manufacturers of PFAS. Both have sites in Lancashire. Working with both companies, we are evaluating the hazard and risk of 12 individual PFAS used or produced at these sites. The completed evaluations will be used to identify the need for any further monitoring investigations or other regulatory activities.

Fluoropolymers and polymers containing residual PFAS additives or processing aids, are a source of PFAS in the environment due to degradation and/or weathering over time. However there is no registration requirement for polymers under REACH. Consequently we cannot estimate the contribution of such polymers to the environmental load of PFAS. This is a significant information gap.

Surveys of five UK-based trade sectors did not provide much additional information about the current use of PFAS in these sectors in the UK and this remains an evidence gap but is being followed up as part of the development of a risk management Options Analysis.

In 2019 we commenced a multi-phase project to enhance our understanding of the environmental occurrence of PFAS in relation to UK sources and to understand the level of risk from source sites. The project looked initially at legacy sources, particularly land contamination associated with historic PFAS use.

Civilian airfields, military airfields and bases, fire-fighting training sites and fire stations, WWTWs, and landfills were identified as having the highest potential risk as a source of PFAS to the environment. Several manufacturing industries including textile and leather, carpets and paper and cardboard manufacture were also identified as potentially significant sources of PFAS, as were chrome plating sites.

A multi-criteria GIS-based risk tool has been developed to help us identify potential PFAS source areas and enable in-depth local assessments of specific areas and sites that present a potential risk to health and the wider environment. Targeted water quality sampling at highlighted sites will form a key component of the evidence base into 2022/23, to validate the model with real data.

Our monitoring data in rivers, lakes, groundwaters, estuaries and coastal waters between 2014 and 2019 suggests it is likely that PFAS is widely present in English surface waters and groundwaters.

Short chain, more mobile PFAS (PFBS, PFHxS, PFHxA, PFPeA) are detected at the highest percentage of sites across both groundwater, fresh and saline water sites sampled. Longer perfluoroalkyl chain PFAS such as PFUnDA and PFDoDA are very rarely detected in water samples.

Data for PFOA and PFOS collected at wastewater treatment works through the UKWIR Chemicals Investigation programme (CIP2) show concentrations are highly variable between works. The CIP data corroborates our own data, demonstrating that PFOS and PFOA are widespread contaminants in surface waters.

Measurements of PFOS and PFOA at sites upstream of CIP2 works, in the effluent and downstream of the discharge indicate that whilst treated sewage effluent adds to the PFAS load, further investigation of sources of PFAS to sewer and within catchments are required. Further exploration of the contribution that transformation of precursor PFAS into arrowhead PFAAs during wastewater treatment makes to the overall load from works is also required.

Our monitoring data shows widespread presence of some PFAS substances in environmental waters. Our analytical method is a targeted screening method so our assessment provides an indication of presence/absence only and requires further targeted investigation. We have shared our data and information with water companies and the DWI.

We have also reported the widespread presence of PFOS in both freshwater and marine fish from English waters. Concentrations range from below the limit of quantification to significantly above the biota EQS $(9.1\mu g/kg)$.

PFOA has not been detected above the limit of quantification (1µg/kg) in any fish sampled in our monitoring programme. However, the presence of PFOA is widely reported in aquatic mammals and other aquatic biota, including some reports of PFOA in marine fish in sampling carried out by other organisations.

We do not currently analyse for any other PFAS in fish, although method development is planned by our labs.

Sediment samples from 15 estuaries around England were sampled in 2020 and analysed for a suite of 31 PFAS which included PFCAs, PFSA, perfluoroalkane sulfonamides, fluorotelomer sulfonates and a number of other PFAS compounds. A range of other PFAS were reported – the number and nature of which varied between locations. PFOS and PFOA were detected most frequently. Other notable PFAS with fairly high frequencies of detection were PFBA, PFHxA, PFDcA, PFHpA and PFHxS. Full results and data presented by site location in estuary are available in <u>Barber et al., (2021)</u>.

A range of PFAS have been measured in otter livers from English sites. The longer perfluoroalkyl chain PFAS - PFOS, PFOA, PFNA and PFDcA - were reported at the highest concentrations. This is consistent with other reports of PFAS in aquatic biota where PFOS and the long chain perfluoroalkyl carboxylic acids PFNA, PFUnA and PFDcA are often reported as the dominant PFAS, as well as the PFOS precursor compound PFOSA.

Additional environmental monitoring for PFAS is continuing in 2021, to expand our existing evidence base. This will include further analysis of PFAS in groundwater, surface water (fresh and saline), fresh water fish, marine fish, landfill leachate, WWTW effluent and sludge (Chemical Investigation Programme (CIP), phase 3).

PFAS are known to be released to air from a variety of sources and may travel significant distances in air, depending on the physico-chemical properties of the substance. The scale and significance of atmospheric emissions of PFAS in the UK, especially emissions from potential sources such as manufacture and formulation sites and landfills is an evidence gap.

The application of materials such as sewage sludge to land in the UK is common practice in the UK for restoration, construction and agricultural purposes. The potential for this practice to be a route for PFAS contamination of soil, plants, animals and groundwater is an evidence gap. Work has commenced through CIP3 to measure levels of PFAS in WWTW sludge and characterise exposure via this route.

The significance of atmospheric transport and subsequent deposition to UK soils is another exposure pathway identified as an evidence gap.

Quantifying the scale and nature of the presence of PFAS in the environment is challenging because of the number of individual PFAS substances. To date our monitoring for PFAS has focused on individual perfluoroalkyl acids (PFAAs) or arrowheads.

Analytical methods for PFAS are rapidly developing and our understanding of the most appropriate techniques for analysis of exposure in wildlife and the environment are evolving. It is not possible to keep pace with the introduction of new PFAS, nor do we have adequate information and uses of PFAS in the UK.

Data from non-target screening analysis and wider intelligence on PFAS use could be used to build our knowledge and understanding of UK relevant PFAS further.

We have expanded the range of PFAS we measure. We have used available evidence to identify those PFAS that are most likely to be relevant in the UK. Water samples collected from 2021 onwards will be analysed using our 'new' PFAS targeted analytical method.

Measurement of individual PFAS through a targeted screening method is likely to significantly underestimate the magnitude of the environmental burden of PFAS. Further work is needed to explore the applicability of strategies that have been developed for estimating total PFAS in environmental samples to assess risk. The suitability of approaches such as TOF and the TOP assay for generating environmental data for regulatory risk management and how such data could be used in conjunction with targeted analysis for assessment against regulatory risk thresholds should be explored further.

Interpretation of environmental monitoring data for PFAS requires risk thresholds or acceptable limits, against which we can assess potential risk to humans and the environment. Typically risk thresholds, such as environmental quality standards, soil screening values and safe limits in food and drinking water are derived using toxicological data. The lack of toxicological data for all but a few legacy PFAS is a significant challenge and to effective risk management.

A UK-based multi-regulator analytical working group is being established in 2021 to work collectively to develop and enhance analytical capability.

Managing the risks from use of PFAS is a complex and challenging issue. Regulators, industry, academia and research organisations will need to work together to increase our knowledge and understanding and develop an effective UK strategy for PFAS.

Appendix 1: Definition of PFAS and overview of types of PFAS

Definitions of PFAS

In 2018, the Organisation for Economic Co-operation and Development (OECD) published the results of efforts by OECD and the United Nations Environment Programme (UNEP) Global PFC Group to identify how many PFAS were on the global market; a total of 4,730 PFAS were believed to be in worldwide use (OECD 2018). These substances were defined as those that contain a perfluoroalkyl moiety with 3 or more carbon atoms ($-C_nF_{2n}-$, $n \ge 3$) or a perfluoroalkyl ether moiety with 2 or more carbon atoms ($-C_nF_{2n}-$, $n \ge 3$) or a perfluoroalkyl ether moiety with 2 or more carbon atoms ($-C_nF_{2n}-$, $n \ge 1$).

