CL:AIRE technical bulletin

TB 22
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CL:AIRE technical bulletins describe specific techniques, practices and methodologies relevant to sites in the UK. This bulletin describes per- and polyfluoroalkyl substances (PFAS) uses and identifies industries and activities which could potentially cause environmental impacts.

An overview of the uses of PFAS to assist with identification of sites of concern

1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a broad group of over 12,000 synthetic chemicals [1, 2], widely applied for bulk industrial uses and in consumer applications since the 1930s [3, 4]. As a result of their detection in drinking water supplies, PFAS are the subject of accelerating environmental regulatory concern globally.

The initial regulatory focus was on two perfluoroalkyl acids (PFAAs), perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), but attention has now widened to an array of additional PFAS, including short chain PFAS, polyfluorinated PFAS (PFAA precursors) and perfluoroalkyl ethers.

CL:AIRE Technical Bulletin TB19 *Managing Risks and Liabilities associated with Per- and Polyfluoroalkyl Substances (PFAS)* should be used as a reference document to this bulletin. It provides summary information on PFAS chemistry; their origin; their properties, fate and behaviour; their regulation; risk assessment of PFAS; and remediation of PFAS-contaminated soil and groundwater.

This technical bulletin, describing PFAS uses and potential sites of concern, aims to provide an overview of some of the bulk, legacy and/or dispersive uses of PFAS, to act as a guide to site investigations of land by assisting with identification of activities which may lead to PFAS being present at concentrations which could pose a risk to environmental or human health receptors.

High concentrations of PFAS can remain at locations where PFAS have been lost to ground, acting as ongoing sources to groundwater or surface waters [5-15]. PFAS may remain in soils and be associated with low permeability deposits [6] or concrete surfaces [8, 9].

Activities where the ongoing and legacy releases of liquid forms of PFAS (in solution) have likely occurred, have been prioritised, as these uses could result in a significant mass of PFAS release to the environment over time. Although many PFAS can be highly mobile in the environment, when released, a significant mass of amphiphilic or cationic/zwitterionic PFAS can remain at release sites and continue to represent a source of PFAS [10, 11, 16].

Some PFAS may be regarded as being ubiquitous at very low concentrations. The presence of PFAS in rain and the spreading of biosolids wastes from wastewater treatment plants to land as a fertiliser, can result in widespread (low level) detections of PFAS in soils [17-21].

Figure 1. Aqueous film forming foam in use.

This bulletin aims to identify industries and activities which could cause significant losses of PFAS to the environment, which may continue to act as a source of PFAS to potentially impact receptors. A brief description of the types of PFAS that are associated with differing activities is then provided.

As a result of the widespread use of PFAS in multiple applications, a comprehensive guide to all potential source areas is not possible. A review, cataloguing which PFAS may be used in multiple applications and by differing industries has recently been published [22, 23]. The multitude of PFAS uses has been described in various publications [23-31], which provide a detailed overview.

2. FIREFIGHTING FOAMS

Firefighting foams containing PFAS termed fluorosurfactants have been used for extinguishment of flammable liquid (Class B) fires since 1962 [32], and continue to be widely used.

The types of firefighting foams that contain PFAS include:
- Aqueous Film Forming Foams (AFFF) (Figure 1) and alcohol resistant derivatives (AR-AFFF);
- Film Forming Fluoroprotein Foams (FFFP) and alcohol resistant derivatives (AR-FFFP); and
- Fluoroprotein Foams (FP) and alcohol resistant derivatives (AR-FP).

Class B firefighting foams continue to be stored and used for fire suppression, fire training, equipment testing and flammable vapour suppression at multiple sites where there is a fire risk from holding flammable liquids such as hydrocarbons (e.g. gasoline, kerosene, diesel, greases, tars, oils), alcohols, solvents and speciality chemicals. If a flammable liquid was or is handled or stored at any location, the nature of the fire suppression system warrants investigation to determine whether a fluorinated firefighting foam has been used.

Class A foams are used to extinguish fires caused by wood, paper, rubber, textiles and vegetation etc. They were developed in the mid-1980s and are generally not considered to contain PFAS. Prior to their availability, Class B foams were used to fight the types of fires that Class A foams now address. There is evidence that certain dry powder firefighting foams contained PFAS [33].

