

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, food packaging, 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, but share the feature of linked carbon atoms bonded to fluorine atoms at most or all available carbon bonding sites. Additional discussion of the definitions of PFAS is included in Section 2.2 of the Guidance Document. Over the years, manufacturing and use of these compounds, in concert with their recalcitrance, has resulted in their widespread occurrence in the environment.

The scientific community is rapidly expanding its understanding of the environmental and health effects of PFAS. Some PFAS, such as perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), are mobile, persistent, and bioaccumulative, and are not known to transform in the environment (USEPA 2003 Ref#858; ATSDR 2020 Ref#1942; NTP 2016; CONCAWE 2016).

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

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.

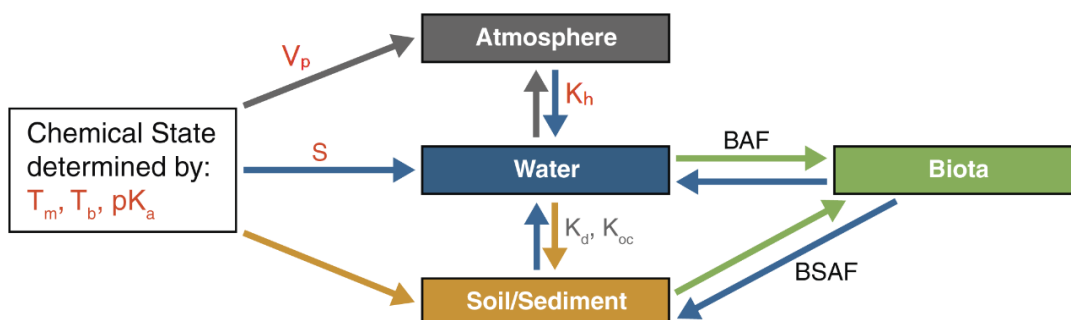


Figure 1. The role of key physical and chemical properties (shown in red) in influencing environmental compound behavior.

Other key distribution coefficients (BAF and BSAF shown in grey) are addressed in the Sections 5.5 (Table 5.1) and 9.2 of the Guidance Document. T_m = melting point; T_b = boiling point; pK_a = acid dissociation constant; V_p = vapor pressure; S = solubility; K_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.

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Physical and chemical properties for a variety of PFAS are available in the literature. While some experimentally derived values are available, the majority of values are estimated using predictive mathematical techniques that predict properties of compounds from knowledge of their chemical structure. A combination of empirically derived physical and chemical properties and modeled values is invaluable to predictive development of conceptual site models, but lacks the site-specific detail required to definitively resolve PFAS behavior and partitioning at impacted sites.

PFAS can be cationic, anionic, or zwitterionic and most site characterization work has focused on anionic perfluoroalkyl acids (PFAAs) with limited attention to the cationic or zwitterionic PFAS. With few exceptions (for example, K_{oc}), much of the data for available properties are based on the acid form of the compound, which is not present at environmentally relevant pH values ($pK_a < 3$).

Common physical and chemical properties of several PFAS, related references, and the uncertainties in the published values, are discussed in Section 4 of the Guidance Document and provided in Table 4-1 (see the External Data Tables on <https://pfas-1.itrcweb.org>). Bioaccumulation factors and bioconcentration factors, which are used to understand bioaccumulation and associated risk, are discussed and presented in Sections 5.5 (aquatic organisms) and 5.6 (plants) and in Tables 5-1 and 5-2 (see the External Data Tables on <https://pfas-1.itrcweb.org>).

3 Fate and Transport Processes

Partitioning, transport, and transformation of PFAS occur across multiple media types. Most regulatory attention focuses on perfluoroalkyl acids (PFAAs), especially PFOS and PFOA, due to their stability and known toxicity at low concentrations. However, processes affecting other PFAS, such as transformation of polyfluorinated precursor PFAS to PFAAs, affect conceptual model development and our ability to assess the potential for PFAS-impacted sites to become long-term PFAA sources. See Section 5 of the Guidance Document for additional discussions of fate and transport.

Partitioning

The PFAS most commonly detected in the environment typically have a hydrophobic fluoroalkyl “tail” and a polar, hydrophilic nonfluorinated “head” consisting of a polar functional group, as illustrated for PFOS and PFOA in Figure 2. PFAAs are typically considered amphiphilic, as they have hydrophilic (head) and hydrophobic (tail) regions.

