



## 5 Environmental Fate and Transport Processes

This section provides current information about PFAS fate and transport in the environment. Understanding relevant fate and transport processes for PFAS is critical in evaluating the potential risk from a release, where to look for PFAS following a release, and what treatment alternatives may be effective. The available information about fate and transport processes varies between the different PFAS. PFAS fate and transport is a rapidly evolving field of science.

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### 5.1 Fate and Transport Introduction

#### 5.1.1 Overview of PFAS Fate and Transport

PFAS fate and transport describes the behavior of these compounds following their release to the environment. This includes the physical, chemical, and biological processes that influence distribution of PFAS in various media, as well as the extent of migration within and between media (for example, plume development, groundwater discharge to surface water). Given the wide variety of PFAS, it is not surprising that they collectively exhibit a wide range of different physical and chemical characteristics that can affect their behavior in the environment. This adds to the complexity of fate and transport assessments and highlights the risk in making broad assumptions based on the behavior of a few well-studied PFAS.

Understanding relevant fate and transport processes for PFAS is critical in answering several key questions:

- **What is the potential risk from a PFAS release?** An understanding of fate and transport processes provides the basis for defensible predictions about occurrence, migration, persistence, and potential for exposure.
- **Where do I need to look for PFAS following a release?** Knowledge of PFAS fate and transport characteristics strongly informs site characterization by providing insight on where efforts should be focused and developing an appropriate CSM.
- **How can I treat PFAS?** Establishing how these compounds behave in the environment is important in developing and/or selecting PFAS treatment strategies because this helps establish the potential effectiveness of a particular treatment.

#### 5.1.2 Factors Affecting PFAS Fate and Transport

Factors that influence PFAS fate and transport can be broadly divided into two categories:

- **PFAS characteristics:** Critical factors include the chain length, the ionic state of the compound (for example, the charge(s) carried by the molecule at a typical environmental pH), the type of functional group(s), and the extent of fluorination (for example, perfluorinated versus polyfluorinated compounds). These properties strongly influence the type and extent of PFAS partitioning and transformation that can be expected to occur. A description of these physical-chemical properties is provided in [Section 4](#).
- **site characteristics:** Site characteristics generally define the nature of the source but also have an effect on PFAS-media interactions. Potentially relevant characteristics include soil type (including properties such as

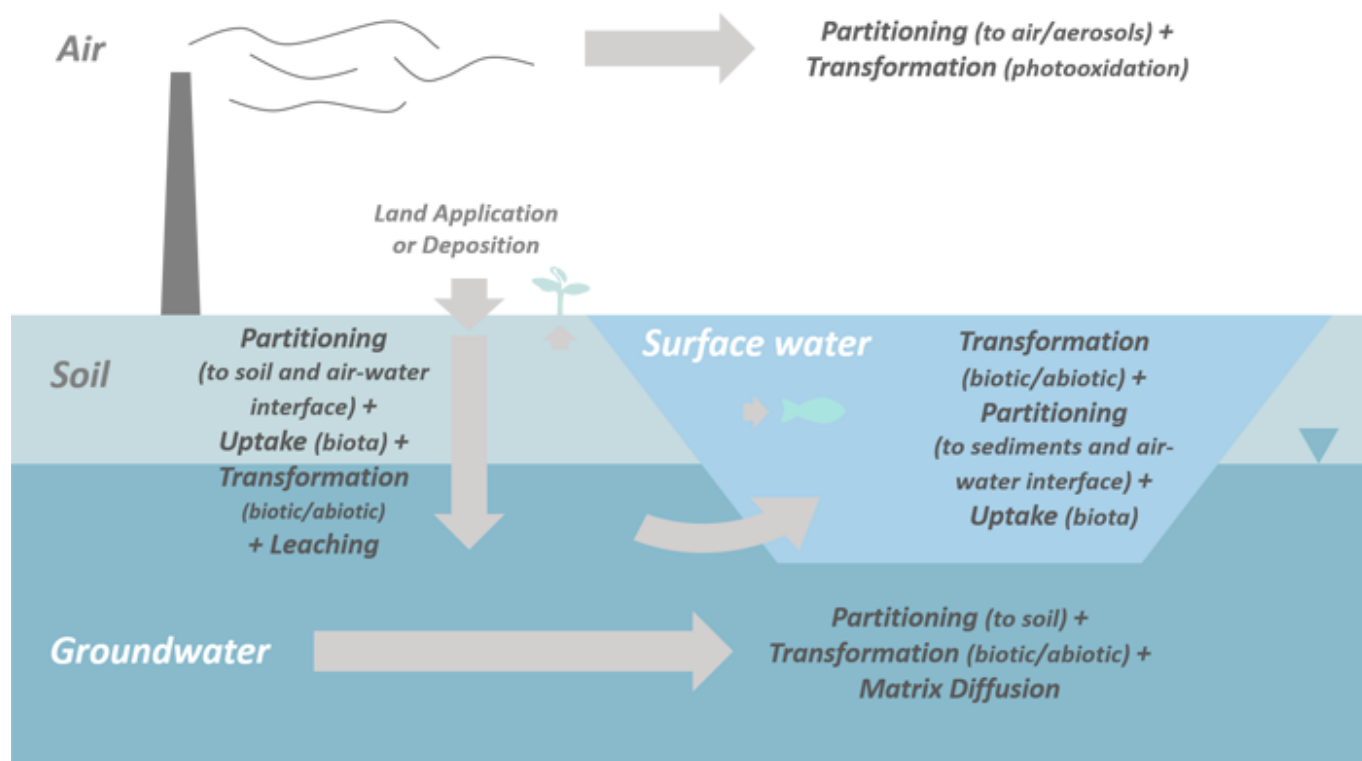
permeability, surface charge, organic carbon content, exchange capacity, mineralogy, water content), depth to groundwater, oxidation-reduction conditions, precipitation/infiltration rates, surface water and groundwater flow rates, prevailing atmospheric conditions, and the presence of co-contaminants.