2.1 Environmental Release

Firefighting foams may be released to the environment as a result of various activities [11, 34], such as:

- Fire training, where periodic and repeat releases of high volumes of foams, to extinguish fires, has occurred;
- Equipment testing, where repeat discharge of foam was required to test or service fire suppression equipment;
- Accidental discharge, such as triggering a fire suppression system (e.g. sprinklers), which causes a high volume of foam to be released;
- Incident responses, where large volumes of foam may have been used to extinguish a fire;
- Losses of foam concentrate during storage or transfer between vessels; and
- Release of waste foam or foam concentrates to wastewater treatment plants, which cannot treat the persistent PFAAs but can convert polyfluoroalkyl PFAS to PFAAs.

2.2 Fire Suppression Systems

Fire suppression systems that incorporate PFAS generally include storage of a foam concentrate, that is diluted using water and released via sprinkler heads for fire extinguishment. However, some fluorinated foam systems may incorporate storage of a premixed foam, which is pressurised using gas when the suppression system is activated.

When assessing whether a facility has applied a fluorinated foam, it can be important to recognise that these foams are dispensed from sprinkler heads (Figure 2). High expansion (Hi-Ex) foams are delivered using foam generators (Figure 3). These Hi-Ex foams are not generally considered to contain PFAS [35-39].

Figure 2. Sprinklers used to dispense PFAS-containing foams (Image courtesy of National Foam).

Figure 3. Foam generators used to dispense high-expansion foams (Image courtesy of National Foam).

2.3 Sites Using Class B Firefighting Foams

Fire training and equipment testing was often done at the following types of sites:

- Chemical, petrochemical and pharmaceutical plants;
- Military sites where fire training or operation using aircraft were common;
- Civil fire stations; and
- Civil airports.

The types of facilities that require fire suppression systems to control flammable liquid fires include:

- Chemical, petrochemical and pharmaceutical plants;
- Military sites where fuels are stored, or have vehicle workshops or aircraft hangars;
- Manufacturing facilities, for example aerospace, coatings, paints, resins etc;
- Chemical and solvent stores;
- Firefighting foam manufacturing, fire testing and foam blending facilities;
- Facilities where vehicles and aircraft are stored or undergo maintenance including automotive workshops and showrooms, aircraft hangars, helipads etc;
- Warehouses and businesses where alcohols are manufactured and stored such as breweries, distilleries, and bonded warehouses;
- Marine operations and shipyards where firefighting foam was stored to be loaded on fireboats, tugs and military vessels;
- Rail yards, where fuels are dispensed;
- Mining operations, used in fire suppression systems built into large vehicles;
- Fire protection for back-up diesel generators for electricity generation in case of power outages, such as at data centres, insurance companies, hospitals etc;
- Commercial kitchens / restaurants cooker hood fire extinguishment systems; and
- Sites where electricity transformers are located and require fire suppression.

Consideration should also be given to sites with a prior history of large liquid hydrocarbon fires e.g. Grangemouth (1987), Buncefield (2005), Stanlow (2018).

2.4 Foam Formulations

The first PFAS-containing firefighting foams, were manufactured by 3M using the electrochemical fluorination process (ECF) and comprised a combination of PFOS and PFOA [32]. The 3M "Light Water" branded foams, sold widely from the late 1960s, contained fluorosurfactants that were dominated by PFOS. From the early 1990s 3M "Light Water" formulations also contained polyfluorinated cationic and zwitterionic PFAS that are mostly precursors to perfluorohexane sulfonate (PFHxS) [40-42]. The general sale of 3M foams containing PFOS ended in 2003 [43], but with long shelf lives, these foams could remain present in fire suppression systems, such as sprinkler systems, or be stored at sites.

Further brands of fluorinated foams, manufactured by the fluorotelomerisation process were sold from the 1970s by several other foam manufacturers such as Ansul, National Foam, Angus, Chemguard, Buckeye and Fire Service Plus [40]. The fluorosurfactants in these foams mainly comprised polyfluorinated precursors to the short-chain perfluorohexanoic acid (PFHxA) (C6) and long-chain PFOA (C8). Other short chain (C2, C3, C4, C5) and long chain PFAS (C9-C14) may also be present [44]. Multiple mixtures of polyfluorinated fluorotelomers may be present in foams [45], these are generally precursors to fluorotelomer sulphonates (FTS) such as 6:2 fluorotelomer sulfonate (6:2FTS) and 8:2 fluorotelomer sulfonate (8:2FTS). 6:2FTS and 8:2FTS can transform in the environment to generate PFHxA and PFOA respectively. The exact composition of PFAS in differing foam formulations can be complex, requiring chemical analysis using non-target methods for a forensic investigation of their content [42, 45-47]. There is current concern regarding the toxicity of the parent polyfluorinated precursors in these fluorotelomer foams, such as 6:2 fluorotelomer alkylbetaine (6:2 FTAB) [48].

