Managing Risks and Liabilities associated with Per- and Polyfluoroalkyl Substances (PFASs)

1. SETTING THE SCENE

Per- and polyfluoroalkyl substances (PFASs) are a broad group of several thousand man-made chemicals [1, 2], widely used in industrial and consumer applications and classed as emerging contaminants. PFASs are the subject of accelerating environmental regulatory concern globally, as a result of their detection in drinking water supplies above acceptable levels. The prior regulatory focus has been on two individual compounds, perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), but an expanding range of PFASs are now regulated in many locations [3-29].

PFASs have been used since the 1940s across a wide range of applications [30], with PFOS introduced for commercial use in firefighting foams in 1964 [31]. They are extremely persistent in the environment, usually highly mobile and able to bioaccumulate within various species including humans and some plants [32-35]. These characteristics and the widespread distribution of PFASs are creating significant public health concerns globally. For example, in 2016, the detection of PFASs in drinking water in the USA, combined with the U.S. Environmental Protection Agency (U.S. EPA) issuing a long-term health advisory level of 70 ng/L (for combination of PFOS and/or PFOA) [36], led to 6.5 million people’s drinking water being considered unsafe [37]. It is very difficult to remove and destroy PFASs using conventional water treatment technologies, so they can recirculate within the water cycle.

This technical bulletin is intended to provide a short summary of this class of chemicals and highlight approaches to effectively and pragmatically manage risks and liabilities associated with PFASs impact to the environment such as soil and groundwater in the UK and globally. A more comprehensive and detailed review considering management of the environmental challenges posed by PFASs is presented in recent publications and guidance documents [38-44].

2. PFAS CHEMISTRY

2.1. Types of PFASs

PFASs are a very diverse class of xenobiotic “man-made” chemicals, united by the common structural element of a fully fluorinated carbon (alkyl) chain, known as the perfluoroalkyl group which is typically 2 to 18 carbon atoms in length. The whole PFAS molecule may be either fully (per-) or partly (poly-) fluorinated, but each compound always contains a perfluoroalkyl group.

This carbon fluorine bond is the strongest in organic chemistry so when multiple fluorine atoms saturate an alkyl chain to create the perfluoroalkyl group, this imparts biological, thermal and chemical stability to the molecule, and brings extreme persistence. The perfluoroalkyl group can also impart both hydrophobic and lipophobic properties and decreased surface tension which are sought-after commercial properties.

2.1.1. Perfluoroalkyl Substances

Perfluoroalkyl substances have previously been referred to as perfluorinated compounds (PFCs) but are now more commonly termed perfluoroalkyl acids (PFAAs) and contain a fully fluorinated carbon chain with no additional carbon to hydrogen bonds in the molecule. PFAAs include polar terminal functional groups such as carboxylic acids; which are present in perfluorocarboxylic acids (PFCAs) such as PFOA, and sulfonic acids; which are found in perfluorosulfonic acids (PFSAs) such as PFOS. Less commonly assessed PFAAs include perfluoroalkyl phosphinic acids (PFPI), perfluoroalkyl phosphonic acids (PFPA) and perfluoroalkyl ether carboxylates (PFECA) such as GenX.

When a polar terminal functional group is combined with an extended perfluoroalkyl chain (e.g. above approximately 6 carbons) this can provide unique surface-active properties to the molecule as a whole. PFASs with smaller perfluoroalkyl chains are less effective as surfactants, less likely to adhere to surfaces, more soluble in water and thus more mobile in the environment [3].

PFOS, containing a chain of 8 fully fluorinated carbon atoms, is the most well studied PFSA [3]. PFOS comprises a mixture of linear and branched isomers, with approximately 70% linear and 30% branched [35]. PFSAs of differing chain lengths can also be production by-products during synthesis of PFOS. The shorter chained PFSAs have been introduced as alternatives for PFOS. For example, PFBS (perfluorobutane sulfonate; C₄F₈SO₃-salt) is one important replacement substance for PFOS [45].

PFOA, also known colloquially as C8, has been the most commonly studied PFCA to date and consists of a chain of 7 perfluorinated carbon atoms and a carboxyl functional group forming an 8 carbon chain (Lindstrom, 2011). As production of the longer perfluoroalkyl chain carboxylates is being phased out, shorter chains such as C6 compounds are expected to be increasingly used.

While previous regulatory focus has been on PFOS and PFOA, additional PFASs are now the focus of regulatory attention in many
locations. It is clear that PFOS and PFOA will usually be accompanied by other PFASs in the environment, as when 116 products containing PFASs were examined they all comprised a mixture of PFASs with multiple perfluoroalkyl chain lengths, not just PFOS and PFOA [46] principally due to production processes (Section 2.2).

More recently developed PFASs include the perfluoroalkyl ethers such as GenX and ADONA (discussed in Sections 2.2, 2.4 and 2.5).

2.1.2 Long-Chain and Short-Chain PFASs
PFASs may also be subdivided into two broad classes, short-chain PFASs and long-chain PFASs, with long-chain PFCAs comprising those that have 7 or more perfluoroalkyl carbon atoms (e.g. PFOA) and long-chain PFASs having 6 or more perfluoroalkyl carbon atoms (e.g. perfluorohexane sulfonic acid (PFHxS) and PFOS) [47]. Studies have been conducted that indicate long-chain PFASs have a higher potential to bioconcentrate and bioaccumulate through trophic levels as compared to shorter-chain PFASs [48]. They are described as exhibiting biopersistence, which describes compounds that tend to remain within an organism, rather than being expelled or broken down, so demonstrate slow clearance from organisms. PFASs typically bioaccumulate in proteins, rather than (the more usual) fats and lipids and have been described as proteinophilic [49].

The increasingly higher water solubility of short-chain PFASs on the other hand make them more mobile in aquifers and less effectively treated by many water treatment technologies, such as granular activated carbon (GAC) [50, 51]. The short-chain PFASs are also found to bioaccumulate in the edible portion of crops such as fruits [32-34, 52].

