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, reduction in PFAS production/use, 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 1999 Ref#82; Buck et al. 2011; KEMI 2015 Ref#657; USEPA 2017 Ref#920). Additional information is available in the Guidance Document.

PFAS have followed a similar pattern of emergence and awareness exhibited by many other anthropogenic environmental contaminants. Figure 1 provides a general timeline of PFAS emergence and awareness that includes categories of 1) synthesis/development, 2) commercial production, 3) health concerns, 4) environmental detection, and 5) reductions/alternatives.

ITRC has developed a series of fact sheets that summarizes 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

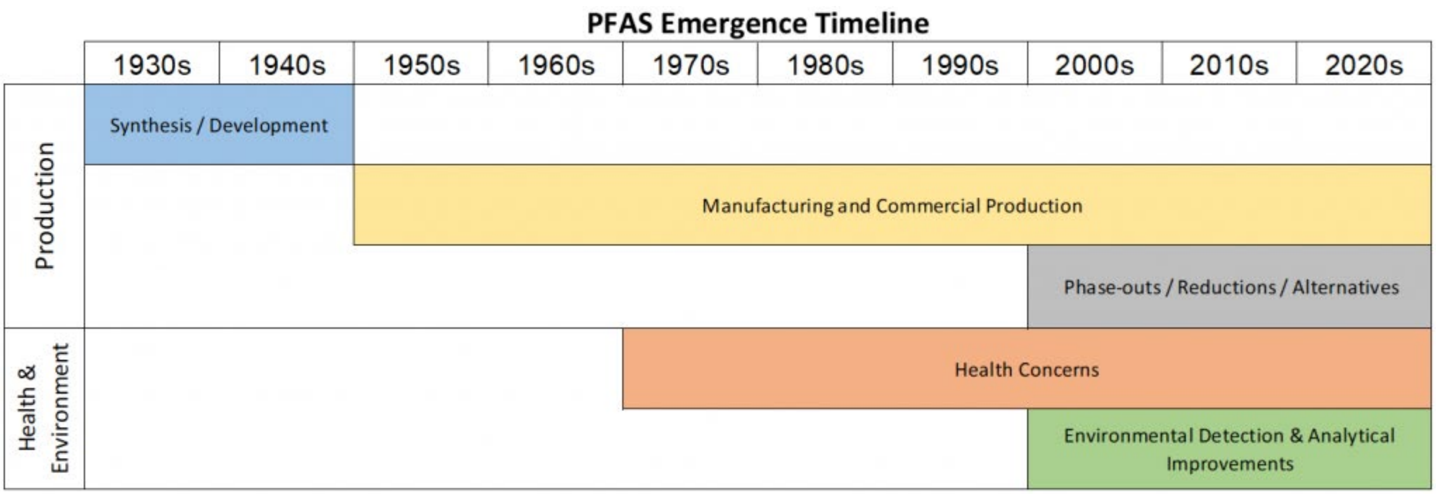

Figure 1. General timeline of PFAS emergence and awareness.

Graphic provides general indication of PFAS emergence and awareness by decade. Specific activities and events are described in more detail within the Guidance Document. "Reductions/alternatives" refers to reduction in production/use and includes other PFAS that have replaced legacy chemistry.

Source: J. Hale, Kleinfelder. Used with permission. PFAS-1, Figure 2-1.

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 been (and are) used to manufacture PFAS substances that contain perfluoroalkyl chains: side-chain fluorinated polymers, perfluoroalkyl acids and polyfluoroalkyl surfactants (USEPA 2003 Ref#858; Benskin, DeSilva, and Martin 2010; KEMI 2015 Ref#658; 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.