The OECD has recently drafted an update to their 2018 definition of PFAS which states "fluorinated substances that contain at least one aliphatic carbon atom that is both saturated and fully fluorinated (without any H/Cl/Br/l atom attached to it), i.e. any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2$ -) in its structure"(OECD, unpublished) and the simplest substance meeting this definition is tetrafluoromethane (CF4) (OECD, unpublished).

These definitions of PFAS supplemented by the classification methodologies of <u>Buck et al.</u> (2011) and <u>Wang et al. (2017)</u> and the overview of terminology provided by <u>OECD (2013)</u> are appropriate for this report. A summary is provided below and the reader is referred to the original reference materials for further detail.

A.1 Non-polymeric PFAS

A.1.1 Perfluoroalkyl substances

Perfluoroalkyl substances are characterised by a fully fluorinated carbon chain where all hydrogen atoms in the alkyl chain are replaced by fluorine atoms (C_nF_{2n+1}) .⁴ They have been manufactured for more than 50 years. Examples include perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA).

A.1.2 Polyfluoroalkyl substances

Polyfluoroalkyl substances are aliphatic substances in which all hydrogen atoms attached to at least one (but not all) of the carbon atoms have been replaced by fluorine atoms in such a manner that they contain the perfluoroalkyl moiety.

Polyfluoroalkyl substances have the potential to be transformed into perfluoroalkyl compounds under appropriate conditions. Examples include fluorotelomer substances such as 8:2 fluorotelomer alcohol (8:2 FTOH), which has 8 fully fluorinated carbon atoms and 2 terminal carbon atoms with no fluorine atoms attached (Buck et al. 2011) and 10:2 fluorotelomer alcohol (10:2 FTOH).

A.2 Polymeric PFAS

Fluorinated polymers are considered to be PFAS if they contain per- or polyfluoroalkyl moieties. Polymeric PFAS are made from one or more PFAS monomers or involve the use of a fluorosurfactant processing aid (<u>Buck et al. 2011</u>).

⁴ Perfluorocarbons (PFCs) consist only of fluorine and carbon atoms.

There are 2 main types. Both can be a source of lower molecular weight PFAS due to degradation of poly/perfluorinated side chains, or the presence of residual manufacturing impurities (such as processing aids) that are PFAS themselves.

A.2.1 Fluoropolymers

'Fluoropolymers' are typically made by the (co)polymerisation of unsaturated monomers – at least one of which contains fluorine atoms bound to one or both of the unsaturated carbon atoms – to form a carbon-only polymer backbone with fluorine atoms directly attached (<u>Buck et al. 2011</u>). Examples include:

- polytetrafluoroethylene (PTFE)
- polyvinylidene fluoride (PVDF)
- fluorinated ethylene propylene (FEP)
- perfluoroalkoxyl polymer (PFA)

<u>Henry et al. (2018)</u> argued that fluoropolymers are distinctly different from other polymeric and non-polymeric PFAS due to their thermal, chemical, photochemical, hydrolytic, oxidative and biological stability. They have negligible residual monomer and oligomer content and low to negligible leachability. Fluoropolymers have very high molecular weights, are practically insoluble in water and are not subject to long-range transport (<u>Henry et al. 2018</u>).

A.2.2 Side-chain fluorinated polymers

Side-chain fluorinated polymers have a non-fluorinated polymer backbone with fluorinated side chains, ending in $-C_nF_{2n+1}$. Examples are polymers derived from 8:2 FTOH.

Figure A.1 Overview of PFAS (From OECD, 2013)



Per- and polyfluoroalkyl substances (PFASs)

Appendix 2: PFAS registrations under the REACH Regulation

The substances listed below were registered on the ECHA public dissemination website⁵ as of 23 November 2018. Those highlighted in grey are former 'new substances' under pre-REACH legislation. Substances supplied at 10 tonnes per year or more are highlighted in orange. The substances are presented in general accordance with PFAS family groups set out in <u>Buck et al. (2011)</u>.

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|--|---------------|---------------------------|---------------------------------|--|--|----------------------|
| Perfluorocarbons (PFCs) | | | | | | |
| Octafluorocyclobutane | 115- 25-3 | 10–100 | F F | - | Formulation into mixtures | - |
| | | | F F | | Electronic component manufacture | |
| | | | F F | | Use for the calibration of analysis equipment | |
| Nonafluoro(trifluoromethyl)cyclo- pentane | 1805- 22-7 | 0–10 | F F F F F F F | _ | Manufacture of the substance | _ |

⁵ https://echa.europa.eu/information-on-chemicals/registered-substances

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|--|--------------|---------------------------|---|--|--|----------------------|
| Perfluoroperhydrophenanthrene | 306- 91-2 | Confide ntial | | _ | _ | _ |
| Perflunafene | 306- 94-5 | 0–10 | | - | Manufacture of the substance Laboratory chemicals Pharmaceuticals | - |
| Docosafluorododecahydrofluore ne | 307- 08-4 | Confide ntial | | _ | - | _ |
| Perfluorooctane | 307- 34-6 | 0–10 | F | _ | Manufacture of the substance | - |
| 1,1,2,2,3,3,4,5,5,6-Decafluoro- 4,6- bis(trifluoromethyl)cyclohexane | 335- 27-3 | 0–10 | | _ | Manufacture of the substance Use of non- reactive processing aid at industrial site | _ |

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|---|--------------|---------------------------|--|--|--|----------------------|
| | | | | | Manufacture of bulk, large scale chemicals (including petroleum products) | |
| Perfluoro(methylcyclohexane) | 355- 02-2 | 0–10 | F F CF ₃ F F F F F F F F F F F F F F F F F F F | - | Manufacture of the substance | _ |
| Octafluoropropane | 76-19- 7 | 10–100 | F F F | - | Manufacture of the substance | - |
| | | | F F | | Processing agent | |
| | | | I I I F F F | | Coolant and detector fluid | |
| | | | | | Calibration of analysis equipment | |
| | | | | | Refrigerant | |
| | | | | | Use as intermediate | |
| | | | | | Solvent in polymerisation process | |
| | | | | | Use for electronic component manufacture | |

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|--|---------------|---------------------------|---|--|--|---|
| | | | | | Industrial use as cleaning/etching | |
| Polyfluorinated polymerisation media | | 10–100 | - | - | Formulation into mixtures | |
| | | | | | Use as non- reactive processing aid at industrial site (no inclusion into or onto articles) | |
| 1,1,1,2,2,3,3,4,5,5,5- Undecafluoro-4- (trifluoromethyl)pentane | 355- 04-4 | 100– 1,000 | $F F F F F F$ $F + F + F$ $F F F F CF_{3}F$ | - | Manufacture of the substance | _ |
| (<i>E</i>)-1,1,1,2,3,4,5,5,5-Nonafluoro- 4-(trifluoromethyl)pent-2-ene ⁵ | 3709- 71-5 | 100– 1,000 | F CF ₃ F | - | Manufacture of the substance | - |
| | | | F F F F | | Industrial use in insulation foams | |
| 1,1,2,3,4,4-Hexafluorobuta-1,3- diene | 685- 63-2 | 10–100 | F F F F F | - | Manufacture of the substance (directly exported) | Appears to be a structural analogue to a known POP (hexachloro–butadiene) |

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|---|----------------|---------------------------|--|--|---|--|
| Poly(1-pentene-2,3,3,4,4,5,5- heptafluoro-co-ethene-co- tetrafluoroethene) | 94228- 79-2 | Confide ntial | $F \xrightarrow{F}_{F} \xrightarrow{F}_{F} \xrightarrow{F}_{F} \xrightarrow{F}_{F} \xrightarrow{F}_{F} \xrightarrow{F}_{F} \xrightarrow{F}_{F} \xrightarrow{Ke^{+}}_{F} KE^$ | _ | _ | _ |
| Perfluoroalkyl acids (PFAAs) | | | | | | |
| Tetraethylammonium heptadecafluorooctanesulfonate | 56773- 42-3 | 0–10 | $F \xrightarrow{F} F \xrightarrow{F} F \xrightarrow{F} F \xrightarrow{F} F \xrightarrow{F} F \xrightarrow{O} H_3C \xrightarrow{OH_3} $ | PFOS | Manufacture of the substance | Addressed by ongoing activity under Stockholm |
| | | | ĊH ₃ | | Manufacture of fabricated metal products, chromium (VI) metal plating | Convention for PFOS |
| Ammonium undecafluorohexanoate [perfluorohexanoic acid (PFHxA), ammonium salt] | 21615- 47-4 | 10–100 | NH ⁺ 40 ⁻ F F F F F F F F F F | PFHxA | Manufacture of polymers | SVHC proposal in 2018 for concerns over drinking water contamination was withdrawn; restriction proposal expected 2019 |
| 1,1,2,2,3,3,4,4,4- Nonafluorobutane-1-sulfonic | 375- 73-5 | 0–10 | | PFBS | Manufacture of the substance | RMOA by Norway, 2018 (SVHC identification and restriction proposal likely) |
| acid [perfluorobutane sulfonate, PFBS] | | | U I I I I O F F F F | | Chemical intermediate | |