2.1.3 Polyfluoroalkyl Substances
Polyfluoroalkyl substances comprise by far the more diverse group of PFASs, as compared to perfluorinated compounds, with thousands of compounds synthesised for a broad array of commercial uses. In addition to the perfluoroalkyl group, polyfluorinated compounds contain carbon to hydrogen bonds, such as fluorotelomers, but also may have more complex functional groups which can be neutral, anionic, cationic or zwitterionic.

Polyfluorinated compounds include fluorotelomer alcohols (FTOHs), fluorotelomer sulfonic acids (FTSs), polyfluorinated alkyl phosphates (PAPs), perfluorooctane sulfonamides (PFOSA) and many thousands more compounds, which have a very wide range of physical and chemical properties. A small number are shown in Figure 1.

Figure 1. Examples of PFASs. Reprinted (adapted) with permission from Backe, W.J., Day, T.C., Field, J.A. 2013. Environ. Sci. Technol. 47 (10), 5226–5234. Copyright © 2013, American Chemical Society.
2.1.4. Polyfluorinated PFASs as Precursors to Perfluorinated Compounds

Polyfluorinated PFASs biotransform in the environment (more rapidly under aerobic conditions) and in higher organisms (often via attack by cytochrome P450 enzymes [53]) to create perfluorinated compounds and are thus termed precursors. The polyfluorinated precursors produce “dead end” perfluorinated daughter products (PFAAs) as the terminal products of transformation. These PFAAs, including PFOS and PFOA, are all extremely persistent and can be more mobile in groundwater than the precursors they originated from.

It should be stressed that none of the several thousand polyfluorinated PFASs produced by industry can fully mineralise by biological processes, they all form extremely persistent PFAAs as biotransformation products.

Precursors biotransform to create a more limited number of PFAAs, which are increasingly subject to regulation, but precursors can go undetected in the environment as most are not detected by conventional analytical techniques. A funnel is shown in Figure 2, to show the biological funnelling of precursors through to the ultra-persistent PFAAs.

2.2. Production

Production of PFASs has been via three main processes: (1) electrochemical fluorination (ECF), (2) telomerisation and (3) oligomerisation. The ECF process yielded 30-45% perfluorooctane sulfonylfluoride (POSF) as the main product and a range of other PFCAs and PFSAs, with both branched and linear isomers. Production of PFOS by ECF ceased in the USA in 2001 due to environmental concerns, but shorter chain compounds (≤ C4) continue to be synthesised, such as perfluorobutane sulfonic acid (PFBS), with PFOS production continuing in China and India. Telomerisation was used to synthesise PFOA and the fluorotelomers and produces only straight chain isomers and even numbered perfluoroalkyl chains. As part of the U.S. EPA PFOA stewardship program, production of PFOA and C8 fluorotelomers ceased in 2015 and PFCAs and their fluorotelomer precursors should now be shorter chain compounds (≤ C6). Alternative replacement C6 fluorotelomers and perfluorinated compounds such as PFBS, perfluoroalkyl ether carboxylates (PFECAs) such as GenX and ADONA are now produced. These PFECAs are generally synthesised using oligomerisation.

2.3. Uses

PFASs were synthesised for use in a large range of applications, including as water and stain resistant coatings for textiles, furniture and carpeting, in the manufacture of polytetrafluoroethylene (PTFE) to make non-stick surfaces (e.g. Teflon, Dyneon, Fluon etc.) and other fluoropolymers such as polyvinylidene difluoride (PVDF). Other uses include within electronics and photographic industries, semiconductor manufacture, performance plastic coatings, water and oil resistant coatings for food packaging (e.g. pizza boxes, microwaveable popcorn bags, dessert and bread wrappers, sandwich and burger wrappers), hydraulic fluids (e.g. Skydrol for aviation use), car wash/wax finishes such as Simoniz, electroplating mist suppressants, lubricant additives, in moulded rubber formulations or manufacture (e.g. Viton), personal products (e.g. shampoo, sun screen and hand-cream), inks, varnishes, waxes, lubricants, other cleaning agents, and pesticides [35, 46, 54-60].
PFASs are also components of the class B (flammable liquid) firefighting foams known as “film forming foams” such as Aqueous Film Forming Foam (AFFF) which have commonly been used in training exercises and fire incidents. Further foams containing PFASs include FFFP (film forming fluoroprotein foam) and FP (fluoroprotein foam) which are used to protect above ground fuel storage facilities.

2.4 Sites of Concern

PFASs have been found at a range of sites including where they are primarily manufactured or used in processing or making various products. For example, PFASs may be used in bulk quantities at facilities for making waterproof textiles and furnishings, locations where leather is treated, photographic development studios, in printing facilities where inks are used in photolithography, where paper coatings are applied and in performance plastics manufacture. PFCAs have been used for over fifty years as processing aids in the manufacture of fluoropolymers such as PTFE and PVDF [61]. Fluoropolymer manufacture is the single largest direct use of PFOA with 2,000 to 4,000 tonnes of PFOA used between 1951 and 2004 [54], with PFOA more recently replaced with a perfluoroalkyl ether such as GenX. The manufacture of PTFE was reported to have started in the UK in 1947 [30].

PFASs are also commonly encountered at airports, military sites, civil fire training areas and other large industrial (e.g., petrochemical) facilities where bulk liquid hydrocarbon storage occurs and/or firefighting/firefighting training has been carried out. PFASs are frequently identified within landfills and their leachates [62-64]. The 5:3 fluorotelomer carboxylic acid, described as the dominant compound detected in landfill leachate, was recently described as showing slow clearance across species [65], indicative of biopersistence.

PFASs are also often associated with effluent and biosolids from waste water treatment plants (WWTPs) treating sewage as conventional water treatment technologies do not effectively remove PFASs. There is generally an increase in detectable PFASs observed in outflows from WWTPs which use biologically-based treatment or advanced oxidation processes (AOP) to destroy conventional contaminants, as polyfluorinated precursors can be converted to PFAAs via these processes. The biosolid wastes from WWTPs are often used for fertilising crops when used for land spreading and PFASs can bioaccumulate in plants [25, 32].

Air deposition of PFASs can also play a role around some facilities which use PFASs in industrial processes involving heat, as PFASs volatilised in air emissions condense and can impact wide areas under the vapour cloud. Widespread, but low level impacts to surficial soils which leach PFASs to groundwater may represent a large source footprint to underlying aquifers [66, 67].