Table 1. Manufacturing processes and potential PFAAs produced

Manufacturing Process	Commonly Found Polyfluorinated Substances	Potential PFAAs Produced
Fluorotelomerization	FTS[1], FTCA[2], and FTOH	Linear PFCAs[3]
Electrochemical fluorination	FASE and FASAA	Branched and linear PFCAs & PFSAs[4]
[1]Fluorotelomer sulfonate (FTS): for example, may be found at aqueous film-forming foam (AFFF) sites; [2]Fluorotelomer carboxylic acids (FTCAs): for example, 5:3 FTCA may be found in landfill leachate; [3]Under certain instances, can produce mixture of linear and branched perfluoroalkyl carboxylates (PFCAs); [4]Perfluoroalkyl sulfonates (PFSAs).		

Glüge et al. (2020) categorized PFAS by uses according to industry application and practical use and identified more than 200 uses for more than 1,400 individual PFAS. An industry survey, reported in Buck et al. (2021), noted that only 256 of the 4,700 PFAS with CAS Registry Numbers are commercially relevant, with others of lesser environmental significance but potentially still occurring in the environment.

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 et al. 2015 Ref#654; CDC 2022). Concentrations of some PFAS (especially PFOS) in human blood have decreased since the early 2000s (ATSDR 2020 Ref#1861), around the same time of the voluntary phaseout of perfluorooctanyl chemistries by a major U.S. manufacturer (see below).

Publicly available health and toxicity studies are limited to only a small fraction of PFAS, and modern commercially available analytical technologies are typically capable of identifying and quantifying about 70 PFAS, but these lists are increasing. In the meantime, ATSDR is undertaking a national, multi-site PFAS health study to evaluate the health impacts of PFAS in drinking water (ATSDR 2020 Ref#1862).

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 early 2000s, analytical methods have been, and continue to be, developed with lower detection limits 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. 2007 Ref#1602; 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). UCMR5 is planned for 2023–2025, and is expected to include 29 PFAS.

Since the UCMR3, 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 2. As of June 2022, USEPA had issued interim health advisories for PFOA and PFOS in drinking water (USEPA 2022 Ref#2311). These replace the values USEPA issued in 2016. In addition, in June 2022 USEPA issued final health advisories for GenX chemicals and PFBS in drinking water (USEPA 2022 Ref#2311). See the ITRC PFAS Water and Soil Values Table posted on the fact sheets page for these values (https://pfas-1.itrcweb.org/fact-sheets).

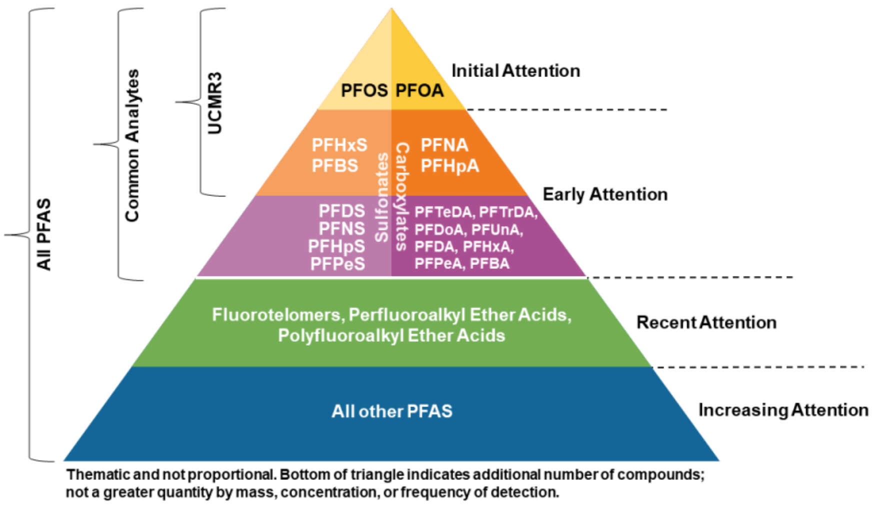

Figure 2. Emerging awareness and emphasis on PFAS occurrence in the environment.
Source: J. Hale, Kleinfelder. Used with permission. PFAS-1, Figure 2-16.

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 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 et al. 2015 Ref#875).