The characteristics of sites with releases of PFAS often share many similarities with sites having releases of other contaminants, although there are some source scenarios that are relatively unique to PFAS (see [Section 2.6](#) for description of source scenarios). Although many PFAS chemicals may share similar characteristics, such as resistance to transformation, those same PFAS may have widely varying physical-chemical properties, such as those associated with partitioning. As a result, PFAS fate and transport in the environment can be quite different from other contaminants.

### 5.1.3 Section Organization

This section includes a detailed description of several processes that are particularly relevant for PFAS fate and transport and are illustrated in [Figure 5-1](#).

- **Partitioning:** Both hydrophobic partitioning to organic carbon and electrostatic interactions between charged surfaces and PFAS are discussed, along with the tendency of PFAS to aggregate at air-water interfaces. These processes can greatly affect migration in the environment by promoting retention within sediments and unsaturated soils, as well as retardation within groundwater. Varying degrees of retention on solids can contribute to differential transport where certain PFAS (for example, short-chain, anionic) are more rapidly transported than others.



**Figure 5-1. Fate and transport processes relevant for PFAS.**

Source: D. Adamson, GSI. Used with permission.

- **Media-specific processes:** The potential impact of processes such as diffusion into low-permeability matrices, atmospheric transport, and leaching from soil to groundwater are described. Unlike the broader processes of partitioning and transformation, most of these processes are unique to specific media or a specific cross-media transport pathway.
- **Transformation:** Although a number of individual PFAS, such as perfluoroalkyl acids and perfluoroalkyl ether carboxylic acids, are highly persistent due to the strength of the C-F bond, a number of polyfluorinated substances can be partially degraded via several different biological and abiotic mechanisms. Transformation of these precursors to PFAAs has been shown to occur in a variety of environmental media and can result in unexpected temporal and spatial trends in PFAS occurrence. The susceptibility of individual PFAS to

transformation processes can also influence how each will bioconcentrate and bioaccumulate within various biotic species.

- **Uptake into biota and plants:** Once released into the environment, PFAS will migrate to both terrestrial and aquatic systems. Uptake into plants can occur within affected areas and may transfer PFAS to wildlife and humans that consume those plants. Some compounds have a propensity to bioaccumulate and then biomagnify up the food chain, with relatively low levels in invertebrates and fish and higher levels observed in animals at the top of the food chain (for example, seals, seabirds, polar bears).