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|---|-----------------|---------------------------|--|--|--|----------------------|
| | | | | | Catalyst | |
| Sodium 1,1,2,2,3,3,4,4,4- nonafluoro-1-butanesulfinate | 10206 1-82-5 | Confide ntial | Na ⁺ 0 F F F F 0 F F F F | PFBS | - | See CAS no. 375-73-5 |
| Perfluorobutanesulfinic acid | 34642- 43-8 | Confide ntial | F F F F O F F F F OH | PFBS | - | See CAS no. 375-73-5 |
| Triphenylsulfonium perfluoro-1- butanesufonate | 14431 7-44-2 | Confide ntial | | PFBS | - | See CAS no. 375-73-5 |
| Dimethyl(phenyl)sulfanium nonafluorobutane-1-sulfonate | 22013 3-51-7 | Confide ntial | $H_3C^{CH_3}$ $F \xrightarrow{F} F \xrightarrow{F} 0^{-0}$ | PFBS | _ | See CAS no. 375-73-5 |
| Tetrabutyl-phosphonium nonafluoro-butane-1-sulfonate ⁶ | 22068 9-12-3 | 1+ | $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | PFBS | Manufacture of the substance | See CAS no. 375-73-5 |
| | | | H ₃ C P ⁺ CH ₃ | | Manufacture of polymer preparations | |
| | | | CH ₃ | | Production of plastic articles | |
| Potassium 1,1,2,2,3,3,4,4,4- nonafluorobutane-1-sulfonate | 29420- 49-3 | 10–100 | O F F F F K ^{+(I)} O ⁻ S | PFBS | Manufacture of the substance | See CAS no. 375-73-5 |
| | | | | Formulation of polymer preparations | | |
| | | | | | Use as an additive/reactant in polymerisation process | |

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|---|-----------------------------|---------------------------|--|--|--|--|
| | | | | | Laboratory use | |
| | | | | | Manufacture of plastic articles | |
| | | | | | Chemical intermediate | |
| N,N,N,-Triethylethanaminium 1,1,2,2,3,3,4,4,4- | 25628- 08-4 | 0–10 | F F F F O H ₃ C CH ₃ | PFBS | Manufacture of the substance | See CAS no. 375-73-55 |
| nonatiuorobutane-1-sulfonate | onafluorobutane-1-sulfonate | | ⊧́⊧́⊧́⊧́́ь́н н₃с́ ⊂сн₃ | | Manufacture of fabricated metal products, except machinery and equipment | |
| Bis(nonafluorobutyl)phosphinic acid | 52299- 0–10 25-9 | 0–10 | | – F | Manufacture of the substance | Substance Evaluation by Germany, 2018 (PBT/vPvB concern) |
| | | | - FFFFOFFF | | Metal surface treatment chemical | |
| | | | | | Laboratory chemical | |
| | | | | | Chemical intermediate | |
| Perfluoroalkane sulfonyl fluorides (PASFs) | - | - | - | - | - | - |
| | | | | | | |

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|--|-----------------|---------------------------|---|--|--------------------------------|-----------------------------------|
| Heptadecafluorooctanesulfonyl fluoride | 307- 35-7 | - | F F F F F F F O F | PFOS | Chemical intermediate | See CAS no. 56773-42-3 |
| 1,1,2,2,3,3,4,4,4- Nonafluorobutane-1-sulfonyl fluoride | 375- 72-4 | - | F F F F O F F F F F O F F F F O | PFBS | Chemical intermediate | See CAS no. 375-73-55 |
| Perfluoroalkane sulfonamides (FASAs) | | | | | | |
| Triphenyl(phenylmethyl)phosph onium 1,1,2,2,3,3,4,4,4- nonafluoro-N-methyl-1- butanesulfonamide (1:1) | 33235 0-93-3 | Confide ntial | $F F F F O P^+$ $F F F F O CH_3$ | PFBS | _ | See CAS no. 375-73-5 |
| Perfluoroalkyl iodides (PFAIs) and perfluoroalkyl bromides (PFABs) | | | | | | |
| Alkyl iodides, C6-18, perfluoro | 90622- 71-2 | - | F F F F F F F $F + F F F F F$ $F + F F F F F F$ $F F F F F F F$ $n=1-7$ | PFOA and long- chain PFCAs | Chemical intermediate | Exempt from EU PFOA restriction?? |

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|--|--------------|---------------------------|--|--|---|---|
| 1-Bromoheptadecafluorooctane | 423- 55-2 | 0–10 | F F F F F F F F F | PFOA | Processing aid in the manufacture of pharmaceuticals | Addressed by EU PFOA restriction |
| 1,1,1,2,2,3,3,4,4,5,5,6,6- Tridecafluoro-6-iodohexane | 355- 43-1 | _ | F F F F F F F + + + + + + + + + + + + + | PFHxA? | Chemical intermediate | - |
| 1,1,1,2,3,3,3-Heptafluoro-2- iodopropane | 677- 69-0 | - | F F F F - F F I F | _ | Chemical intermediate | _ |
| Other perfluoroalkyl substances | | | | | | |
| 1,1,1,3,4,4,4-Heptafluoro-3- (trifluoromethyl)butan-2-one | 756- 12-7 | 0–10 | | _ | Use of substance as an insulator in closed electrical/ electronic equipment | _ |
| | | | FF | | Closed heat transfer agent in thermal management systems | |
| 1,1,1,2,2,4,5,5,5-Nonafluoro-4- (trifluoromethyl)-3-pentanone | 756- 13-8 | 1,000+ | F F, | _ | Formulation into mixtures | Dossier Evaluation on a testing proposal ECHA |
| | | | | | Use as a cover gas | restriction |
| | | | F F F | | Use as a functional fluid in a closed system | |

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|--|----------------|---------------------------|--|--|---|--|
| 1,1,1,2,2,4,5,5,5-Nonafluoro-4- (trifluoromethyl)-3-pentanone | 756- 13-8 | 0–10 | | _ | Gaseous fire suppression Use as a functional fluid in a closed system | Dossier Evaluation on a testing proposal. ECHA Decision dated 14 September 2011 |
| 1-Propanamine, 1,1,2,2,3,3,3- heptafluoro- <i>N,N</i> - bis(1,1,2,2,3,3,3- heptafluoropropyl)- [Perfluamine] | 338- 83-0 | 100– 1,000 | | | Manufacture of the substance Formulation of mixtures Functional fluid at industrial sites Non-reactive processing aid at industrial sites | Substance Evaluation by Belgium, 2020 (suspected PBT/vPvB) |
| 2,3,3,3-Tetrafluoro-2- (trifluoromethyl)propanenitrile | 42532- 60-5 | 0–10 | F F F F F F F F N | - | Functional fluid (insulator on manufacture of computer, electronic and optical products, electrical equipment; electricity, steam, gas water supply; and sewage treatment) | _ |

