

1 Introduction

Understanding the fate and transport of a chemical in the environment is fundamental to the investigation and remediation of any contaminated site. This fact sheet focuses on how the unique chemical and physical properties of PFAS affect their behavior in the environment. Additional information is available in the Guidance Document.

PFAS are a large family of compounds used in or to create non-stick coatings, textiles, paper products, some firefighting foams, and many other products. These compounds have many manufacturing and product applications because they repel oil and water, resist temperature extremes, and reduce friction. PFAS include compounds that vary in molecular weight and can have multiple structures and functional groups. Over the years, manufacturing and use of these compounds has resulted in their presence in the environment.

The scientific community is rapidly recognizing the environmental and health effects of PFAS. Some of the perfluoroalkyl acids (PFAAs), such as perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), are mobile, persistent, and bioaccumulative, and are not known to degrade in the environment (USEPA 2003b; ATSDR 2015; NTP 2016; CONCAWE 2016).

2 Physical and Chemical Properties

The physical and chemical properties of PFAS, in concert with the characteristics of the environmental system, determine the environmental behavior, including the compound's state and partitioning behavior (Banks, Smart, and Tatlow 1994). Partitioning can occur between neutral and ionic molecular forms, solid and liquid states, and between different media and biota (aqueous, pure phase, soil/sediment, biota, and atmospheric). The environmental behavior of many PFAS is further complicated by their surfactant properties.

Figure 1 illustrates key chemical and physical properties and distribution coefficients. Comparing the chemical and physical properties of different PFAS provides insight into similarities and differences in their environmental behavior and can inform investigation design:

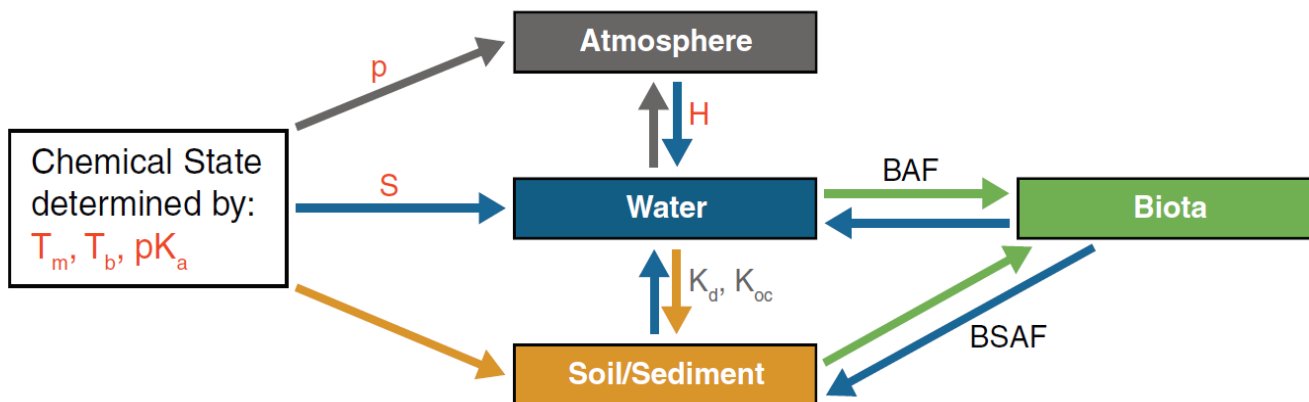


Figure 1. The role of key physical and chemical properties (shown in red) in influencing environmental compound behavior.

Other key distribution coefficients (BAF and BSAF shown in grey) are addressed in the Sections 5.1 (Table 5.1) and 9.2 of the Guidance Document. T_m = melting point; T_b = boiling point; pK_a = acid dissociation constant; p = vapor pressure; S = solubility; H = dimensionless Henry's law constant; K_d = soil and sediment partitioning coefficient; K_{oc} = organic carbon partitioning coefficient; BAF = bioaccumulation factor; and BSAF = biota-sediment accumulation factor.

