

History and Use of Per- and Polyfluoroalkyl Substances (PFAS) found in the Environment

1 Introduction

This fact sheet provides a summary of the discovery and application of PFAS, emergence of known health effects, PFAS reduction, and environmental impacts. PFAS are a family of thousands of chemicals that vary widely in their chemical and physical properties, as well as their potential risks to human health and the environment. The unique physical and chemical properties of PFAS impart oil, water, stain, and soil repellency, chemical and thermal stability, and friction reduction to a range of products. These products have application in many industries, including the aerospace, semiconductor, medical, automotive, construction, electronics, and aviation industries, as well as in consumer products (such as carpets, clothing, furniture, outdoor equipment, food packaging), and firefighting applications (3M Company 1999a; Buck et al. 2011; KEMI 2015a; USEPA 2017b). Additional information is available in the Guidance Document.

2 Discovery and Manufacturing

PFAS chemistry was discovered in the late 1930s. Since the 1950s, many products commonly used by consumers and industry have been manufactured with or from PFAS. Two major processes, *electrochemical fluorination (ECF) and fluorotelomerization*, have

ITRC has developed a series of fact sheets that summarize recent science and emerging technologies regarding PFAS. The information in the fact sheets is more fully described in the *ITRC PFAS Technical and Regulatory Guidance Document (Guidance Document)*

(https://pfas-1.itrcweb.org/).

This fact sheet provides an overview of the:

- discovery and development of PFAS
- detection in the environment
- emerging concerns related to human health effects of PFAS
- efforts to reduce use, replace, or both
- potential major sources of release to the environment

been (and are) used to manufacture PFAS substances that contain perfluoroalkyl chains: side-chain fluorinated polymers, perfluoroalkyl acids and polyfluoroalkyl surfactants (USEPA 2003b; Benskin, DeSilva, and Martin 2010; KEMI 2015b; OECD 2018). Table 1 summarizes types of perfluoroalkyl acids (PFAAs) produced by these processes. More than 600 intermediate processes have also been used to further produce certain PFAS and the associated final products.

Manufacturing Process	Commonly Found Polyfluorinated Substances	Potential PFAAs Produced
Fluorotelomerization	FTSA ¹ , FTCA ² , & FTOH	Linear PFCAs ³
Electrochemical fluorination	FASE & FASAA	Branched & linear PFCAs & PFSAs

Table 1. Manufacturing processes and potential PFAAs produced

¹Fluorotelomer sulfonate: for example, may be found at aqueous film-forming foam (AFFF) sites; ²Fluorotelomer carboxylic acids: for example, 5:3 acid may be found in landfill leachate; ³Under certain instances, can produce mixture of linear and branched perfluoroalkyl carboxylates (PFCAs)

3 Emerging Health and Environmental Concerns

Awareness of Public Health Impacts

Awareness of the presence of PFAAs can be attributed to occupational studies in the 1970s that found detections of some PFAS in the blood of exposed workers, and further studies in the 1990s that reported detections in the blood of the general human population (Buck et al. 2011). In recent years, the presence of several long-chain PFAAs (PFOA, PFOS, PFNA, and PFHxS) have been measured in the low parts per billion (ppb, equivalent to nanograms per milliliter (ng/ml)) range in the blood serum of almost all residents of the United States and other industrialized nations (Kato 2015; CDC 2018). These PFAS are present whether or not people were exposed in the workplace, likely due to the widespread use of PFAS in consumer products and industries (Kannan et al. 2004; Kärrman et al. 2006; Olsen et al. 2003). PFAS concentrations (especially PFOS) in human blood have decreased steadily since 2000 (ATSDR 2020a) with the voluntary phaseout of perfluorooctanyl chemistries by a major U.S. manufacturer.