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|---|-------------------|---------------------------|---|--|--|--|
| Polyfluoroalkyl substances | | | | | | |
| Triethoxy(3,3,4,4,5,5,6,6,7,7,8,8, 9,9,10,10,10- heptadecafluorodecyl)silane | 10194 7-16-4 | Confide ntial | F F F F F F F F F F F F F F F F F F F | PFNA/PFOA | - | Addressed by restriction of PFOA and higher homologues |
| Potassium 3,3,4,4,5,5,6,6,7,7,8,8,8- | 59587- 38-1 | 0–10 | 0 | PFHpA/PFHxA, 6:2 FTOH | Manufacture of the substance | See CAS no. 21615-47-4 |
| tridecafluorooctanesulfonate | | | | | Manufacture of plastics products, including compounding and conversion | |
| 3,3,4,4,5,5,6,6,7,7,8,8,8- Tridecafluorooctanesulfonic acid | 27619- 10 97-2 | 10–100 | O HO—S— FFFFFFF | PFHpA/PFHxA, 6:2 FTOH | Formulation for metal treatment | See CAS no. 21615-47-4 |
| | | | U FFFFFF FFFFFF | | Industrial use as fluoropolymer and fluoroelastomer processing aid | |
| N -[3-(Dimethylamino)propyl]- 3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctane-1- sulfonamide | 34455- 22-6 | - | | PFHpA/PFHxA, 6:2 FTOH | Chemical intermediate | See CAS no. 21615-47-4 |
| N -[3-(Dimethylamino)propyl]- 3,3,4,4,5,5,6,6,7,7,8,8,8- | 80475- 32-7 | 10–100 | CH3 0 [−] N ⁺ CH3 | PFHpA/PFHxA, 6:2 FTOH | Manufacture of the substance | See CAS no. 21615-47-4 |
| tridecafluorooctanesulfonamide N -oxide | | | | | Formulation into mixtures | |
| | | | | | Industrial use in paint | |

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|---|---|--|----------------------------------|--|---|--|
| | | | | | Professional use in fire-fighting foams | |
| 4,4,5,5,6,6,7,7,8,8,9,9,9- Tridecafluorononyl methacrylate | 12283 50-17- | 0–10 | F F F | PFHpA/PFHxA | Manufacture of the substance | See CAS no. 21615-47-4 |
| | 1 $H_2C \xrightarrow{CH_3} F \xrightarrow{F} F$ | H_2C G F | 6:2 FTOH | Manufacture of fine chemicals | | |
| 1,1,1,2,2,3,3,4,4,5,5,6,6- Tridecafluoro-8-iodooctane | 2043- 57-4 | - | | PFHpA/PFHxA, 6:2 FTOH | Manufacture of the substance Chemical | See CAS no. 21615-47-4 |
| | | | F | | intermediate | |
| 3,3,4,4,5,5,6,6,7,7,8,8,8- Tridecafluorooctyl methacrylate | 2144- 53-8 | 100– 1,000 | H ₃ C-CH ₂ | PFHpA/PFHxA, 6:2 FTOH | Manufacture of the substance | Substance Evaluation by Germany, 2016 (endocrine |
| | | | | | Monomer for manufacture of | disruption and PBT concerns) |
| | | | · F F F F F F | | polymers | See CAS no. 21615-47-4 |
| 3,3,4,4,5,5,6,6,7,7,8,8,8- Tridecafluorooct-1-ene | 25291- 17-2 | 10–100 | | PFHpA/PFHxA | Manufacture of intermediate | See CAS no. 21615-47-4 |
| | | | FFFFFFCH ₂ | | Monomer in polymerisation processes | |
| | | | | | Non-metal surface treatment products | |

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|--|----------------|---------------------------|---|--|---|------------------------|
| Thiocyanic acid, 3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctyl ester | 26650- 09-9 | - | F S | PFHpA/PFHxA, 6:2 FTOH | Manufacture of the substance for use as an isolated intermediate | See CAS no. 21615-47-4 |
| 3,3,4,4,5,5,6,6,7,7,8,8,8- Tridecafluorooctanesulfonyl chloride | 27619- 89-2 | - | F F F F F F O F F F F F F G F F F F F F G O O | PFHpA/PFHxA, 6:2 FTOH | Manufacture of the substance for use as an isolated intermediate | See CAS no. 21615-47-4 |
| Carboxymethyldimethyl-3- [[(3,3,4,4,5,5,6,6,7,7,8,8,8- | 34455- 29-3 | 100– 1,000 | | PFHpA/PFHxA, 6:2 FTOH | Manufacture of the substance | See CAS no. 21615-47-4 |
| tridecafluorooctyl)sulfonyl]amino]propylammonium hydroxide | | | | F Formulation i mixtures | Formulation into mixtures | |
| | | | | | Industrial use in inks and films | |
| | | | | | Professional use in fire-fighting foams | |
| | | | | | Consumer use in portable fire extinguishers | |
| 3,3,4,4,5,5,6,6,7,7,8,8,8- Tridecafluorooctane-1-thiol | 34451- 26-8 | 0–10 | F | PFHpA/PFHxA, 6:2 FTOH | Use as intermediate | See CAS no. 21615-47-4 |

| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|--|-----------------|---------------------------|--|--|---|--|
| 1,1,1,2,2,3,3,4,4,5,5,6,6- Tridecafluorotetradecane ⁶ | 13333 1-77-8 | 10–100 | H ₃ C F F F F F F F F F F F F F F F F | PFHpA/PFHxA 6:2 FTOH | Manufacture of the substance Use at industrial sites leading to inclusion into/onto article | See CAS no. 21615-47-4 |
| 3,3,4,4,5,5,6,6,7,7,8,8,8- Tridecafluorooctyl acrylate | 17527- 29-6 | 100– 1,000 | $F F F F F F F F$ $F F F F F F F$ $F F F F F F F$ $H_2C = 0$ | PFHpA/PFHxA, 6:2 FTOH | Manufacture of the substance Monomer for manufacture of polymers | Substance Evaluation by Germany, 2016 (endocrine disruption and PBT concerns) See CAS no. 21615-47-4 |
| 4-[(3,3,4,4,5,5,6,6,7,7,8,8,8- Tridecafluorooctyl)thio]butane-1- thiol | 36097- 07-1 | 0–10 | F F F F F F F F F F F F F F F F F F F | PFHpA/PFHxA, 6:2 FTOH | Chemical intermediate | See CAS no. 21615-47-4 |
| Trimethoxy(3,3,4,4,5,5,6,6,7,7,8, 8,8-tridecafluorooctyl)silane | 85857- 16-5 | 10–100 | $\begin{array}{c ccccc} & & F & F & F & F & F & F \\ & & & & & &$ | PFHpA/PFHxA, 6:2 FTOH | Manufacture of the substance Formulation into mixtures Non-metal surface treatment Laboratory chemical | See CAS no. 21615-47-4 |
| Substance1 (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|---|----------------|---------------------------|--|--|---|------------------------|
| Triethoxy(3,3,4,4,5,5,6,6,7,7,8,8, 8-tridecafluorooctyl)silane | 51851- 37-7 | 10–100 | $F = F = F = F = F = F = CH_3$ | PFHpA/PFHxA, 6:2 FTOH | Manufacture of the substance Preparation of pre-treatment solutions Use of non-metal surface treatments Use as a chemical intermediate at the production site | See CAS no. 21615-47-4 |
| Trichloro(3,3,4,4,5,5,6,6,7,7,8,8, 8-tridecafluorooctyl)silane | 78560- 45-9 | 10–100 | F | PFHpA/PFHxA, 6:2 FTOH | Manufacture of the substance Non-metal surface treatment agent Use as an intermediate at production site and by downstream users | See CAS no. 21615-47-4 |
| 2-Propenoic acid, γ-ω-perfluoro- C8-14-alkyl esters | 85631- 54-5 | 100– 1,000 | F = F = F = F = O = O = O = O = O = O = | PFHpA/PFHxA, 6:2 FTOH and higher homologues | Manufacture of the substance Formulation and re-packing Monomer in polymerisation | See CAS no. 21615-47-4 |

| CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern2 | Use according to registration3 | Regulatory activity4 |
|----------------|---|---|---|--|---|
| | | | | processes at industrial sites | |
| 68391- 08-2 | - | | PFHpA/PFHxA, 6:2 FTOH and higher homologues | Manufacture of the substance | See CAS no. 21615-47-4 |
| | | | | Chemical intermediate | |
| | | n=2-5 | | | |
| 85995- 91-1 | - | F F F F F F F $F + F F F F F$ $F + F F F F F F$ $F F F F F F F F$ $n=1-4$ | PFHpA/PFHxA, 6:2 FTOH and higher homologues | Chemical intermediate | See CAS no. 21615-47-4 and PFOA restriction |
| 62880- 93-7 | 0–10 | о 0 9 4.С — Сн. | PFHpA/PFHxA, 6:2 FTOH | Use in fire-fighting foams | See CAS no. 21615-47-4 |
| | | Na F F F F F F F | | Use in coatings and paints, thinners, paint removers | |
| | no. 68391- 08-2 85995- 91-1 62880- | no. tonnage band band - 68391- - 08-2 - 85995- - 91-1 - 62880- 0-10 | no. tonnage band $ \begin{array}{c} 68391- \\ 08-2 \\ 08-2 \\ \hline F \\ F \\$ | no. tonnage band transformation product of concern2 68391 08-2 $-F + F + F + F + F + F + F + F + F + F +$ | no. tonnage band transformation product of concern2 registration3 processes at industrial sites 68391 $B^{F} F F F F F} F F F F F F F F F F F F F$ |

| Substance ¹ (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern ² | Use according to registration ³ | Regulatory activity ⁴ |
|---|----------------|---------------------------|---|---|--|----------------------------------|
| 3,3,4,4,5,5,6,6,7,7,8,8,8- Tridecafluorooctan-1-ol [6:2 fluorotelomer alcohol, 6:2 FTOH] | 647-42- 7 | _ | Pi HOFFFFFF FFFFFFFFFFFFFFFFFFFFFFFFFF | PFHpA/PFHxA, 6:2 FTOH | Chemical intermediate | See CAS no. 21615-47- 4 |
| Dichloromethyl(3,3,4,4,5,5, 6,6,7,7,8,8,8- tridecafluorooctyl)silane ⁵ | 73609- 36-6 | 0–10 | F F F F F F F $F F F F F F$ $F F F F F F F$ $G = CI$ | PFHpA/PFHxA, 6:2 FTOH | Manufacture of the substance Chemical intermediate | See CAS no. 21615-47- 4 |
| 1,1,1,2,2,3,3,4,4,5,5,6,6- Tridecafluorooctane | 80793- 17-5 | 0–10 | $H_{3}C F F F F F F F$ $H_{3}C F F F F F F F$ $F F F F F F F$ | PFHpA/PFHxA, 6:2 FTOH | Used as a solvent Used as a heat transfer fluid | See CAS no. 21615-47- 4 |
| 4,4,5,5,6,6,7,7,8,8,9,9,9- Tridecafluorononan-1-ol | 80806- 68-4 | - | HO F F F F F F F F F F F F F F F F F F F | PFHpA/PFHxA, 6:2 FTOH | Chemical intermediate | See CAS no. 21615-47- 4 |
| 2-Hydroxy-N,N,N-trimethyl- 3- [(3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctyl)thio]propa n-1-aminium chloride | 88992- 45-4 | 0–10 | H_{3C} CH_{3} OH F | PFHpA/PFHxA, 6:2 FTOH | Use in fire- fighting foams Use in coatings and paints, thinners, paint removers | See CAS no. 21615-47- 4 |

| Substance ¹ (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern ² | Use according to registration ³ | Regulatory activity ⁴ |
|---|----------------|---------------------------|---|---|--|----------------------------------|
| 3,3,4,4,5,5,6,6,7,7,8,8,8- Tridecafluorooctyl 2- chloroacrylate | 96383- 55-0 | 0–10 | CI CH_2 F | PFHxA, 5:2 FTOH | Chemical intermediate | See CAS no. 21615-47- 4 |
| (2,2,3,3,4,4,5,5,6,6,7,7,7- Tridecafluoroheptyl)oxirane | 38565- 52-5 | - | F F F F F F F F F F F F F F F F F F F | PFHpA/PFHxA, 6:2 FTOH | Chemical intermediate | See CAS no. 21615-47- 4 |
| 3,3,4,4,5,5,6,6,7,7,8,8- Dodecafluorodeca-1,9- diene | 1800- 91-5 | 0–10 | H ₂ C F F F F F F F F F F F F F F F F F F F | _ | Manufacture of the substance Manufacture of rubber products for the automotive industry | _ |
| Silane, trimethoxy(3,3,4,4,5,5,6,6,6 -nonafluorohexyl)- | 85877- 79-8 | Confide ntial | $F F F F F H_{3}C O CH_{3}$ $F F F F F F H_{3}C O H_{3}$ | PFPeA 4:2 FTOH | - | Dossier Evaluation concluded |
| Dichloromethyl(3,3,4,4,5,5, 6,6,6- nonafluorohexyl)silane | 38436- 16-7 | 0–10 | $F F F F F - Si - CH_3$ $F - F F F F - Si - CH_3$ $F - F F F F$ | PFPeA 4:2 FTOH | Substance is manufactured and used as a monomer in polymer production outside the EU. The polymer does not contain the registered substance as it | _ |

| Substance ¹ (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern ² | Use according to registration ³ | Regulatory activity ⁴ |
|--|-----------------|---------------------------|--|---|---|----------------------------------|
| | | | | | reacts fully during polymerisation | |
| Polyfluorinated monomer | | 100– 1,000 | - | - | Monomer for manufacture of (imported) polymers | |
| | | | | | Chemical intermediate | |
| Methyl heptafluorobutyrate | 356-24- 1 | - | F F F O $F F F O$ $F F F O$ | PFBA | Chemical intermediate | _ |
| 2,2,3,3,4,4,5,5- Octafluoropentan-1-ol | 355-80- 6 | - | F F F F OH F F F F | - | Chemical intermediate | - |
| 2,2,3,3,4,4,5,5- Octafluoropentyl methacrylate | 355-93- 1 | 10–100 | $F F F F F H_3C$ $F F F F F O CH_2$ CH_2 | CAS no. 355–80–6 | Manufacture of the substance Formulation into cosmetic products | - |
| 3,3,4,4,5,5,6,6-Octafluoro- 6-iodohex-1-ene | 203929- 12-8 | _ | F F F F F H H H F H H H I F F F CH ₂ | 2 | Chemical intermediate Use as chain transfer agent in | _ |

| Substance ¹ (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern ² | Use according to registration ³ | Regulatory activity ⁴ |
|--|----------------|---------------------------|---|---|---|----------------------------------|
| | | | | | polymerisation reactions | |
| 1,1,2,2,3,3,4,4,4- Nonafluoro-N-(2- | 34454- 97-2 | 10–100 | F F F F O CH ₃ F F F S N | PFBS | Manufacture of the substance | See CAS no. 375-73-5 |
| hydroxyethyl)-N- methylbutane-1- sulfonamide | | | F F F F O | | Use as intermediate or monomer in form of flakes or liquid substance | |
| | | | | | Monomer in imported polymers | |
| 2-[Methyl[(nonafluorobutyl)- sulfonyl]amino]ethyl | 67584- 55-8 | 100– 1,000 | | FFBS | Manufacture of the substance | See CAS no. 375-73-5 |
| acrylate | | | O O O N V F F F C H ₃ O C H ₃ O | - | Monomer in polymerisation processes at industrial sites | |
| 2-[Methyl[(nonafluorobutyl)- sulfonyl]amino]ethyl | 67584- 59-2 | 10–100 | H ₂ C F F F | PFBS | Manufacture of the substance | See CAS no. 375-73-5 |
| methacrylate | | | O O O O O S F F F CH ₃ F CH ₃ CH ₃ | | Monomer for (imported) polymers (inclusion or not into/onto article) | |