It is important that the potential presence of PFASs at such sites is considered and, if appropriate, assessed during site redevelopment / acquisition, due diligence and contaminated land investigations in order to assess potential human health and environmental risks and manage liabilities.

2.5 Alternatives & Product Stewardship

Many industries are looking to reduce their exposure to potential risks associated with use of PFASs.

In response to global regulatory initiatives to limit the production and use of long-chain PFASs, many class B firefighting foam suppliers have developed effective completely fluorine free foams (F3) which contain no PFASs (Figure 3). There are also short-chain (C6) PFASs foams available, but there are concerns over their long-term environmental persistence, toxicity and high mobility leading to long range transport and frequent detections in drinking water supplies [25, 68-70].

It is important that sites give careful consideration to both safety and environmental risk factors, and consult with fire safety experts, when determining the optimal foam type for any given application. Environmental considerations are becoming more prominent when considering current firefighting foam use as well as from legacy foam uses and foam disposal options.

Figure 3. Royal Danish Airforce in action, after adopting fluorine free firefighting foams. Source: Ian Ross, Arcadis.
Many industries are engaged in the transition away from long-chain PFASs with, for example, the replacement of PFOA used in the production of PTFE for non-stick coatings by perfluoroalkyl ethers (e.g. GenX compounds) and short-chain PFASs such as PFHxS and PFBS increasingly used as stain repellents [3].

Although the shorter chain compounds show some reduction in their aquatic and human bioaccumulation potential, they biocumulate in the edible portion of crops (fruits), are equally as persistent as long-chain PFASs, more mobile and difficult to remove from water using multiple treatment technologies, with limited understanding regarding their toxicity. As a result concerns have been raised over continuing production of PFASs as they are becoming increasingly present in the global environment [71].

3. PROPERTIES, FATE AND BEHAVIOUR

3.1. Physicochemical Properties

PFASs are widely distributed in the global environment, but most investigations have so far focussed on PFOS and PFOA, with increased attention more recently on the shorter chain PFASs. Their extreme persistence and high aqueous solubility, coupled with their ineffective treatment by most water treatment technologies, means that they have widespread low level (ng/L) distribution in the biosphere [72-79].

Long-chain PFASs typically consist of a hydrophobic, perfluoroalkyl group chain and a hydrophilic functional group such as a sulfonate or carboxylate. This amphiphilic (both hydrophobic and hydrophilic) characteristic of the longer chain PFASs makes them ideal for use as surfactants and can also cause them to accumulate at soil, water and air interfaces. However, in contrast to conventional surfactants, the perfluorinated carbon chain also has a lipophobic characteristic which renders many PFAS coatings resistant not only to water, but also to oil, grease, other non-polar compounds and dirt particles.

PFAAs are typically very soluble in water (e.g. the solubilities of PFOS and PFOA are 520 mg/L and 3,400 mg/L, respectively at 20°C), although the solubility can reduce significantly in brackish or saline water. Most PFASs do not readily partition from groundwater into air as they have relatively high aqueous solubility and are polar anions, so generally remain charged at environmental pHs, decreasing their volatility from water.

Physicochemical properties for a number of PFASs, derived from scientific literature [80], can be found in the CONCAWE Report on PFAS [35].

3.2. Fate and Transport

The persistence of PFASs, coupled with their solubility and low/moderate sorption to soils, make many PFASs highly mobile resulting in extremely long groundwater plumes (multiple kilometres) which have the potential to impact groundwater abstraction wells and other receptors over a much wider area than conventional contaminants (such as methyl tert-butyl ether (MTBE) or chlorinated hydrocarbons). Predicted retardation factors from experimentally derived data [81] and aquifer properties were proposed as follows: PFOS 39, PFOA 5, PFHxS 7, PFHxA 1.1, PFPeA, 1.4, PFBA 5, PFBS 4 [82], with sorption described to not be only explained by interaction with the fraction of organic carbon (F OC).

A tracer study after concomitant release of both PFOS and MTBE into the Chalk aquifer after the Buncefield Oil Storage Terminal Fire (2005) incident found that PFOS travelled at 29 m/year whilst MTBE moved 17 m/year in the same aquifer, indicating the relatively higher mobility of PFOS vs MTBE [83].

The transport of PFASs is very dependent on the type of precursor (i.e. cationic, zwitterionic, anionic, neutral), but the anionic PFAAs are generally very mobile. Further site specific criteria such as soil mineralogy and groundwater geochemistry are required to understand and predict PFASs mobility.

There are multiple sorption mechanisms which control the degree of PFASs sorption to sediments and soils during transport in water [84]. Hydrophobic sorption to soil organic particles (estimated using PFAS specific partition coefficients) generally increases with increasing chain length and with increasing solid phase FOC. PFASs can sorb to the surface of charged mineral surfaces by ion exchange processes. Sulfonic and carboxylic acid functional groups associated with PFSA and PFCAs are anionic (negatively charged) under almost all natural conditions and are, therefore, repelled and poorly sorbed by negatively charged mineral surfaces (e.g. clay particles) [83]. In addition, PFAA precursors may contain cationic (positively charged) or zwitterionic (both positively and negatively charged) functional groups which may result in greater sorption and retardation in some matrices. There has also been a description of a “molecular brush” effect where perfluoroalkyl chains self-assemble at interfaces and pack closely together. This is reported to allow formation of a dense layer of PFASs which repels both water and oil, which is described to be more pronounced for longer perfluoroalkyl chains lengths [85].

Due to the surfactant nature of the longer chain PFASs, there is potential for micelle and hemimicelle formation as their concentrations increase. The individual critical micelle concentrations (CMC) for PFAAs may appear not particularly relevant when considering aquifer concentrations ranging from 100s of ng/L to 1000s of µg/L (i.e. the CMC for PFOS and PFOA reported as around 4.5 g/L and 15.7g/L , respectively [86, 87]). However, it has been suggested that amphiphilic compounds may adsorb onto minerals in hemimicelles when the organic ions are present at 0.001 to 0.01 of the CMC [87]. Long-chain PFASs have been found to concentrate in the surface of concrete and pose a potential ongoing source to surface waters for many decades at firefighting training pads [88].