ITRC has developed a series of fact sheets that summarize recent science and emerging technologies regarding PFAS. The information in this and other PFAS 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 describes:

- Physical and chemical properties of PFAS that effect compound state and partitioning in the environment
- Partitioning and transport behavior of PFAS
- Abiotic and biotic transformation of select PFAS in the environment

Fate and Transport for Per- and Polyfluoroalkyl Substances (PFAS) *continued*

There is a large variation in published data on chemical and physical properties of PFAS. Reliable physical and chemical properties of PFAS are scarce (for example, vapor pressure and Henry's law constants), and some of the available values are modeled, as opposed to directly measured. With a few exceptions (for example, Koc), many of the available properties are based on the acid form of the PFAA, which is not present in the environment in aqueous media, unless at pH <3, which is not typical. Table 1 provides a general summary of the available chemical and physical property information for PFCAs and the sensitivity of this information in relation to the acid vs. anionic form. For some properties, such as bioconcentration factor and bioaccumulation factor properties the anionic forms of PFOA and PFOS do have documented information (Martin et al. 2003), while other properties are not readily available.

See the Guidance Document for a detailed description of these properties and the uncertainties in the published values. The Physical and Chemical Properties Table provided as a separate spreadsheet to the Guidance Document summarizes some of the physical and chemical properties that are available for PFAS (<https://pfas-1.itrcweb.org/4-physical-and-chemical-properties/>).

Table 1. Available physical and chemical properties for PFCAs.

PFAA State	CAS No.	S _w	P ^o	K _h	K _{ow}	K _{oc}	Environmentally Relevant?
Acid	Y	Y	Y	E	E	E	No
Cation:							No
NH ⁺	Y	Y	N	N	N	N	
Li ⁺	Y	Y	N	N	N	N	
Na ⁺	Y	Y	N	N	N	N	Yes
Anion	M	N	N	N	N	Y	

S_w = solubility in water P^o = vapor pressure K_h = Henry's Law Constant K_{ow} = octanol/water partition coefficient
 K_{oc} = organic carbon partition coefficient Y = data available N = no data available M = data may be available for some
 E = data estimated, not directly measured

3 Fate and Transport Processes

Partitioning, transport, and transformation of PFAS occurs across multiple media types. While most research literature focuses on PFAAs (especially PFOS and PFOA), processes affecting precursor PFAS that can degrade to PFAAs over time are also important. See Section 5 of the Guidance Document for additional discussions of fate and transport.

Partitioning

PFAS most commonly detected in the environment typically have a carbon-fluorine "tail" and a nonfluorinated "head" consisting of a polar functional group, as illustrated for PFOS and PFOA in Figure 2. The tail is hydrophobic and lipophobic, while the head groups are polar and hydrophilic.

Important PFAS partitioning mechanisms include hydrophobic and lipophobic effects, electrostatic interactions, and interfacial behaviors. The hydrophobic and lipophobic effects drive the association with organic carbon in soils. Electrostatic interactions are a function of the charge of the polar functional group at the head of the molecule. Because the head and the tail compete, partitioning to interfaces of environmental media such as soil/water, water/air, and water/NAPL co-contaminants can occur (Guelfo and Higgins 2013; McKenzie et al. 2016; Brusseau 2018).

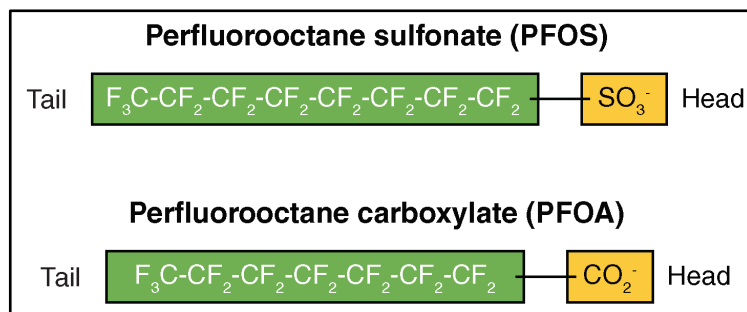


Figure 2. The head and tail structure of PFOS and PFOA.