Laboratory studies using animals and epidemiological studies of human populations show that exposure to some PFAS may be associated with a wide range of adverse human health effects (USEPA 2016c, d; ASTDR 2018e). Toxicity studies are discussed in more detail in Section 7.1 of the Guidance Document. More recently, the toxicology of other PFAS, such

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as fluorotelomers and shorter chain PFAAs, as well as replacement PFAS chemicals (such as GenX chemicals), have received increased attention (CONCAWE 2016; USEPA 2016e; USEPA 2018g).

Awareness and Detection in the Environment

Although some PFAS have been manufactured since the 1950s, PFAS were not widely documented in environmental samples until the early 2000s, as PFAS testing was not widely available until that time. Since the 2000s, methods have been, and continue to be, developed with lower detection limits in water that are commensurate with levels of potential human health effects.

Initially, investigations focused mainly on major releases from manufacturing sources and uses such as firefighting foam application sites. But since the early 2000s, the occurrence of PFAS in the environment has been a very active area of research, with occurrence of certain PFAS reported in a wide variety of matrices (Kannan et al. 2004; Yamashita et al. 2005; Higgins et al. 2005; Rankin et al. 2016). With more sensitive analytical methods available, PFAS (especially PFAAs) have been widely detected around the world. Nationwide testing in 2012 of drinking water supplies under the USEPA's Third Unregulated Contaminant Monitoring Rule (UCMR3) led to four additional PFAAs (PFHpA, PFNA, PFBS, PFHxS) gaining greater attention. The UCMR3 sampling detected PFAS in 4% of drinking water supplies across the country (Hu et al. 2016).

In 2016, USEPA issued a Lifetime Health Advisory (LHA) for two of the most widely detected PFAAs, PFOA and PFOS. The LHA was set at 70 nanograms per liter (ng/L, equivalent to parts per trillion [ppt]) in drinking water and applies to PFOS and PFOA individually or in combination (USEPA 2016c, d). Since the UCMR3 and the LHA, other polyfluoroalkyl substances are receiving increased attention and many state regulatory agencies now request or require testing for an expanded list of long- and short-chain PFAAs, and some potential precursors to PFAAs, such as fluorotelomers, as illustrated in Figure 1.



not a greater quantity by mass, concentration, or frequency of detection.

Figure 1. Emerging awareness and emphasis on PFAS occurrence in the environment.

Source: J. Hale, Kleinfelder. Used with permission.

Phaseout of Long-Chain PFAS

Due to concerns about the potential health and environmental impacts, there has been a reduction in the manufacture and use of certain long-chain PFAAs. Long-chain PFAAs include PFCAs with eight or more fully fluorinated carbons (for example, PFOA) and perfluorinated sulfonates (PFSAs) with six or more fully fluorinated carbons (for example, PFHxS and PFOS), their salts, and precursor compounds capable of forming long-chain PFAAs (Buck et al. 2011; OECD 2013; Wang, Cousins, et al. 2015).

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- In May 2000, 3M, the principal worldwide manufacturer and sole U.S. manufacturer of PFOS, announced a voluntary phaseout of perfluorooctanyl chemistries, which included PFOS, PFHxS, PFOA, and related precursors. (USEPA 2003b; USEPA 2017e; 3M Company 2017).
- Since 2002, USEPA has issued multiple Significant New Use Rules (SNURs) under the Toxic Substances Control Act (TSCA) to require notification to USEPA before any manufacture, use, and/or import of certain chemicallyrelated PFAS (USEPA 2020c).
- In January 2006, USEPA initiated the PFOA Stewardship Program (USEPA 2006b) in which the eight major manufacturing companies committed to reducing PFOA, other longer-chain PFCAs, and related precursors (USEPA 2017e).
- The Stockholm Convention on Persistent Organic Pollutants (POPs) is a United Nations treaty signed in 2001 aimed at reducing or eliminating the production, use, and release of key POPs (KEMI 2004, 2015b; USEPA 2017j). The Stockholm Convention has since been amended to include PFOS, PFOA, and discontinuation of previously allowed uses.

PFAS are manufactured globally, and recently increased international production of PFAS have potentially offset the global reduction anticipated with the U.S. phaseout (OECD 2015b). Further, the phaseout efforts do not prevent the import of materials containing PFAS to the United States. Additional details related to the phaseout of certain PFAS chemistries can be found in Section 2 of the Guidance Document.