Some fluorosurfactant manufacturers committed to reduce the C8 content of PFAS in foam formulations as part of the voluntary USEPA PFOA stewardship program (2010-2015) [49]. Alternative foam formulations, termed C6-foams, were produced with reduced C8 content, but elimination of long-chain PFAS from these foams is not possible. The C6 foams should meet the European regulatory requirements for <1 mg/L PFOA-precursors and <25 µg/L PFOA [50].

These C6 fluorinated firefighting foams are still available for sale and used widely, with regulations advancing in Europe proposing elimination of all PFAS [51, 52]. Alternative fluorine-free firefighting (F3) foams have been available since 2002 and have demonstrated comparable or superior performance for extinguishment of flammable liquid fires [53-56].

3. TEXTILES, CARPET AND LEATHER INDUSTRIES

PFAS have been used in the manufacture of textiles, upholstery, carpets, leather products (genuine and artificial). The major use being to provide water- and stain-repellence [57, 58] (Figure 4). PFAS are used in the manufacture of outer garments (outdoor clothing, workwear for medics, pilots and firefighters [59]) and umbrellas, bags, sails, tents, parasols, car seat covers, leather articles, shoes, carpets etc. [60].

Facilities which manufacture, process, finish or reproof these goods may require investigation to assess environmental impacts from PFAS.

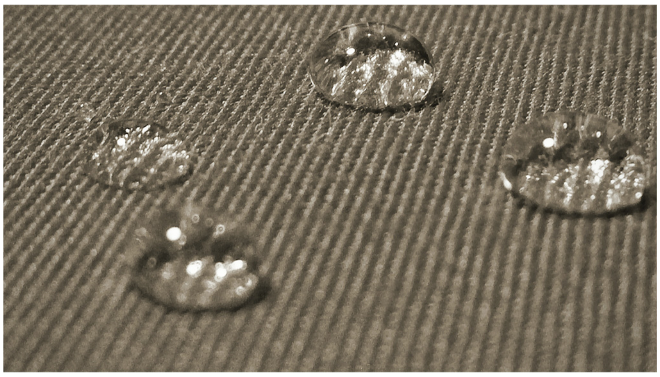

Figure 4. Water beading on a fabric.

Polytetrafluoroethylene (PTFE) is used in highly porous fabrics (such as Gore-Tex®) [60] with a variety of PFAS, including PFOA detected on Gore-Tex® [61].

Side-chain fluoropolymers, such as fluorotelomer-based acrylate polymers are used as surface treatments (finish) to improve surfaces and to make textiles, carpets and leather, water-, grease- and dirt-repellent. These polymers can represent a source of monomeric PFAS to the environment, as breakage of covalent bonds integrating perfluoroalkyl chains into polymer network can cause their release as monomers [62]. Fluorotelomer-based acrylate polymers can break down to generate volatile fluorotelomer alcohols (such as 8:2FTOH and 6:2FTOH) which transform to create PFOA and PFHxA respectively [60]. Carpets, leather and outdoor materials have also been found to contain PFOS [62].

The 3M Scotchgard product has been used to protect surfaces of clothing, furniture and carpets since the mid-1950s [63]. Formulations prior to 2002 contained precursors to PFOS, after reformulation Scotchgard continues to be sold containing precursors to perfluorobutane sulfonate (PFBS) [64]. Links between Scotchgard applications and exposure to PFHxS has been reported suggesting Scotchgard formulations may have contained PFHxS or PFHxS precursors [65].

PFAS are also present in aqueous solutions of aftermarket stain and water repellent reproofers [66] and dry cleaning fluids [22]. Releases to the soil and water environment can also occur through leaching of PFAS from fabrics during commercial dry cleaning and laundering activities [67].

4. PAPER AND CARDBOARD MANUFACTURING

Fluorochemicals are used in the paper and cardboard industries to manufacture grease- and water- repellent materials, which includes food packaging as a food contact material [60] (Figure 5). These include plates, popcorn bags, burger wrappers, greaseproof paper, microwaveable containers, biscuit, bread and pastry packaging and pizza boxes.