Sorption of PFASs can also be influenced by the presence of co-contaminants such as non-aqueous phase liquid (NAPL) and non-fluorinated surfactants [89]. In addition, for PFASs, sorption typically increases with decreasing pH and increasing concentration of Ca²⁺ (ionic strength) [90].

3.2.1. Precursor Fate and Transport

While many studies have been published on the behaviour of PFASs and PFCAs within the environment, little data is available for precursor substances due to the difficulty inherent in their identification and analysis.
Precursors are likely to have different physical and chemical properties to the perfluorinated daughter products they will transform to. They may be more or less mobile depending on the size, hydrophobicity and charge of the functional group [91] or contain more complex neutral, anionic, cationic, zwitterionic or volatile functional groups, leading to differences in their transport behaviour. The PFAA precursors can biotransform to create PFAAs, which is generally more rapid under aerobic conditions.

However, using advanced analytical techniques (described in Section 4.2), precursors have been identified migrating within groundwater from Fire Training Area (FTA) source zones [92] and within PFASs impacted drinking water supplies [91].

4. CHEMICAL ANALYSIS METHODS

4.1. Overview of Standard Methods

Worldwide there are a variety of standard methods available for the analysis of PFAs, including the international standard ISO 25101:2009(E) for the analysis of PFOA and PFOS and the U.S. EPA Method 537 for the analysis of PFAAs. Most of the international available standards are based on liquid chromatography with tandem Mass Spectrometry (MS) detectors (LC-MS/MS) and analyse for around 12-30 compounds, principally PFAAs with a handful of known polyfluorinated precursors for which standards are available. The analysis of branched PFOs isomers should also be undertaken and mass labelled standards used for quantification. Laboratories have been working towards achieving lower Limits of Reporting (LOR) in response to ever more stringent regulatory standards with LORs typically around 1 ng/L (waters) and 5-10 µg/kg (soils). Some analytical laboratories are currently capable of reporting 0.65 ng/L (EU Inland Surface Water Environmental Quality Standard (EQS) for PFOS) for PFOS/PFOA in clean water, but can struggle to achieve such limits in ‘dirty’ water samples.

4.2. Advanced Analytical Techniques

While standard methods are available for the analysis of PFAAs, the quantitative analysis of other PFASs is often difficult due to the large number of compounds and lack of appropriate reference materials. Therefore, the full extent and distribution of PFASs impacts from precursors and their eventual dead-end daughter products, as well as the associated long-term liabilities, have not generally been assessed.

To address this difficulty, analytical techniques have been developed which can assess the total mass of PFASs. There are four methods available to measure the total concentration of PFASs in multiple matrices:

- The Total Oxidisable Precursors (TOP) Assay allows quantification of the sum of PFASs, including PFAA precursors, by converting them to detectable PFAAs, via an oxidative digest with LC-MS/MS analysis undertaken before and after this digest [93, 94]. This allows the PFAAs evolved from the precursors to be measured by conventional LC-MS/MS with an LOR of around 2 ng/L. The TOP Assay also provides indicative data regarding the perfluoroalkyl chain length of the precursors, which can assist with assessing the source of the PFASs contamination as well as their potential to bioaccumulate.

- The TOP Assay is increasingly being adopted for PFASs site assessments, notably within Scandinavia and Australia, and is specifically recommended within the Queensland Department for Environment and Heritage Protection Foam Policy [95, 96] for use in characterising the composition of firefighting foams. Soil, sediment, water and biota are also now routinely subject to analysis using the TOP Assay in Australia.

- The Adsorbable Organofluorine (AOF) method uses combustion ion chromatography which involves sorption of PFASs onto a synthetic activated carbon (thus excluding inorganic fluoride) followed by combustion and measurement of evolved fluoride by ion chromatography. AOF provides a single measurement of organofluorine content with an LOR of ~1 µg/L. Extractable Organofluorine (EOF) analysis, based on a similar process, has also recently been developed for soils with an LOR of 50 µg/kg.

- Particle Induced Gamma Emission (PIGE) spectroscopy involves initial separation of PFASs via solid phase extraction cartridges followed by proton bombardment and the measurement of the unique gamma ray signature emitted from any fluorine present. This analysis also provides a single measure of total organofluorine with an LOR of ~2 µg/L.

- Quadrupole Time of Flight - Mass Spectroscopy (QTOF-MS) can identify multiple PFASs, including precursors, via mass ion capture and accurate mass estimation to give likely empirical formulae. This method is not widely available commercially and is best placed as a technique for forensic analysis.

The use of such advanced analytical techniques to develop robust conceptual site models (CSMs) is discussed in Section 8.1.

4.3. Sampling

Specific precautions have to be taken in the sampling of environmental media since PFASs adsorb strongly to glass. PTFE-containing materials can lead to increased blank values if AOF is analysed, and may also interfere with the analysis by adsorbing PFASs. Currently the most appropriate material for sampling seems to be polyethylene or polypropylene. Additional precautions regarding cross-contamination from waterproof clothing, cosmetic products and other equipment should also be considered and robust decontamination procedures employed and validated (e.g. via field and sampling blanks), especially on sensitive sites.

5. TOXICITY

Available data on PFASs toxicity is dominated by PFOS, PFOA and also PFHxS due to the widespread detection of these long-chain PFAAs in humans and the environment, and concern that these could biomagnify to a level whereby humans consuming fish may be adversely affected. Much less data is available on the toxicology of other PFASs, and this is often inconsistent and fragmentary. For the less investigated polyfluorinated chemicals, toxicology is often estimated based on structure-activity relationships, or structural homologues. However, the toxicity of the fluorotelomer precursors has been described to be greater than the inert perfluoroalkyl acids they transform to create [97].

Human exposure to PFASs is mainly by ingestion of contaminated food or water [98, 99], although household dust and breast milk may be important exposure pathways for infants and young children.
Both in animals and humans, PFOS and PFOA can cross the placenta and so cause exposure to the developing foetus. PFASs are not metabolised [3, 101], bind to proteins (not to fats) and are mainly detected in blood, liver and kidneys [3]. Elimination of PFOS, PFHxS and PFOA from the human body takes some years [102], whereas elimination of shorter chain PFASs is in the range of days. The half-life of PFOS and PFOA in rodents is in the range of months [102-104] which differs significantly from humans and can cause extrapolation issues in tests.