As noted previously, the physical-chemical properties of PFAS, and the influence of these properties on PFAS fate and transport within environmental media, are critical in determining how these compounds behave after they are released. To date, our understanding of PFAS fate and transport has relied largely on assumptions based on these physical-chemical characteristics, even though the specific parameter values have proven challenging to estimate; however, there is an increasing amount of lab- and field-derived data that has improved the empirical basis for understanding PFAS fate and transport. This section focuses on findings from peer-reviewed studies that directly evaluated PFAS fate and transport and provided key insight on the processes described above. The material in this section is also intended to provide a technical basis for subsequent sections on site characterization ([Section 10](#)) and treatment of PFAS ([Section 12](#)).

## 5.2 Phase Partitioning

### 5.2.1 Introduction

PFAS most commonly detected in the environment typically have a carbon-fluorine tail and a nonfluorinated head consisting of a polar functional group (see [Section 2.2](#) for more information about naming conventions and terminology). The tail is hydrophobic and generally lipophobic (attracted neither to water nor to nonpolar organic matter), while the head groups can be polar and hydrophilic (attracted to water) ([Buck et al. 2011](#)). The competing tendencies of the head and the tail can lead to a widespread yet uneven distribution in the environment. Given the heterogeneity of subsurface environments, soils with different surface charges, organic carbon, interfaces between air and water, and interfaces with water and hydrocarbon co-contaminants, multiple partitioning mechanisms should be considered when characterizing PFAS fate and transport. PFAS may also exhibit different behavior depending on concentration, such as the tendency to form micelles at high concentrations ([Section 5.2.2.2](#)). Although the structure of PFAS makes them generally oil- and water-resistant in many products (for example, dry surface coatings), in the aqueous phase, PFAS may not exhibit lipophobic tendencies, as shown by the ability of a variety of PFAS to partition to phospholipid bilayers (bacterial membranes) ([Jing, Rodgers, and Amemiya 2009](#)) ([Fitzgerald et al. 2018](#)).

Important PFAS partitioning mechanisms include hydrophobic effects, electrostatic interactions, and interfacial behaviors. The hydrophobic effects drive the association with organic carbon in soils, a process PFAS have in common with other organic contaminants (for example, chlorinated solvents). Electrostatic interactions are a function of the charge of the polar functional group at the head of the molecule. For instance, natural soils and aquifer materials often have a net negative surface charge that can repel the negatively charged heads of PFAAs, which are usually present as anions in environmental media. Due to the competing properties of the head and the tail, partitioning to interfaces of environmental media can occur, such as soil/water, water/air, and water/nonaqueous phase liquid (NAPL) co-contaminants ([Guelfo and Higgins 2013](#); [McKenzie et al. 2016](#); [Brusseau 2018](#)).