The partitioning behavior of perfluoroalkyl carboxylates (PFCAs) and perfluoroalkane sulfonates (PFSAs) has been studied more in depth than that of other PFAS. At relevant environmental pH values, PFCAs and PFSAs are present as anions and are therefore relatively mobile in groundwater (Xiao et al. 2015) but tend to associate with the organic carbon fraction that may be present in soil or sediment (Higgins and Luthy 2006; Guelfo and Higgins 2013).

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Sorption and retardation generally increase with increasing perfluoroalkyl tail length (Guelfo and Higgins 2013; Sepulvado et al. 2011), indicating that the short-chain PFASs and PFCAs are retarded less than their long-chain counterparts (PFOS and PFOA, respectively). In addition, PFASs tend to sorb more strongly than PFCAs of equal chain length (Higgins and Luthy 2006), and branched isomers appear to have less sorption than linear (Kärman et al. 2011).

Transport

The resistance of most PFAS to biotic or abiotic degradation (except for precursor transformation discussed herein) means that physical transport processes are critical for PFAS transport and potential for exposure.

Advection, Dispersion, Diffusion

Processes such as advection, dispersion, and diffusion can strongly influence the migration of PFAS within and between media. Advection (the flow-related transport of compounds within a fluid such as water or air) drives PFAS mobility in many cases. Advection, however, does not reduce concentration along the flow path.

Small-scale changes in air and surface water velocities can disperse contaminants in multiple directions, contributing to rapid vertical mixing of PFAS and cross-media transport (for example, surface water to sediment and deposition from air to surface soil).

In air and water, molecules moving in response to a concentration gradient is known as diffusion. In surface water and air, mixing caused by turbulence is also referred to as eddy diffusion. Diffusion in groundwater is often ignored because diffusion rates are slow relative to advection. However, diffusion of contaminant mass into lower permeability soils or site materials such as clays, bedrock, and concrete may enhance the long-term persistence of PFAS in groundwater.

Deposition

While many PFAS exhibit relatively low volatility, airborne transport of some PFAS is a relevant migration pathway through industrial releases (for example, stack emissions). Once airborne, some PFAS are subject to photooxidation and transport, but they can eventually accumulate to measurable levels in soil and surface water through atmospheric deposition (Young and Mabury 2010; Ahrens and Bundschuh 2014; Rankin et al. 2016). Atmospheric deposition can occur as dry or wet deposition, both of which are relevant for PFAS (Barton, Kaiser, and Russell 2007, 2010; Dreyer et al. 2010; Taniyasu et al. 2013). During dry deposition, PFAS that are preferentially associated with liquid or particle phases in air (aerosols) can be naturally deposited onto surfaces by sedimentation, diffusion, or other processes. When precipitation washes out these PFAS-containing aerosols, the process is known as wet deposition.

Leaching

PFAS present in unsaturated soils are subject to downward leaching during precipitation or irrigation events that promote dissolution of soil-bound contaminant mass (Sepulvado et al. 2011; Ahrens and Bundschuh 2014). This process is a potential driver of PFAS transport from surface soils to groundwater and surface water, because releases often involve surface applications or atmospheric deposition. Leaching is also potentially relevant for plant uptake and transport of PFAS contained in landfill waste without adequate leachate control (Benskin, Muir, et al. 2012; Yan et al. 2015; Lang et al. 2017). Leaching potential is a function of both media properties (for example, pH and increased partitioning with organic-rich soil) and PFAS structural properties (for example, ionic charge, and chain length) (Gellrich, Stahl, and Knepper 2012).

Surfactant Properties and Micelle Formation

PFAS exhibit surfactant properties because they often contain hydrophobic and hydrophilic portions, which affect transport in ways that are complex and not well understood. By design, many PFAS preferentially form films at the air-water interface, with the hydrophobic carbon-fluorine (C-F) tail oriented towards the air and the hydrophilic head group dissolved in the water (Krafft and Riess 2015). This behavior influences aerosol-based transport and deposition and suggests that PFAS accumulates at water surfaces (Prevedouros et al. 2006). This preference for the air-water interface may also influence vadose zone transport, where unsaturated conditions provide significant air-water interfacial area. Adsorption of PFOS and PFOA at the air-water interface can increase the retardation factor for aqueous-phase transport.