Facilities which manufacture, process, or finish papers or cardboard may require investigation to assess environmental impacts from PFAS.

PFAS coatings applied to paper and cardboard tend to be blends or polymers, potentially comprising >100 differing polyfluorinated PFAS [68, 69]. A wide variety of polyfluorinated surfactants, side-chain fluorinated polymers and sulfonamido phosphate diesters

Figure 5. Greaseproof burger wrapper.

(SAmPAPs), that transform to generate PFOS, were used in food contact materials, until 3M ceased production in 2000 [70]. PFAS coatings containing side-chain fluorinated polymers and phosphate diesters (diPAPs) based on 8:2 fluorotelomers (PFOA precursors) have been replaced by products based on 6:2 fluorotelomers (PFHxA precursors) [71, 72]. In addition, food contact materials have been manufactured that are based on perfluoropolyethers (PFPE).

5. METAL PLATING / ELECTROPLATING SITES

PFOS was the primary surfactant utilised in electroplating solutions from the 1950s [73]. Salts of PFOS have been used as wetting agents and mist-suppressing agents in decorative plating and non-decorative hard plating [70] (where 'hard' chrome plating refers to application of layers that are 0.2 mm or thicker [74]). Electroplating involves the deposition of a thin layer of metal on an article by passing an electric current through an aqueous solution of the relevant metal salt [75] (Figure 6). PFAS usage has been especially prevalent in chromium plating, and has also been utilised in zinc, nickel, copper and tin plating [23].

Figure 6. Electroplating process.

In Europe, salts of 6:2 FTS are used as an alternative to PFOS [70] for metal plating. Also a perfluorobutane sulfonate-based defoamer (Bis-[2-(N.methylperfluorobutanesulfonamido) ethoxy]phosphoric acid ester) which comprises a PFBS-precursor, was reported in 2003 as being used in electroplating [76]. In China, several producers have used a chlorinated perfluoroalkyl ether termed 9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS; also known as 6:2 Cl-PFESA or by its trade name "F53-B") for metal plating since the late 1970s [70, 77, 78]. There have been detections of 9Cl-PF3ONS in the River Thames, in London [79] and it was added to the analyte requested for PFAS analysis in raw UK water supplies by the Drinking Water Inspectorate (DWI) in 2021 [80]. Facilities involved in metal plating may require investigation to assess environmental impacts from a variety of differing PFAS.

6. ELECTRONICS INDUSTRIES

There are multiple uses of PFAS in the electronics, optoelectronic and semiconductor industries, with the electronics industry using by far the largest mass of non-polymeric PFAS in Scandinavia [81] (Figure 7).

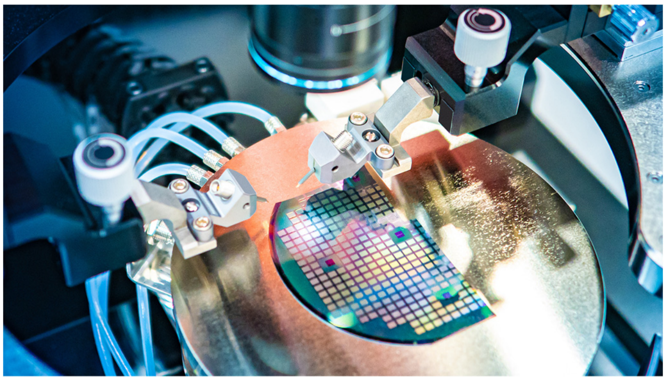

Figure 7. Computer chip manufacture.

In the semiconductor manufacturing industry, PFAS are used as solutions and reagents in multiple steps in the photolithography process to apply antireflective coatings, etchants, barrier layers, photoresists and cleaning solutions.

Multiple PFAS, including 10 perfluoroalkyl acids (PFAAs) have been detected in wastewaters emanating from electronics, optoelectronics and semiconductor industries with PFOS, PFOA and perfluorodecanoic acid (PFDA) found to constitute the largest proportion of PFAS detected [82].

Facilities where electronics, optoelectronic and semiconductors have been manufactured or processed may require investigation to assess environmental impacts from a variety of differing PFAS.