| Substance ¹ (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern ² | Use according to registration ³ | Regulatory activity ⁴ |
|---|------------------|---------------------------|--|---|--|----------------------------------|
| Poly(α-fluoro-ω- methacryloyloxyethylpoly(di fluoro-methylene)-co-3- chloro-2- hydroxypropylmethacrylate) | 101896- 32-6 | Confide ntial | | Unknown | - | - |
| Tridecafluorooctyl- phosphonic acid sodium salt (1:1) | 118905 2-95-6 | 0–10 | 0 0 0 0 0 0 0 F F F F F F F F F F F F F | C8–PFPA (perfluorooctyl phosphonic acid) | Fragrance and cosmetics | _ |
| 1,1,2,2,3,3,4- Heptafluorocyclopentane ⁶ | 15290- 77-4 | 0–10 | $F \xrightarrow{F} F$ | _ | Semiconductor s Washing and cleaning product Manufacture of computer, electronic and optical products, electrical equipment | _ |

| Substance ¹ (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern ² | Use according to registration ³ | Regulatory activity ⁴ |
|--|-----------------|---------------------------|--|---|--|---|
| 1,1,2,2-tetrafluoro-2- [(trifluorovinyl)oxy]ethanesu | 29514- 94-1 | 0–10 | | - | Manufacture of the substance | - |
| lfonyl fluoride | | | | | Manufacture of plastics products, including compounding and conversion | |
| 1,1,2,2,3,3,4,4-Octafluoro- 1,4-diiodobutane | 375-50- 8 | - | F F F F F F I F F F | - | Chemical intermediate | - |
| 1,6-Diiodoperfluorohexane | 375-80- 4 | - | F F F F F F F F F F F F F I F F F F F | - | Chemical intermediate | - |
| ammonium 2,2,3 trifluor-3- (1,1,2,2,3,3-hexafluoro-3- trifluormethoxypropoxy), propionate (ADONA) | - | 0–10 | | | Use as a non- reactive processing aid at industrial sites | Substance Evaluation by Germany, 2017 (PBT concern) |
| | | | | | Used in polymer production | |
| 2,2,3-Trifluoro-3- [1,1,2,2,3,3-hexafluoro-3- (trifluoromethoxy)- propoxy]propanoic acid | 919005- 14-4 | _ | $F \xrightarrow{F} O = F \xrightarrow{F} O = O = O = O = O = O = O = O = O = O $ | _ | Chemical intermediate | _ |

| Substance ¹ (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern ² | Use according to registration ³ | Regulatory activity ⁴ |
|--|------------------|---------------------------|---|---|---|---|
| Ammonium difluoro[1,1,2,2- tetrafluoro-2- (pentafluoroethoxy)ethoxy] acetate | 908020- 52-0 | 10–100 | $F \xrightarrow{F} F \xrightarrow{F} F \xrightarrow{F} O O O \xrightarrow{F} O O \xrightarrow{F} O O \xrightarrow{F} O O \longrightarrow{F} O O \xrightarrow{F} O O \xrightarrow{F} O O \xrightarrow{F} O $ | 3 — | Use as a non- reactive processing aid at industrial sites | Substance Evaluation by Germany, 2017 (PBT concern) |
| Ammonium difluoro{[2,2,4,5-tetrafluoro- | 119093 1-27-1 | 10–100 | F F~ / | - | Manufacture of the substance | - |
| 5-(trifluoromethoxy)-1,3- dioxolan-4-yl]oxy}acetate | | | H_4^+ O F F F F F F O F F O F O F O F O O O F O | | Polymerisation aid in fluoropolymer production | |
| Potassium difluoro{[2,2,4,5- tetrafluoro-5- (trifluoromethoxy)-1,3- dioxolan-4-yl]oxy}acetate | 119093 1-39-5 | - | | | Chemical intermediate | _ |

| Substance ¹ (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern ² | Use according to registration ³ | Regulatory activity ⁴ |
|--|------------------|---------------------------|---|---|--|---|
| Difluoro{[2,2,4,5-tetrafluoro- 5-(trifluoromethoxy)-1,3- dioxolan-4-yl]oxy}acetic acid | 119093 1-41-9 | - | | | Chemical intermediate | _ |
| Ammonium 2,3,3,3- tetrafluoro-2- (heptafluoropropoxy)propa noate (FRD-902 or GEN-X) | 62037- 80-3 | 10–100 | $F = F = NH_4^+$ $F = F = 0$ $F = F = F$ | - | Processing aid for polymerisation | Substance Evaluation by Germany and Netherlands, 2017 (PBT concerns) RMOA by Netherlands, 2018 |
| N-[2,5-Dichloro-4- (1,1,2,3,3,3- hexafluoropropoxy)-phenyl- aminocarbonyl]-2,6- difluorobenzamide (Lufenuron) | 103055- 07-8 | Confide ntial | $ \begin{array}{c} F \\ F $ | _ | (Known to be used as a pesticide but no approvals in UK) | _ |

| Substance ¹ (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern ² | Use according to registration ³ | Regulatory activity ⁴ |
|--|-----------------|---------------------------|--|---|--|----------------------------------|
| 2-(1,2-Dichloro-1,2,2- trifluoroethoxy)-1,1,2,2- tetrafluoroethanesulfonyl fluoride | 144728- 59-6 | - | F = F | _ | Chemical intermediate | _ |
| 1,2-Dichloro-1- [difluoro(trifluoromethoxy)m ethoxy]-1,2,2- trifluoroethane, | 874288- 98-9 | - | $F \xrightarrow{F} CI CI CI F F F F F F F F F F F F F F F $ | - | Chemical intermediate | - |
| 1-[3-[4- ((Heptadecafluorononyl)oxy)-benzamido]propyl]-N,N,N- trimethylammonium iodide | 59493- 72-0 | Confide ntial | $H_{3C} \xrightarrow{OH_{3}} H_{3C} \xrightarrow{H_{3C}} H_{4C} \xrightarrow{H_{3C}} H_{4C} \xrightarrow{H_{3C}} H_{4C} \xrightarrow{H_{4C}} H_{4$ | - | - | - |
| {Difluoro[(1,2,2- trifluoroethenyl)oxy]- methoxy}trifluoromethane | 700874- 87-9 | 10–100 | | _ | Manufacture of the substance Monomer in polymerisation processes | _ |

| Substance ¹ (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern ² | Use according to registration ³ | Regulatory activity ⁴ |
|--|-----------------|---------------------------|------------------------------|---|--|--|
| Trifluoro(pentafluoroethoxy) ethylene | 10493- 43-3 | 0–10 | | - | Import in another monomer Intermediate | _ |
| | | | | | Polymer preparations and compounds | |
| | | | | | Manufacture of plastics products, including compounding and conversion | |
| Trifluoro(trifluoromethoxy)et hylene | 1187- 93-5 | 100– 1,000 | | - | Monomer for manufacture of (imported) polymers | Dossier Evaluation on a testing method proposal. ECHA Decision dated 25 November 2014 |
| 1,4-Dichloro-2-(1,1,2,3,3,3- hexafluoropropoxy)-5- nitrobenzene ⁶ | 130841- 23-5 | - | | _ | Manufacture of the substance Chemical intermediate | _ |



| Substance ¹ (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern ² | Use according to registration ³ | Regulatory activity ⁴ |
|--|-----------------|---------------------------|------------------------------|---|--|---|
| Hexafluoropropene, oxidised, oligomers, reduced, fluorinated | 161075- 00-9 | 10–100 | | _ _ | Manufacture of the substance Formulation into mixtures Heat transfer fluid at industrial sites | Dossier Evaluation on a testing proposal ECHA Decision concluded |
| Polyfluorinated monomer | | 100– 1,000 | - | - | Manufacture of the substance Monomer for manufacture of (imported) polymers | |
| 1,1,1,2,3,3-Hexafluoro-2- (heptafluoropropoxy)-3- [(trifluorovinyl)oxy]propane | 1644- 11-7 | 0–10 | | _ | Manufacture of the substance Monomer for manufacture of polymers | _ |