Animal studies mainly show effects from PFOS on the liver, the gastrointestinal tract and on thyroid hormone levels [105-108]. In general, PFOS is more toxic than PFOA.

Carcinogenic effects of PFOS and PFOA have also been studied (human and animal studies) without focus on other PFASs. The U.S. EPA concludes that evidence of carcinogenicity of PFOS is “suggestive”, but not definitive, because the tumour incidence does not indicate a dose response [109]. Based on a risk assessment study performed in 2005 [110], PFOA’s carcinogenicity was also categorised as “suggestive”.

Probable links with high cholesterol, thyroid disease, pregnancy-induced hypertension, ulcerative colitis, testicular cancer and kidney cancer, have been published for PFOA based on a large population human health screening study [111] whilst similar studies are ongoing in Sweden for PFOS [112] and U.S. epidemiological studies have recently been described [113]. Recent publications have suggested a series of correlations with PFOA and male diabetes and in both sexes, statistically significant rate ratios were detected for all causes of mortality, diabetes, cerebrovascular diseases, myocardial infarction and Alzheimer’s disease. In females, rate ratios significantly higher than 1.0 were also observed for kidney and breast cancer, and Parkinson’s disease [114-116]. Immunotoxicity has also been suggested [117-119]. A recent review of >200 human epidemiological studies, considering PFOS and PFOA, by the European Food Safety Agency (EFSA) is described in section 6.2.

6. REGULATION

Initial concern and regulatory focus has been on PFASs with longer perfluoroalkyl chains (see Section 2.1.2) as these show greater aquatic bioaccumulation potential and have longer half-lives within the human body [48]. However, more recently, international regulatory concerns have focussed on the shorter chain replacements, PFECAs such as GenX, and some polyfluorinated precursors [3-25, 120].

6.1. Global / European Treaties and Conventions

In 2009, PFOS was added to Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs), meaning that measures must be taken to restrict its production and use. With global restrictions now in place for PFOS, further regulation is proposed in Europe and elsewhere to restrict the manufacture and use of any PFAS substance that contains a C7 or C8 perfluorocarbon moiety in its molecular structure.

In June 2015, the European Union (EU) submitted a proposal to list PFOA, its salts (e.g. ammonium pentadecaffluoroacetanoate (APFPO)) and PFOA-related compounds (e.g. B 2 FTOH) in Annexes A, B and/or C6 of the Stockholm Convention. During 2017 PFOA and PFHxS were added to compounds proposed to be listed under the Stockholm Convention [121].

On 14th June 2017 the EU published measures to regulate PFOA, its salts and related substances in a wide range of products under Annex XVII of the Regulation, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation. The new law will be implemented in phases, starting 4th July 2020 [122]. The European Environmental Bureau commented that a lower limit should have been set and that these proposals are meaningless in terms of reducing global consumption and emissions of PFOA [123].

There are additional emerging methods to evaluate environmental hazards posed by PFASs. These include assessing persistence, mobility, and toxicity (PMT) and the assessment of very persistent and very bioaccumulative (vPvB) compounds [25, 124] and very persistent and very mobile compounds (vPvM) [120]. The use of these additional criteria to assess environmental effects of PFASs will potentially lead to the identification of a far wider range of PFASs to be restricted under future environmental regulations. The Zurich statement published by over 30 regulators and academics in 2018, considered that regulatory schemes should be adapted to cover PFASs that are highly persistent in the environment but fail to meet key bioaccumulation criteria [125].

There are several other international conventions and agreements that cover PFASs in some way of note are The Organisation for Economic Cooperation and Development (OECD) and the United Nations Environment Program (UNEP) Global PFC Group. These organisations aim to develop and promote international stewardship programmes and regulatory approaches for PFASs and include establishing a global emission inventory for PFASs and promotion of information on alternatives to PFASs in key industries.

6.2. National Legislation and Guidance Outside the UK

Advancing science and a recognition that a major route of public exposure to PFASs has been via impacted drinking water has led to regulators globally reviewing national standards with overall trends towards regulating a greater number of PFASs (including shorter chain lengths) and towards lower acceptable concentrations. Underlying the regulatory changes are diminishing acceptable daily exposure levels for the general population known as tolerable daily intakes (TDIs) measured in ng/kg body weight/day (ng/kg bw/day), which have fallen significantly in many jurisdictions.

In May 2016, based on new TDIs for a combination of PFOS and/or PFOA (20 ng/kg bw/day), the U.S. EPA issued a Federal long-term exposure Health Advisory Level (HAL) for drinking water of 0.07 µg/L [36]. Some U.S. states have proposed levels as low as 0.05 µg/L for PFOS and PFOA, such as in Pennsylvania [126] and Michigan [127]. Australia matched the U.S. EPA TDI and drinking water target for PFOS in April 2017 but added PFHxS to drinking water standards, so the sum of PFOS and PFHxS should not exceed 0.07 µg/L [128, 129].

The Agency for Toxic Substances and Disease Registry (ATSDR), published a draft report in 2018, recommending reference doses of 2 and 3 ng/kg bw/day for PFOS and PFOA respectively which potentially results in drinking water criteria of 7 ng/L for PFOS and 11 ng/L for PFOA [130].
In 2015, New Jersey announced that it had developed recommendations for an enforceable drinking water limit, called a maximum contaminant level (MCL) for perfluorononanoic acid (PFNA) at 13 ng/L, which was enforced in 2018. MCLs for PFOS and PFOA have been proposed at 13 ng/L and 14 ng/L respectively and are currently being applied as guidance values [131]. These levels were also adopted by the State of California [132]. The State of New York has recommended MCLs of 10 ng/L for PFOS and PFOA [133]. U.S. states including Massachusetts and Connecticut have applied the U.S. EPA HAL to a combination of 5 PFAAs including a short-chain PFAA, whilst Vermont has applied a standard of 20 ng/L to these same PFAAs.