7. FLUOROCHEMICAL, RUBBER AND PLASTICS INDUSTRIES

PFAS synthesis and production facilities can hold large volumes of fluorochemicals. The production of fluorinated polymers / fluoropolymers entails reacting monomeric PFAS to generate oligomers and polymers, where polymerisation processing aids such as PFOA and a variety of perfluoroalkyl ethers may be required [70, 83].

PFAS are used in rubber moulding, mould release and anti-blocking agents for rubber in addition to fluoropolymers being applied in rubber compounding [23] (Figure 8). Production of rubber products which comprise fluoroelastomers (e.g. Viton) can involve use of perfluoroalkyl ethers. The use of PFOS in rubber manufacture was discontinued in 2015, as result of exemption from Stockholm convention restrictions [74].

Fluorinated polymers include: PFPE (e.g. Fluorolink, Optool, Fomblin, Krytox); PTFE and ethylene tetrafluoroethylene (ETFE) (e.g. Teflon™, Dyneon®, Fluon™); Fluorinated ethylene-propylene copolymer (FEP); Perfluorosulfonic acid resins and membranes (e.g. Nafion); Perfluoroalkoxy polymers (PFAs) (e.g. Hyflon PFA, Teflon PFA, Neoflon PFA and Chemfluor PFA); Fluoroelastomers (e.g Viton, Kalrez, Technoflon) and polyvinylidene fluoride (PVDF) (e.g. Solef®) [83].

Figure 8. Rubber mould production.

In the UK, mass production of PTFE began in 1947 [3], with transition away from use of PFOA reported between 2006 and 2015 [84]. A perfluoroalkyl ether termed EEA-NH4 or SAA-1000 (Perfluoro (2-ethoxy-2-fluoroethoxy)acetic acid ammonium salt) is currently used as a replacement for PFOA [70, 85]. EEA-NH4 is not currently included as one of the analytes requested for analysis in raw water supplied by DWI [80]. Facilities involved in the manufacture or processing of fluorochemicals, fluoropolymers, fluorinated polymers and rubber may require investigation to assess environmental impacts from a variety of differing PFAS.

8. PRINTING AND PHOTOGRAPHIC DEVELOPMENT INDUSTRIES

PFOS-related substances have been used in the photographic industry for the manufacture of film, film paper and photographic plates [60] (Figure 9). More than 100 identified PFAS have been found associated with the photographic industry [74].

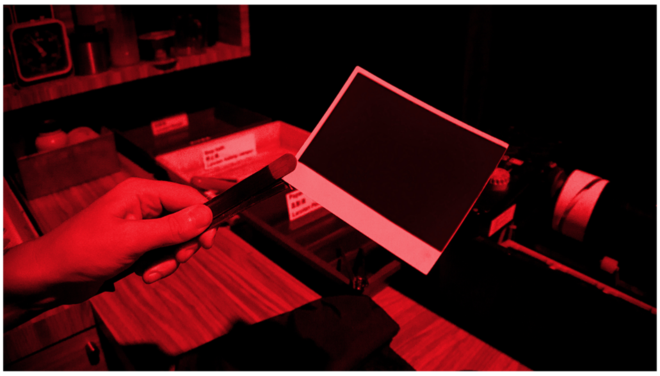

Figure 9. Photographic development in a dark room.

For printing inks, PFAS enhance ink flow and levelling, improve wettability and aid with pigment dispersion in addition to imparting water repellency. Precursors to PFOS have been identified as additives in printing inks [86].

Sites where printing has been carried out may require investigation for PFAS.

9. AVIATION / AEROSPACE INDUSTRIES

The aviation industry has used Class B firefighting foams for fire training, equipment testing and fire suppression in aircraft hangars as described in section 2.

Hydraulic systems in the aviation industry have used PFOS or PFOS-related substances [60] (Figure 10). Currently a cyclic PFAS, perfluoroethylcyclohexanesulfonate (PFECHS) is used [87] which is included on the analytes requested for analysis in raw water supplied by DWI [80].

Figure 10. Hydraulic system of an aircraft.

Per- and polyfluoroalkylether substances (PFAEs) and PTFE may be present in lubricants (e.g. Krytox^{TM}, Fomblin and Dennum) potentially used in the aviation industry in landing gear, gearboxes, fuel pumps, hydraulic pumps etc., which may give rise to release of a variety of perfluoroalkyl ethers [83].