- In 2000, 3M, the principal worldwide manufacturer and sole U.S. manufacturer of PFOS, announced a voluntary phaseout of perfluorooctanyl chemistries, which included PFOS, PFHxS, PFDS, PFOA, and related precursors. (USEPA 2003 Ref#858; USEPA 2017 Ref#923; 3M Company 2017 Ref#172).
- In January 2006, USEPA initiated the PFOA Stewardship Program (USEPA 2006 Ref#861) in which the eight major manufacturing or processing companies committed to reducing the use of PFOA, other longer-chain PFCAs, and related precursors (USEPA 2017 Ref#923).
- 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; KEMI 2015 Ref#658; USEPA 2017 Ref#929). 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 has potentially offset the global reduction anticipated with the U.S. phaseout (OECD 2015 Ref#742). Further, the phaseout efforts do not prevent the import of materials containing PFAS to the United States.

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 polyfluoroalkylether acids (for example, GenX chemicals and ADONA) and other types of PFAS (Hori et al. 2006; OECD 2007 Ref#737; Herzke, Olson, and Posner 2012; Wang et al. 2013 Ref#872; Wang et al. 2015 Ref#875; Holmquist et al. 2016).

Many PFAS alternatives are structurally similar to their predecessors and manufactured by the same companies (CONCAWE 2016; Wang et al. 2015 Ref#875). 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 Ref#454). Several studies suggest some of the alternate PFAS chemistries may be similarly hazardous to the long-chain predecessors, although publicly available information on most replacement chemicals is limited (Wang et al. 2015 Ref#875; RIVM 2016; OECD 2015 Ref#742). Additional information related to replacement chemistries can be found in the Guidance Document.

4 PFAS Releases to the Environment

PFAS are and have been used in many industrial and consumer applications that may affect the environment or receptors by various mechanisms and to various degrees.

Some uses of PFAS are summarized in Table 2-5 of the Guidance Document, including (but not limited to):

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

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).

Figure 3 illustrates a conceptual PFAS life cycle.

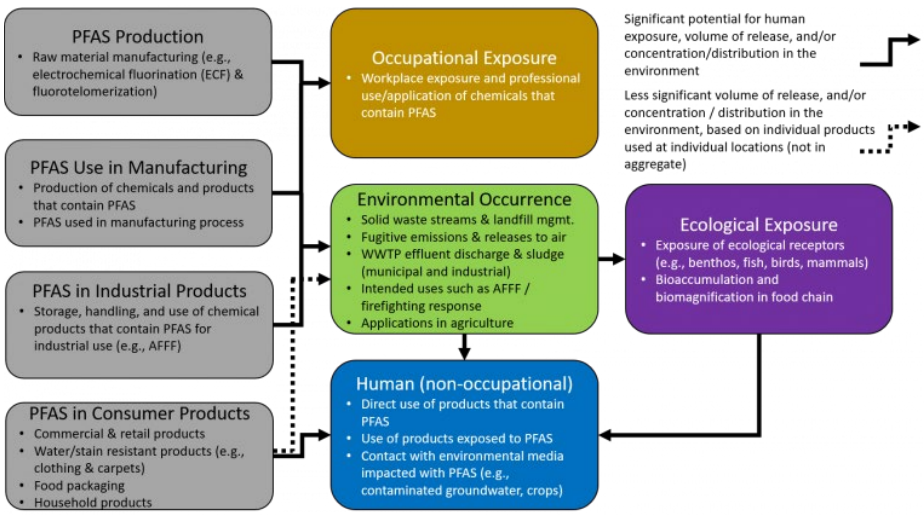

Figure 3. Generalized PFAS uses and relative exposure and environmental impact potential from PFAS life cycle. *Source: PFAS-1, Figure 2-2.*

5 References and Acronyms

The references cited in this fact sheet and further references can be found at https://pfas-1.itrcweb.org/references/. Reference numbers are included in this fact sheet for non-unique citations in the Guidance Document reference list.

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

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