Across Europe, the most stringent drinking water guidelines are found in Scandinavia - Denmark’s are set at 0.1 µg/L for the sum of 12 PFAAs [28] and Sweden’s are set at 0.09 µg/L for the sum of 11 PFASs [29] - and in certain states in Germany such as Bavaria with 13 individual PFAAs regulated to varying acceptance criteria between 0.1 µg/L and 10 µg/L [26].

In December 2018 EFSA published revised tolerable weekly intake (TWI) levels for PFOS and PFOA [134]. After reviewing over >200 epidemiological studies, with approximately 20 differing endpoints, EFSA concluded that, for PFOS/PFOA, three endpoints are considered likely to be causal and adverse as a result of consistent data. These comprise (1) increased serum cholesterol (PFOS & PFOA), (2) impaired vaccination responses in children (PFOS) (3) high serum alanine transferase (ALT) (PFOA).

The EFSA TWIs result in TDIs of 1.8 ng/kg bw/day for PFOS and 0.8 ng/kg bw/day for PFOA, which theoretically generate drinking water criteria of 12.6 ng/L for PFOS and 5.6 ng/L for PFOA (based on 70 kg, 2L water/day and 20% allocation). It is noted that EFSA is also reviewing the risks to human health related to 17 additional PFASs.

More comprehensive regulations are developing to cover other PFASs introduced as replacements for PFOS and PFOA led by certain U.S. states and European countries.

A monitoring system for identifying unregulated emerging contaminants via a Contaminant Candidate List (CCL) has been undertaken in the U.S. since 2001, using the Unregulated Contaminants Monitoring Rule (UCMR) applied for drinking water protection [135].

6.3. UK Regulations and Guidance

The use of legacy firefighting foam products containing >0.001 wt% PFOS has been banned in the EU since 27th June 2011 and PFOS is a ‘Hazardous Substance’ under the Water Framework Directive (WFD) (2000/60/EC) (WFD) and Groundwater Daughter Directive (2006/118/EC) (GDD) and so input into groundwater must be prevented.

The UK Technical Advisory Group (UK TAG) has advised that for PFOS, the concentration in groundwater below which the danger of deterioration in the quality of the receiving groundwater is avoided is an annual mean of 1 µg/L (derived from 75% of the WFD threshold), where that threshold is used for the protection of groundwater as a long-term drinking water resource.

PFOS and its derivatives are also considered ‘Priority Hazardous Substances’ (PHS) under the WFD, having been included in Annex I of the Priority Substances Directive (2013/39/EC). The EU annual average environmental quality standard (AA-EQS) for PFOS in surface freshwater is set at a very low criterion of 0.65 ng/L, based on the potential for secondary poisoning in humans due to fish consumption [35]. The EQS was applied in December 2018 with the aim of achieving good chemical status in surface waters by 2027. A supplementary monitoring programme and draft programme of measures for PFOS was required to go to the European Commission by the end of 2018 [136].

The AA-EQS of 0.65 ng/L is derived from starting points that are considered as conservative [137]. It is lower than background levels typically recorded in many European surface waters; for example 238 ng/L PFOS was reported in the River Severn (flowing at 33 m³/s) [75]. As a result of this EQS, analytical laboratories have successfully achieved lower detection levels to accurately measure PFOS to below 0.65 ng/L, by achieving detection limits at 0.09 ng/L.

In the UK, tiered Drinking Water Guidance (2009) has been produced by the Drinking Water Inspectorate (DWI) for PFOS and PFOA with a first tier at 0.3 µg/L above which consultation and monitoring must be undertaken [138]. However, the guidance only requires measures to reduce concentrations to below 1 µg/L for PFOS and 5 µg/L for PFOA, which is higher than many other countries and reflects the higher TDIs, published in 2008 by EFSA and still adopted in the UK (150 ng/kg bw/day PFOS; 1,500 ng/kg/ bw/day PFOA). As mentioned above, EFSA has recently finalised new TWIs for PFOS and PFOA which are significantly lower those presently used in the UK. It is anticipated that there may be downward revision of UK drinking water standards for PFOS and PFOA based on the recent EFSA opinion.

Soil Screening Values (SSV) for PFOS and PFOA have also been published by the Environment Agency [139] at 0.014 mg/kg Dry Weight (DW) (normalised to 3.4% Soil Organic Matter (SOM)) and 0.022 mg/kg DW (normalised to 3.4% SOM) based on secondary poisoning to birds and mammals.

Public Health England has produced four guidance documents relating to the incident management and toxicology of PFOS and PFOA [105-108] but which are not considered to be fully up to date, particularly with regard to the toxicological information assessed (which was published no later than April 2009).

Looking forward, the UK government’s strategic approach to managing chemicals includes a goal in the Department for Environment, Food and Rural Affairs (DEFRA) 25 year plan [140] to publish an overarching Chemicals Strategy which sets out its approach as the UK leaves the EU, exploring options to consolidate monitoring and horizon-scanning work to develop an early warning system for identifying emerging chemical issues.

7. Current Condition of UK Waters

An assessment of the occurrence of PFASs within UK waters was undertaken by the Environment Agency in 2006 [141] which identified PFASs at 26% of selected groundwater sites (including at sites located away from potential sources), at 52% of surface water sites at drinking water abstraction points and at 67% of ‘high risk’
surface water sites. PFOS was the PFAS identified most frequently and at the highest concentrations. This study indicates PFASs to be widespread at µg/L concentrations within the UK surface and groundwaters assessed. However, it is difficult to draw conclusions from this limited study as results were not repeatable and method detection limits were relatively high (0.1 µg/L).

In 2007, the DWI undertook a survey of the prevalence of PFOS and PFOA within UK drinking water at 20 sites over a 1 year period [142]. The very limited survey found that PFOS and PFOA did not appear to be widespread within UK raw and treated drinking water and that when detected PFOS was below UK drinking water guidance values (0.3 µg/L) and associated with specific incidents (i.e. the Buncefield Terminal Fire in 2005) or local sources of contamination (e.g. an airfield). However, detections of PFOS within treated drinking water at concentrations up to 0.13 µg/L were measured and little treatment of PFOS or PFOA was observed within treatment plants (although GAC present at two sites had not been replaced for several years). This limited data set, coupled with concentrations of PFOS reported in UK surface waters and aquifers, indicates that drinking water in some UK locations may exceed acceptable levels applied in many other countries e.g. U.S. EPA HAL of 0.07 µg/L (as described in section 6.2).