| Substance ¹ (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern ² | Use according to registration ³ | Regulatory activity ⁴ |
|---|-----------------|---------------------------|---|---|--|--|
| Methyl 2,2,3,3,4,4- hexafluoro-4-[(1,2,2- trifluoroethenyl)oxy]butano ate | 19190- 61-5 | 0–10 | | _ 3 | Monomer bound within an imported polymer | - |
| 3-Ethoxy- 1,1,1,2,3,4,4,5,5,6,6,6- dodecafluoro-2- (trifluoromethyl)-hexane ⁶ | 297730- 93-9 | 0–10 | F F F F F F F F F F | - | Use of functional fluid at industrial site and in motor vehicles | Substance Evaluation by Spain, 2018 (suspected PBT/vPvB) |
| 2- [Difluoro(methoxy)methyl]- 1,1,1,3,3,3- hexafluoropropane | 382-26- 3 | - | F + F + F + F + F + F + F + F + F + F + | _ | Chemical intermediate | _ |

| Substance ¹ (trade name if available) | CAS no. | Annual tonnage band | Chemical structure (example) | Potential terminal transformation product of concern ² | Use according to registration ³ | Regulatory activity ⁴ |
|--|-----------------|---------------------------|--|---|--|----------------------------------|
| N-(2-Methylsulfinyl-1,1- dimethyl-ethyl)-N'-{2- methyl-4-[1,2,2,2- tetrafluoro-1- (trifluoromethyl)ethyl]phenyl }-phthalamide | 371771- 07-2 | - | O H H F F F F F F F | - | Chemical intermediate | _ |
| Methyl 2,2,3-trifluoro-3- [1,1,2,2,3,3-hexafluoro-3- | 958445- 54-0 | - | F | - | Manufacture of the substance | - |
| (trifluoromethoxy)propoxy]p ropanoate | | | F F F F F F F F F F | | Chemical intermediate | |
| 2,2,3,3,5,5,6,6-Octafluoro- 4- | 382-28- 5 | 100– 1,000 | F | - | Manufacture of the substance | - |
| (trifluoromethyl)morpholine | | | F-F | | Formulation of mixtures | |
| | | | | | Use of functional fluid at industrial sites | |
| 1,1,2,2,3,3-Hexafluoro-1- | 40573- | 10–100 | F, | | Manufacture of | - |
| trifluoromethoxy-3- trifluorovinyloxypropane | 09-9 | | | | the substance Monomer in polymerisation | |



Notes:

¹ Substances highlighted in grey are former 'new substances' under pre-REACH legislation. Substances supplied at 10 tonnes per year or more are highlighted in orange.

² This is an additional consideration to any potential intrinsic hazard of an individual substance which may aid grouping or targeted assessment. It is based on the chemical structure of the substance rather than any specific evidence of degradation. For example, a fully fluorinated C8 carbon chain attached to another carbon atom may degrade to a C9 carboxylic acid (PFNA) or potentially a C8 carboxylic acid (PFOA).

³ Chemical Safety Reports have not been evaluated for this report. The information presented is publicly available.

⁴ ECHA, PACT search dated 10 December 2018 ()

⁵Two registrations are listed for this substance.

⁶ Also listed under N

Appendix 3: Substances included in Environment Agency analytical scan methodology (2014 - 2019; water samples)

| Compound Name | Acronym | Carbon chain length | CAS number | Approximate date added to the LC- MS scan |
|--------------------------------|---------|---------------------------|---------------|--|
| Perfluoropentanoic acid | PFPeA | C5 | 2706-90-3 | Oct-14 |
| Perfluorohexanoic acid | PFHxA | C6 | 307-24-4 | Oct-14 |
| Perfluoroheptanoic acid | PFHpA | C7 | 375-85-9 | Oct-14 |
| Perfluorooctanoic acid | PFOA | C8 | 335-67-1 | Oct-14 |
| Perfluorononanoic acid | PFNA | C9 | 375-95-1 | Oct-14 |
| Perfluorodecanoic acid | PFDA | C10 | 335-76-2 | Oct-14 |
| Perfluoroundecanoic acid | PFUnDA | C11 | 2058-94-8 | Oct-14 |
| Perfluorododecanoic acid | PFDoDA | C12 | 307-55-1 | Oct-14 |
| Perfluorotetradecanoic acid | PFTeDA | C14 | 376-06-7 | Oct-17 |
| Perfluorobutane sulfonic acid | PFBS | C4 | 375-73-5 | Apr-14 |
| Perfluoropentane sulfonic acid | PFPeS | C5 | 630402221 | Jan-19 |
| Perfluorohexane sulfonic acid | PFHxS | C6 | 108427-53-8 | Feb-18 |
| Perfluorooctane sulfonic acid | PFOS | C8 | 1763-23-1 | Oct-14 |
| Perflurorobutanoic acid | PFBA | C4 | 375-22-4 | Aug-18 |
| Perfluorooctyl sulfonamide | PFOSA | C8 | 754-91-6 | Apr-15 |

Appendix 4: List of PFAS substances in targeted PFAS analysis 2021 onwards

Substances in blue are already included in our targeted screening method for emerging contaminants, but included within this list for completeness.

| Name | Acronyms | CAS number |
|--|--------------------------|------------|
| Perfluorobutanoic acid | PFBA; HFBA | 375-22-4 |
| Perfluoropentanoic acid | PFPA, PFPeA | 2706-90-3 |
| Perfluorohexanoic acid | PFHxA | 307-24-4 |
| Perfluoroheptanoic acid | PFHpA | 375-85-9 |
| Perfluorooctanoic acid | PFOA | 335-67-1 |
| Perfluorononanoic acid | PFNA | 375-95-1 |
| Perfluorodecanoic acid | PFDA | 335-76-2 |
| Perfluoroundecanoic acid | PFUnA; PFUdA | 2058-94-8 |
| Perfluorododecanoic acid | PFDoA | 307-55-1 |
| Perfluorotridecanoic acid | PFTrDA; PFTriA | 72629-94-8 |
| Perfluorotetradecanoic acid | PFTeA; PFTreA; PFTeDA | 376-06-7 |
| Perfluorohexadecanoic acid | PFHxDA | 67905-19-5 |
| Perfluorooctadecanoic acid | PFODA | 16517-11-6 |
| Perfluorobutane sulfonic acid | PFBS | 375-73-5 |
| Perfluoropentane sulfonic acid | PFPeS | 2706-91-4 |
| Perfluorohexane sulfonic acid | PFHxS | 355-46-4 |
| Perfluoroheptane sulfonic acid | PFHpS | 375-92-8 |
| Perfluorooctane sulfonic acid | PFOS | 1763-23-1 |
| Perfluorononane sulfonic acid | PFNS | 68259-12-1 |
| Perfluorodecane sulfonic acid | PFDS | 335-77-3 |
| Perfluoroundecane sulfonic acid | PFUnDS | |
| Perfluorododecane sulfonic acid | PFDoS | 79780-39-5 |
| Perfluorotridecane sulfonic acid | | |
| Hexafluoropropylene oxide dimer acid (Gen X) | HFPO-DA (Gen X) | 13252-13-6 |
| Hexafluoropropylene oxide trimer acid | HFPO-TA | 13252-14-7 |