Critical PFAS transport processes include: advection, dispersion, diffusion, atmospheric deposition, and leaching.

- Atmospheric transport and subsequent deposition can lead to measurable PFAS accumulation away from their point of release.
- Downward leaching of PFAS in unsaturated soils during precipitation or irrigation events is site specific and occurs as a function of media and PFAS structural properties.
- At high concentrations PFAAs can form micelles, which could enhance or reduce adsorption on carbon and minerals.

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At higher concentrations, PFAAs can form aggregates in which the hydrophilic portions interact with the water phase and the hydrophobic portions interact with each other (for example, micelles or hemimicelles). This tendency to aggregate may cause PFAAs to act differently at high concentrations and to enhance or reduce adsorption in the environment.

PFAS Transformation

Both biotic and abiotic transformations of some polyfluorinated substances (precursors) may form PFAAs. However, PFAAs likely do not degrade or otherwise transform under ambient environmental conditions. Unlike the fully fluorinated PFAAs, precursor PFAS contain carbon-hydrogen (C-H) and carbon-oxygen (C-O) bonds that are subject to a variety of biotic and abiotic reactions that ultimately form terminal end products. While available studies on both biotic and abiotic transformation of precursor PFAS primarily consist of controlled laboratory experiments (discussed below), a number of field studies have demonstrated the importance of precursors at a variety of sites (for example, Weber et al. 2017; Dassuncao et al. 2017).

- Precursor PFAS can transform to PFAAs via biotic and abiotic processes.
- Transformation rates are highly variable and site specific.
- PFAAs are not known to transform under ambient environmental conditions.

Abiotic Transformation

Abiotic processes that can transform precursors under ambient environmental conditions include hydrolysis, photolysis, and oxidation. Hydrolysis of some precursors, followed by subsequent biotransformation, can produce PFCAs and PFSAAs. For example, PFOS is produced from perfluorooctane sulfonyl fluoride (POSF) (Martin et al. 2010) and PFOA and other PFCAs are produced by the hydrolysis of fluorotelomer-derived precursors (Washington and Jenkins 2015). While direct photolysis of PFAS has not been observed, indirect photolysis of some precursors, notably fluorotelomer alcohols (FTOHs), does occur in the atmosphere and can contribute to PFCA deposition (Armitage, MacLeod, and Cousins 2009; Yarwood et al. 2007).

Perfluoroalkane sulfonamides can also degrade abiotically through oxidation in the atmosphere to form PFCAs in yields that may be 10 times greater than FTOHs (Martin et al. 2006). Shorter-chain PFSAAs such as PFBS also can be produced by oxidation reactions between hydroxyl radicals and sulfonamido derivatives (D'Eon et al. 2006). Finally, in some cases, abiotic precursor transformations may not initially produce any PFAA though eventual formation of PFAAs may still be possible (Martin et al. 2010).

Biotic Transformation

While PFOA, PFOS, and other PFAAs are resistant to microbial degradation, numerous studies have reported biotransformations of various precursors similar to the abiotic transformations discussed herein. The current literature indicate that numerous aerobic biotransformation pathways exist, with relatively rapid kinetics and all polyfluorinated precursors may have the potential to aerobically biotransform to PFAAs. Fewer studies have been published regarding anaerobic biotransformation of PFAS. FTOHs have been observed to biotransform anaerobically, but appear to form stable polyfluorinated acids rather than PFCAs or PFSAAs (Zhang, Szostek et al. 2013; Allred et al. 2015). Defluorination of PFOA and PFOS was observed during anaerobic oxidation of ammonium under iron reducing conditions (Huang and Jaffé 2019).

4 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/acronyms/>.



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