A report by the Environment Agency in 2008 [143] developed partition coefficients for a number of PFASs across a range of aquifer materials and also summarises the occurrence of PFASs in UK waters with reference to three incidents described in [142] and [144] (Buncefield depot, Jersey airport and a major air base). The report also found some evidence that PFASs were more likely to be found at sites with other pollutants also present and that thick drift deposits decreased the likelihood of detecting PFASs in groundwater.

A number of academic studies have included monitoring for PFASs in UK rivers [75, 141, 145] which indicate widespread exceedances of the EU EQS in both EU and UK surface waters with some detections linked to WWTP discharges. A report of results of PFOS analysis of surface waters in the UK via the Chemical Investigations Programme (CIP2) showed very serious fails, versus the EQS, for 69% of samples assessed for PFOS, with serious fails for the remaining samples. All waters sampled for PFOA were reported as fails, with 13% described as serious fails [146].

8. CONCEPTUAL SITE MODELS AND RISK ASSESSMENT

8.1. Conceptual Site Models

A robust, site specific CSM is the corner stone of assessing potential environmental and human health risks within the land contamination sector. The types, properties and fate and transport of PFASs have been outlined above along with the aerobic biotransformation of precursors which are all crucial aspects in conceptualising PFASs sources, pathways and receptors.

As a significant mass of PFAA precursors, in addition to free PFAAs, has been detected in both AFFF impacted soil and groundwater; a revised CSM to describe PFASs fate and transport is hypothesised and presented in Figure 3.

Cationic PFAA precursors (and some zwitterions) will be retained in the soils at the source zone via ion exchange processes (sorbed to negatively charged soil particles) and more hydrophobic PFASs will be retained in surficial soils more strongly via interaction with the fraction of organic carbon. The source zones are likely to be anaerobic as a result of the presence of residual hydrocarbons used in fire training, so precursors will biotransform extremely slowly due to the prevailing biogeochemical conditions and may present an ongoing source of anionic PFAAs, slowly released from the source. Anionic PFAA precursors will migrate away from the source and enter the redox recharge zone where conditions become increasingly aerobic thus promoting in situ generation of detectable PFAAs from the, often undetected, anionic PFAA precursors.

It is therefore crucial to employ advanced analytical techniques (such as the TOP Assay or AOF) in order to characterise PFASs impacted sites and develop a robust CSM. Furthermore, investigations
employing the TOP Assay have identified PFASs source areas which had not been identified previously by conventional analysis [147] with other studies demonstrating precursors transport within the aquifer and using the TOP Assay to distinguish between different PFASs sources [92].

### 8.2. Risk Assessment and Analysis

In order to provide pragmatic, cost-effective solutions to managing potential risks from PFASs, as with more familiar contaminants, site specific risk-based approaches can be employed based on identifying active source-pathway-receptor (SPR) linkages and ensuring suitability for end use.

These approaches may begin with portfolio risk analysis and site sensitivity screening to assess PFASs usage, site sensitivity and potential SPR linkages. This may be as part of land acquisition, due diligence, site redevelopment or environmental liability provisioning, for example. In some cases, this may warrant site investigations which should employ advanced analytical techniques to fully characterise potential liabilities, considering both current and future regulations.

Site specific Detailed Quantitative Risk Assessments (DQRAs) can also be undertaken to support decision making and sustainable remediation end points. A DQRA was undertaken in relation to the Buncefield Oil Terminal fire where Site Specific Assessment Criteria (SSAC) were developed based on the UK Drinking Water Guidelines with fate and transport modelling also undertaken to assess the relative transport of MTBE and PFOS within the fractured Chalk aquifer [83].

Where physiochemical properties and toxicity thresholds can be identified and selected then potential human health risks from a PFAS compound can be assessed as they can be for any other common contaminant including using the Environment Agency’s Contaminated Land Exposure Assessment (CLEA) tool [148]. While there is currently a lack of physicochemical and toxicological data for many individual PFASs which may introduce uncertainty, these data gaps are being increasingly addressed. In addition, complex groups of contaminants have been tackled by the land contamination sector before with familiar approaches such as grouping contaminants according to structure, chemical class and/or properties (e.g. speciated petroleum hydrocarbons) or using indicator compounds (e.g. benzo(a)pyrene, naphthalene etc.) providing potential future options for assessment.

During a foam spillage incident at Brisbane Airport in 2017, as PFASs other than PFOS, PFHxS and PFOA were not assessed by existing Australian screening levels, a ‘conservative but protective’ approach was adopted based on assessing compounds with similar structures and likely similar properties to PFOS and PFOA [149]. In addition, TOP Assay data, which includes assessment of PFAAs and PFAA precursor concentrations, was considered suitable for evaluating the characteristics of the foam spilled as well as in remediation planning and in agreeing endpoints [149].

### 9. SOIL AND GROUNDWATER REMEDIATION

The remedial options available to address PFASs contamination are limited by the unique physical and chemical properties of these compounds. Many remediation methods utilised to address hydrocarbon contamination, such as air stripping, sparging, soil vapour extraction and bioremediation, are ineffective due to the low volatility of these compounds and their resistance to microbial degradation. The overall strategy for PFASs remediation often requires multiple treatment technologies as some PFASs can quickly transit GAC and so are not removed effectively. Remedial technologies which stimulate aerobic biodegradation, such as air sparging and biosparging, plus conventional forms of chemical oxidation are likely to increase the mass flux of PFAAs from the impacted material, as precursor transformation to PFAAs is accelerated, so are not recommended.

For all remediation techniques, particularly emerging technologies, care should be taken to assess the likely efficacy, implementability and cost of each technique as well as the ability to address the range of PFASs required for the project, e.g. precursors [90].

#### 9.1 Management of Potential Releases

Approaches to manage potential future release of PFASs can include the redesign of an FTA which can be engineered to contain foams and fuels used within fire training, prevent discharge to ground and minimise water use and discharge through rain harvesting. This would generally be undertaken alongside management of any historic contamination.