| Name | Acronyms | CAS number |
|--|-------------------------------|-------------|
| 4,8-Dioxa-3H-perfluorononanoic acid (ADONA) | DONA; ADONA | 919005-14-4 |
| 2H,2H,3H,3H-Perfluorooctanoic acid | 5:3 FTCA | 914637-49-3 |
| 6:2 Fluorotelomer phosphate diester | 6:2 diPAP | 57677-95-9 |
| 9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (F-53B Major) | 6:2 CI-PFESA; 9CI- PF3ONS | 756426-58-1 |
| 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (F-53B Minor) | 8:2 CI-PFESA; 11CI-PF3OUdS | 763051-92-9 |
| 4:2 Fluorotelomer sulfonic acid | 4:2 FTSA; 4:2 FTS | 757124-72-4 |
| 6:2 Fluorotelomer sulfonic acid | 6:2 FTSA; 6:2 FTS | 27619-97-2 |
| 8:2 Fluorotelomer sulfonic acid | 8:2 FTSA; 8:2 FTS | 39108-34-4 |
| 10:2 Fluorotelomer sulfonic acid | 10:2 FTSA | 120226-60-0 |
| Perfluorobutylsulfonamide (perfluorobutane sulfonamide) | FBSA | 30334-69-1 |
| Perfluorohexanesulfonamide | FHxSA | 41997-13-1 |
| Perfluorooctanesulfonamide | FOSA; PFOSA | 754-91-6 |
| N-methylperfluorooctanesulfonamide | MeFOSA; N- MeFOSA | 31506-32-8 |
| N-Ethylperfluorooctanesulfonamide | EtFOSA; N- EtFOSA | 4151-50-2 |
| 2-(N-Methylperfluorooctanesulfonamido)acetic acid | NMeFOSAA; MeFOSAA | 2355-31-9 |
| 2-(N-Ethylperfluorooctanesulfonamido)acetic acid | NEtFOSAA; EtFOSAA | 2991-50-6 |
| N-Methyl-N-(2- hydroxyethyl)perfluorooctanesulfonamide | MeFOSE | 24448-09-7 |
| N-Ethyl-N-(2- hydroxyethyl)perfluorooctanesulfonamide | EtFOSE | 1691-99-2 |
| Perfluoro[(2-ethyloxy-ethoxy)acetic acid], ammonium salt | EEA-NH4 | 908020-52-0 |
| Perfluorobutylethlyene | PFBE | 19430-93-4 |
| 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl methacrylate | | 2144-53-8 |
| 1-Propanamine, 1,1,2,2,3,3,3-heptafluoro-N,N- bis(1,1,2,2,3,3,3-heptafluoropropyl)- [Perfluamine] | | 338-83-0 |
| Carboxymethyldimethyl-3- [[(3,3,4,4,5,5,6,6,7,7,8,8,8- | 6:2 FTAB | 34455-29-3 |

| Name | Acronyms | CAS number |
|--|----------|------------|
| tridecafluorooctyl)sulfonyl]amino]propylammonium hydroxide | | |
| N-[3-(Dimethylamino)propyl]- 3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctanesulfonamide N-oxide | FTSAAm | 80475-32-7 |

Appendix 5: Major Product Categories and Applications for perfluorooctyl sulfonates



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List of abbreviations

| Abbreviation | Definition |
|--------------|---|
| AA | Annual average |
| AFFF | Aqueous Film Forming Foam (used in fire-fighting) |
| AOF | Adsorbable organic fluorine |
| BAT | Best available technology |
| BCF | British Coatings Federation |
| BGS | British Geological Survey |
| CAS | Chemical Abstract Service |
| CEFAS | Centre for Environment, Fisheries and Aquaculture Science |
| CIC | Combustion ion chromatography |
| CIP | Chemicals Investigations Programme |
| CIP2 | Chemicals Investigations Programme, phase 2 |
| CIP3 | Chemicals Investigations Programme, phase 3 |
| CPI | Confederation of Paper Industries |
| СТРА | Cosmetics, Toiletry and Perfumery Association |
| Defra | Department for the Environment, Food and Rural Affairs |
| DrWPA | Drinking water protected areas |
| DWI | Drinking Water Inspectorate |
| DWOR | Durable water and oil repellents |
| ECHA | European Chemicals Agency |
| EEA | European Economic Area |
| EOF | Extractable organofluorine |
| EQS | Environmental quality standard |
| ETFE | Ethylene-tetrafluoroethylene |
| F3 | Fluorine free foam |
| FSA | Food Standards Agency |
| GAC | Granular activated carbon |
| GIS | Geographic information system |
| GWQMN | Ground water quality monitoring network |

| Abbreviation | Definition |
|--------------|---|
| HSE | Health and Safety Executive |
| IF | Inorganic fluorine |
| ITRC | Interstate Technology and Regulatory Council |
| LOD | Limit of Detection |
| MAC | Maximum allowable concentration |
| MRV | Minimum reporting value |
| NLS | National Laboratory Service |
| NRW | Natural Resources Wales |
| OECD | Organisation for Economic Co-operation and Development |
| OSPAR | The OSPAR convention is the Convention for the Protection of the Marine Environment of the North-East Atlantic. See https://www.ospar.org/convention. |
| PBMS | Predatory Bird Monitoring Scheme |
| PBT | Persistent, bioaccumulative and toxic |
| PFAA | perfluororalkylated acids |
| PFAA | Perfluoroalkyl acid |
| PFAS | Poly- and perfluoroalkyl substances |
| PFBA | Perfluorobutanoic acid |
| PFBS | Perfluorobutane sulfonic acid |
| PFC | Perfluorinated chemicals |
| PFDA | Perfluorodecanoic acid |
| PFDoDA | Perfluorododecanoic acid |
| PFHpA | Perfluoroheptanoic acid |
| PFHxA | Perfluorohexanoic acid |
| PFHxS | Perfluorohexane sulfonic acid |
| PFNA | Perfluorononanoic Acid |
| PFOA | Perfluorooctanoic acid |
| PFOS | Perfluorooctane sulfonic acid |
| PFOSA | Perfluorooctanesulfonamide |
| PFPeA | Perfluoropentanoic acid |
| PFPeS | Perfluoropentane sulfonic acid |
| PFTDA | Perfluorotridecanoic acid |
| PFUnDA | Perfluoroundecanoic acid |
| PI | Pollution inventory |
| PIGE | Particle-induced gamma-ray emissions |
| POP | Persistent Organic Pollutant |
| | |

| Abbreviation | Definition |
|--------------|--|
| PTFE | Polytetrafluoroethylene |
| qTOF | quadrupole time-of-flight |
| REACH | Registration, Evaluation, Authorisation and restriction of CHemicals |
| SSVs | Soil screening values |
| SVHC | Substance of Very High Concern |
| TF | Total fluorine |
| TOF | Total organofluorine |
| TOMPS | Toxic Organic Micro-Pollutants |
| ТОР | Total oxidizable precursor |
| ΤΟΡΑ | Total organic precursors |
| UKWIR | UK Water Industry Research https://ukwir.org/ |
| UNEP | United Nations Environment Program |
| uPBT | Ubiquitous persistent, bioaccumulative and toxic |
| US EPA | US Environmental Protection Agency |
| VMD | Veterinary Medicines Directorate |
| WFD | Water Framework Directive |
| WWTW | Waste water treatment works |
| | |

Glossary

Adsorb

A sorption process in which one substance becomes attached to another via adhesion to the surface.

Arrowheads

The formation of highly persistent final degradation products (perfluorinated terminal products)

Bioaccumulate

The accumulation of a substance, such as a toxic chemical, in various tissues of a living organism.

Bioavailability

The extent to which a substance can be absorbed by a living organism

Biota

The animal and plant life of a particular region, habitat, or geological period

Moiety

A distinct part of a large molecule

OSPAR

The mechanism by which 15 governments and the EU cooperate to protect the marine environment of the North-East Atlantic.

PBT

Persistent, bioaccumulative and toxic. These substances are a class of compounds that have high resistance to degradation from abiotic and biotic factors, high mobility in the environment and high toxicity.

PFOS related substances

Any or all of the substances which contain the PFOS moiety that may break down in the environment to give PFOS

Pollution Inventory

The inventory collates data from large regulated industrial sites on emissions of specified substances to air and controlled waters and sewers, as well as quantities of waste transferred off site. The thresholds for reporting are generally lower than those under the UK PRTR.

Sorption

A physical or chemical process in which one substance takes up or holds another

Stockholm Convention

The Stockholm Convention is a global treaty to protect human health and the environment from persistent organic pollutants (POPs) and came into force in May 2004.

UK PRTR

The register collates data from industrial and business facilities on emissions to air, water and soil, as well as data on quantities of waste transferred off site. Data from the PI that meet the required reporting thresholds form a subset of the UK PRTR, as well as data from Local Authorities.

uPBT

Ubiquitous PBT. PBTs that are widespread and found everywhere

Wet weight

Whole weight, fresh weight and wet weight refer to the sample as it is received whole or wet, regardless of whether it is a whole organism or parts of the organism.

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