10. SURFACE CLEANERS, CAR WAXES AND TREATMENTS

Commercial car washes may give rise to PFAS impacts, with use of car waxing products (e.g. Simoniz) being associated with PFAS detections in groundwater, where car washing was performed [88]. High concentrations of PFOA-precursors have been detected in car polishes manufactured by Turtle Wax and Autoglym [89].

The manufacture and disposal of cleaning products and polishes, such as floor polishes, (which can contain ~200 mg/L fluorosurfactants), may give rise to PFAS impacts to the environment [90, 91] (Figure 11).

Figure 11. Use of a floor cleaner.

Sites where significant volumes of car waxes or cleaning products have been disposed to ground, may warrant investigation for PFAS.

11. COATINGS, PAINTS AND VARNISH INDUSTRIES

Coatings in which PFAS are used can be divided into five broad types: powder coatings, radiation curable coatings, anti-reflective coatings, cable and wiring coatings and coatings used in the energy sector such as solar panel coatings [92]. Coating via gas phase fluorination has been identified as a technique that is used for fluorinating high density polyethylene (HDPE) to confer resistance from chemical attack when used in e.g. containers for pesticides [93] and liners for tanks in the chemical industry [94]. Powder coatings usually consist of PVDF or ethylene chlorotrifluoroethylene (ECTFE), however a variety of polymers can be used such as PTFE and FEP [92].

Paint formulations can include fluoropolymers (such as PVDF, PTFE, ETFE etc.), fluorosurfactants (C4-fluorinated polyethers), PFBS-precursors and/or C6-fluorotelomers (PFHxA-precursors) (Figure 12). Varnishes may contain C6-fluoropolymers and fluorosurfactants, C4-fluorinated polyethers, methyl nonafluoroisobutyl ethers, and PFBS-precursors [92].

Figure 12. Paint formulations.

The manufacture, processing and commercial applications of coatings, paints and varnishes could give rise to environmental release of PFAS.

12. WASTEWATER TREATMENT PLANTS

Wastewater treatment plants receive PFAS in waste waters from consumer and industrial use of products containing PFAS (Figure 13). A variety of consumer products may contain PFAS which can impact domestic sewerage, such as cosmetics, stain protection, clothing, cookware, coatings, dishwasher rinse aids, car waxes, etc. [22, 23, 89, 91]. Landfill leachates are usually treated using biologically-based wastewater treatment plants, with biological processes being ineffective for treatment of PFAS.

Figure 13. Wastewater treatment plant.

Wastewater treatment plants may also be a source of PFAS to the environment, through liquid effluent discharge, through re-use of biosolids, and through air emissions [95].

Approximately half of the mass of the PFOS entering a wastewater treatment plant can be concentrated in the sewage sludge [96], which can be disposed of in pits on site, or on land applied as a fertiliser. Biosolid disposal in pits has been shown to represent a long-term source of PFAS to groundwater [10].

Multiple types of PFAS can be associated with wastewater treatment plant operations. Usually, polyfluorinated PFAS undergo some degree of transformation to ultimately generate PFAAs, which is favoured in aerobic conditions [96].

13. LANDFILLS

Multiple PFAS have been detected in landfill leachate, including those that receive municipal, construction and industrial waste [97-99] (Figure 14). The use of PFAS in multiple consumer and industrial products which have been disposed to landfill, provides a plethora of differing sources.

Figure 14. Landfill.

The concentration of 70 PFAS in 95 samples of leachates from US landfills of varying climates and waste ages, was surveyed. All leachates contained a range of PFAAs, but the highest detectable concentration for an individual PFAS was for 5:3 fluorotelomer carboxylic acid (5:3 FTCA), with concentrations significantly higher than PFOA and PFOS combined. The fluorotelomer carboxylic acids (FTCAs) are known to be several orders of magnitude more toxic to freshwater organisms than perfluorocarboxylic acids (such as PFOA and PFHxA) [97, 100, 101] and 5:3 FTCA has been described to exhibit biopersistence in higher organisms [102].

Multiple types of landfills are expected to be sources of PFAS, as a result of the widespread legacy and ongoing use of PFAS.

14. CONCLUSIONS

A broad array of differing PFAS have been applied in multiple commercial products with historical and ongoing use by many sectors. Bulk uses of liquid products containing PFAS are more likely to result in an environmental release that potentially causes harm to receptors. A range of polyfluoroalkyl PFAS are described to be present in multiple PFAS-containing products, which can be detected using a combination of chemical analytical tools (outlined in CL:AIRE Technical Bulletin TB19).

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