On any active site, it is important that any PFASs-containing materials or waste streams are effectively identified, characterised and managed, particularly with respect to waste water treatment and potential release to the environment.

#### 9.2 Soil Remediation

Conventional soil treatment methods include excavation and disposal to landfill, however, in addition to cost, the potential long-term liability of this option should be carefully considered given PFASs persistence and limited PFASs treatment or monitoring in most landfill leachates. Landfill operators in several countries (notably Australia and Sweden) are becoming increasingly restrictive regarding PFASs-impacted wastes.

Excavated soils may be incinerated at high temperatures (>1,100°C) to destroy PFASs although this may be prohibitively expensive for many sites. In the UK, waste containing PFOS (as a Persistent Organic Pollutant (POP)) above 50 mg/kg may require destruction even if classified as Non-Hazardous [150].

Capping of soil impacts left *in situ* or containment of excavated soil within engineered stockpiles to prevent infiltration and leaching to groundwater have both been undertaken with long-term management, continued liability as well as restrictions on redevelopment being key considerations.

Soil washing may be suitable to minimise volumes of PFASs-impacted soil waste for larger projects and for soils with relatively low fines content, however, water treatment and fines treatment/disposal may be complex and expensive, with a lack of data demonstrating effectiveness on PFAA precursors [90].
9.2.1 Emerging Soil Remediation Technologies

Approaches involving stabilisation and solidification using binding reagents to prevent leaching to groundwater are becoming of increasing focus for source zone impacts (despite potential long-term liability considerations) given the cost of alternatives. Several proprietary formulations are available and thorough preliminary assessments of efficacy are required which reflect the properties of PFASs and the likely ground conditions (e.g. acidic conditions may increase PFASs sorption so some leaching protocols designed to emulate acid rain leaching may not be the most conservative, such as the U.S. EPA Method 1312 - Synthetic Precipitation Leaching Procedure.

In addition, *ex situ* Low Temperature Thermal Desorption (LTTD) has been evaluated for the treatment of soil containing PFASs, with the principle being that PFASs are volatilised from the soil to then be combusted in the vapour phase at high temperatures. There are concerns over treatment efficiency considering precursors and the generation of hydrogen fluoride and fluorinated organics in the evolved vapours.

9.3 Groundwater Remediation

Typical responses to address PFASs in groundwater employ pump-and-treat based systems using GAC to treat abstracted groundwater. However, while PFOS and PFOA can be effectively treated using GAC, their sorption capacities are relatively low and short-chain PFASs and the polyfluorinated precursors can breakthrough GAC much more rapidly [91]. Dissolved natural organic matter (NOM) strongly competes with PFASs for binding sites on GAC, so where NOM levels are high, such as in surface waters, treatment of PFASs with GAC could be challenging and expensive. GAC is an established technology which can be easily implemented to remove PFOS and PFOA but lifecycle operational and maintenance costs are high and costs can increase if other short-chain PFAAs and precursors also require treatment or NOM levels are high [90].

Reverse Osmosis (RO) and Nanofiltration (NF) have been shown to be extremely effective in removing PFASs regardless of chain length [151], however, these systems are expensive and typically employed with large-scale drinking water systems. For groundwater applications, the suspended solids and water geochemistry must be assessed and managed to prevent fouling or deterioration of the RO/NF membrane. This approach also generates a low volume, high concentration rejectate which requires treatment or disposal.

While several studies have indicated some forms of Advanced Oxidation Processes (AOP) may be capable of destroying PFCAs such as PFOA [90, 152], extreme conditions seem to be required. PFSAs such as PFOS are reported to be much more recalcitrant towards AOP [153]. The potential to create PFAAs from precursors via incomplete or ineffective oxidation should be considered.

9.3.1 Emerging Groundwater Remediation Technologies

Emerging technologies include electrochemical oxidation of PFCAs [154]. Degradation is via direct electron transfer on the surface of the anode and may also be suited to low volume, high concentration waste streams. However, short-chain PFASs are less well treated and potential issues of electrode corrosion and the formation of high concentrations of by-products (e.g. short-chain PFASs, hydrogen fluoride, perchlorate, bromate) must be considered [90, 152]. The use of sonolysis as a technology that can mineralise all PFASs, without creating by-products, at ambient temperatures using high frequency ultrasound is emerging as a destructive treatment option [90].

Several Ion Exchange Resins (IERs) have been assessed and developed which employ a range of functional groups (often involving quaternary ammonium groups) to enable selectivity. While many IERs are effective for either long or short-chain anionic PFASs, more novel resins are reported to have higher sorption capacities for both long-chain and some short-chain PFASs compared with GAC. The performance of IERs on a wider range of PFASs including PFAA precursors, cationic and zwitterionic species etc. has not been reported. While IER media may be more expensive than GAC and often require pre-treatment, the potential for higher sorption capacities, shorter contact times, smaller equipment footprints and ability to regenerate may be more favourable for some applications [90, 151, 152]. Single use IERs have also been developed and IERs can be employed after GAC as a polishing step [90].

A proprietary flocculation / precipitation approach for PFOA and PFOS has been developed for higher concentration liquid waste streams whereby a coagulant is added to the water which adsorbs PFOA and PFOS (employing electrostatic and hydrophobic interactions) and is then precipitated and filtered as a sludge waste for disposal [155]. This is intended to prolong the life of subsequent treatment, e.g. GAC, which is typically required as a polishing step.

Ozofractionation involves sparging waste water with ozone to strip dissolved PFASs into the foam fractionate which can then be treated or disposed (Figure 5). This approach may be more suited as a preliminary step prior to a polishing step, such as nanofiltration [90].

Figure 5. Ozofractionation system in action to remediate PFASs in a C6 fluorotelomer foam spill in Brisbane, Australia. Source: Ian Ross, Arcadis/ EVOCRA.
10. CONCLUSIONS

As the understanding of the types, properties and environmental behaviour of PFASs increases, so do the tools and techniques available to the UK land contamination sector. This dramatically increased understanding and focus on PFASs allows informed assessment of potential liabilities, development of robust CSMs and provision of pragmatic, risk-based management solutions relevant to an evolving global regulatory climate.

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REFERENCES