Replacement Chemistry

Manufacturers have been developing replacement technologies, including reformulating longer-chain substances or substituting them with nonfluorinated chemicals, alternate technologies, or shorter-chain perfluoroalkyl or polyfluorinated substances. Some alternate PFAS include, but are not limited to, compounds produced with ECF and fluorotelomerization, such as: FTOH, PBSF-based derivatives, per- and polyfluoroalkylethers (for example, GenX chemicals and ADONA) and other types of PFAS (Hori et al. 2006; OECD 2007; Herzke, Olson, and Posner 2012; Wang, Cousins, et al. 2015; Holmquist et al. 2016).

Many PFAS alternatives are structurally similar to their predecessors and manufactured by the same companies (CONCAWE 2016; Wang, Cousins, et al. 2015). Some of the replacement chemicals are said to achieve the same performance effectiveness of some of their predecessors; however, it is not yet clear if this is true for all replacement PFAS (Danish EPA 2015). Several studies suggest some of the alternate PFAS chemistries may or may not be less hazardous than the long-chain predecessors, although publicly available information on most replacement chemicals is limited (Wang, Cousins, et al. 2015; RIVM 2016; OECD 2015b). Additional information related to replacement chemistries, including challenges of laboratory analysis and treatment technologies, can be found in the Guidance Document.

4 PFAS Releases to the Environment

PFAS are used in many industrial and consumer applications. For example:

- PFAS is produced at primary manufacturing facilities and used in manufacturing processes at secondary facilities.
- Industrial products including AFFF.
- Consumer products including stain and water repellent material, food packaging, retail products.

As increased environmental sampling for PFAS occurs, it is likely that additional sources may emerge.

PFAS have been and still are widely used, but not all types and uses of PFAS result in the same level of environmental impact and exposure. When considering potential environmental impacts from PFAS, it is critical to be as specific as possible not only about the particular PFAS involved, but also where and how they are released to the environment. Figure 2 illustrates a conceptual PFAS life cycle.

Some uses of PFAS are summarized in Table 2-4 of the Guidance Document, including (but not limited to):

- Building and Construction
- Cable and Wiring
- Metal Finishing and Plating
- Industrial Surfactants and Fluoropolymer Production
- Paper Products and Packaging
- Photolithography/Semiconductor Industry
- Textiles, Leather, and Apparel (Including Carpet and Furniture)

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Figure 2. Generalized PFAS uses and relative exposure and environmental impact potential from PFAS life cycle.

Release mechanisms at primary and secondary manufacturing facilities include air emission and dispersion, spills, and disposal of manufacturing wastes and wastewater. Potential impacts to air, soil, surface water, stormwater, and groundwater are present not only at release areas, but potentially across the surrounding area (Shin et al. 2011).

Environmental releases associated with the use of PFAS-containing products may be related to management of wastes, but the type and concentration of PFAS vary greatly among landfills and among wastewater discharges due to variations in the waste streams. Landfills and other legacy disposal areas can be sources of PFAS because they are repositories for PFAS-contaminated industrial waste, sewage sludge from wastewater treatment facilities, and waste from site mitigation, as well as for PFAS-bearing consumer wastes, such as goods treated with hydrophobic, stain-resistant coatings (Busch et al. 2010; Eggen, Moeder, and Arukwe 2010). Consumer and industrial use of PFAS-containing materials, including disposal of landfill leachate and firefighting foam, may discharge PFAS-containing wastewater to municipal and industrial WWTPs (Lin, Panchangam, and Lo 2009; Ahrens et al. 2009), private septic systems, or other wastewater disposal systems.

5 References and Acronyms

The references cited in this fact sheet and further references can be found at https://pfas-1.itrcweb.org/references/. The acronyms used in this fact sheet and in the Guidance Document can be found at https://pfas-1.itrcweb.org/references/.



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