The predominant mechanisms driving PFAS partitioning include hydrophobic and lipophobic effects, electrostatic interactions, and interfacial behaviors. Electrostatic effects are a function of the charge of the polar functional group at the head of the molecule and is one of the processes that generally drive the association with organic carbon in soils. As is the case for all surfactants, the competing nature of the head and tail groups results in accumulation along interfaces of environmental media such as soil/water, water/air, and water/NAPL co-contaminants (Guelfo and Higgins 2013; McKenzie et al. 2016; Brusseau 2018).

The partitioning behaviors of perfluoroalkyl carboxylates (PFCAs) and perfluoroalkane sulfonates (PFASs) have been studied more in depth than that of other PFAS. At relevant environmental pH values, PFCAs and PFASs are present as anions and are therefore relatively mobile in groundwater (Xiao et al. 2015) but may tend to associate with the organic carbon fraction present in soil or sediment or aggregate at the air-water interface within the vadose zone (Higgins and Luthy 2006; Guelfo and Higgins 2013). PFAS partitioning due to electrostatic interactions has been shown to be nonlinear in some cases; Xiao et al. (2019) demonstrated that the variation in the coefficient of sorption for several zwitterionic PFAS to soils (for example, loams, clay loams) implies an increase in sorption as the PFAS concentrations decreased. The significant non-linearity of zwitterionic PFAS observed by Xiao et al. (2019) also exhibited a high degree of hysteresis that was not related to soil organic matter or surface complexation and was postulated to be due to entrapment. Generally, cationic and zwitterionic PFAS can be expected to sorb to soils and sediment more strongly than anionic PFAS due to their higher electrostatic attractions to negatively charged organic matter and clays. Both solid phase and interfacial sorption and, as a result, retardation generally increase with increasing perfluoroalkyl chain length (Guelfo and Higgins 2013; Sepulvado et al. 2011; Psillakis et al. 2009), indicating that the short-chain PFASs and PFCAs are retarded less than their long-chain counterparts. In addition, PFASs tend to sorb more strongly than PFCAs of equal chain length (Higgins and Luthy 2006; Psillakis et al. 2009), and branched isomers appear to have less solid phase sorption than linear (Kärman et al. 2011).

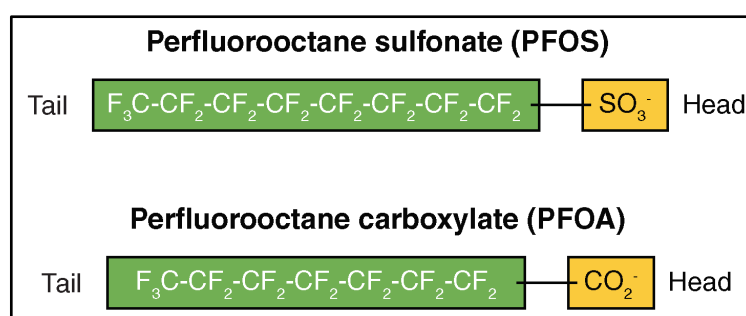


Figure 2. The tail and head structure of PFOS and PFOA.

Source: PFAS-1, Figure 2-7.

Transport

The resistance of most PFAS to biotic or abiotic transformation (except for precursor transformation) 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. Recently there has been an increase in the focus on biosolids contribution to PFAS leaching into receiving waters as a result of the practice of land application of biosolids as fertilizer (Schaefer et al. 2022).

Leaching is also potentially relevant for plant uptake and transport of PFAS contained in landfill waste without adequate leachate control (Benskin et al. 2012 Ref#10; Yan et al. 2015 Ref#278; Lang et al. 2017). Leaching potential is a function of both media properties (for example, affinity for the air-water interface, 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 (Brusseau 2018). At higher concentrations, PFAAs may form aggregates in which the hydrophilic portions interact with the

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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water phase and the hydrophobic portions interact with each other (for example, micelles or hemimicelles), but more research is needed to understand this behavior.

PFAS Transformation

Both biotic and abiotic transformations of some polyfluorinated substances (precursors) may form PFAAs. However, PFAAs likely do not 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 have the potential to 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 with half-lives of 50–90 years are produced by the hydrolysis of fluorotelomer-derived precursors at neutral pH (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 transform 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 transformation, 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 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/>. 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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