### 5.2.2 Considerations for PFAS Partitioning

#### 5.2.2.1 Pure Phase PFAS

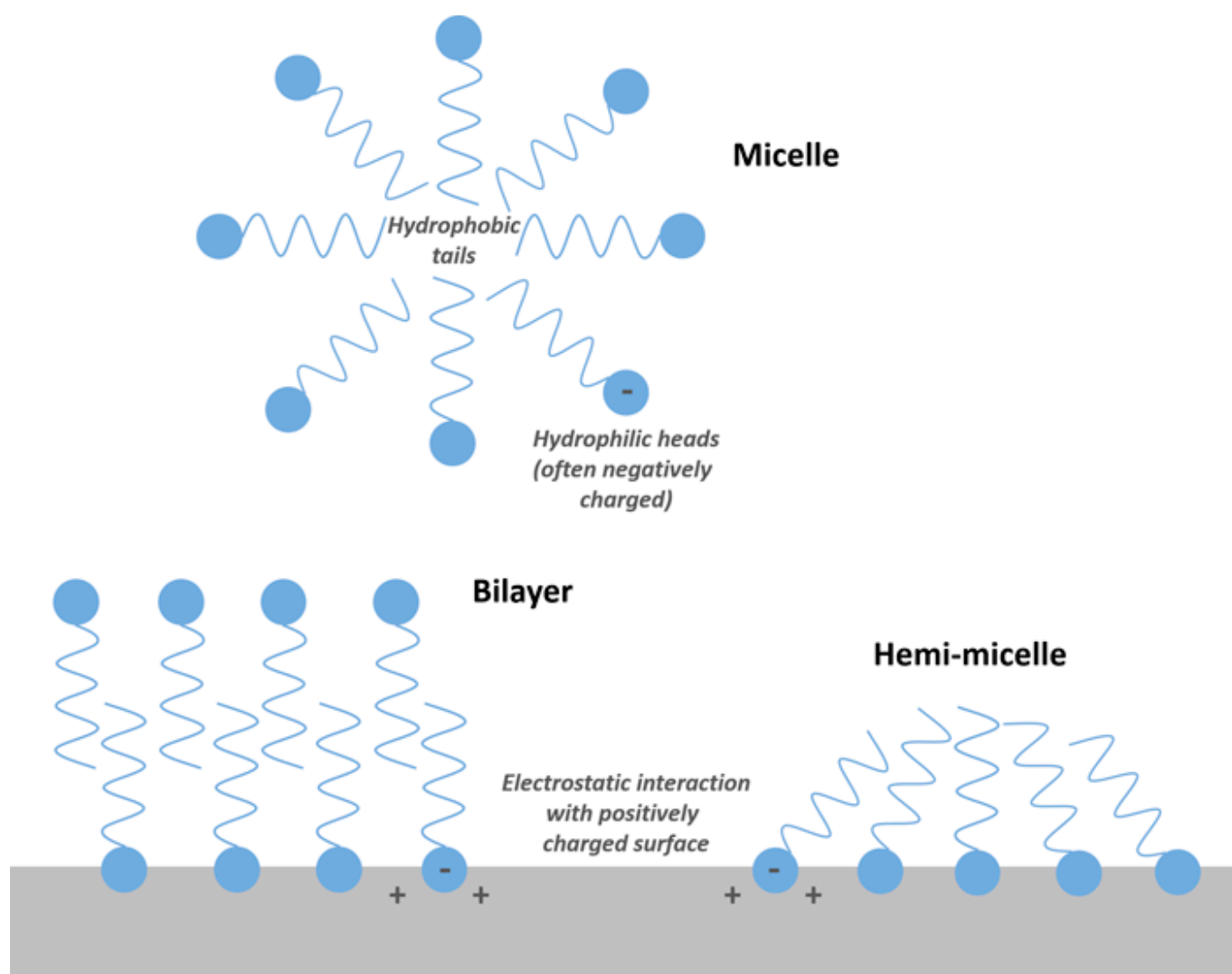
Due to high aqueous solubility, PFAS occurrence as a separate phase in the environment (for example, solid PFAS, LNAPL PFAS, or DNAPL PFAS) is uncommon. Although PFAS may exist as solid salts, typical product applications involve miscible solutions that are frequently mixtures of many different compounds. Several of these compounds exhibit relatively high solubility in water (the Physical and Chemical Properties Table, [Table 4-1](#) provided as a separate Excel file), defined by [Ney \(1995\)](#) as exceeding 1,000 mg/L water. For example, PFOA has a reported solubility of 9,500 mg/L at 25°C ([USEPA 2017n](#)). Note that PFAS interactions with NAPL co-contaminants within the subsurface have been reported and can impact migration in the subsurface ([Section 5.2.5](#)).

#### 5.2.2.2 PFAS Forms Micelles and Foam

A surfactant is a substance that tends to lower the surface tension of a liquid into which it is dissolved. Because PFAS exhibit

this property and are heat stable, they have frequently been used as wetting agents, including in AFFF to form a thin film of water over the fuel source. As a consequence of lowering the surface tension of water, foaming may result. The lipophobic/hydrophobic nature of the fluorocarbon tail and the reduction in surface tension can contribute to aggregation at air-water interfaces, potentially retarding PFAS migration in the subsurface (Brusseau 2018).

At higher concentrations, PFAAs can aggregate into single-component or mixed micelles, where the hydrophilic portions interact with the water phase and the hydrophobic portions interact with each other. These aggregates can take the form of micelles, hemimicelles, or even simple bilayer structures (Figure 5-2) (also see Section 4.2.7). For PFOS, the concentration above which micelles will form (that is, the critical micelle concentrations (CMC)) has been cited as 500–5,000 mg/L, but hemimicelles may form at concentrations as low as 0.001 times the CMC (Yu et al. 2009) (Du et al. 2014) (Brusseau 2018). This tendency to aggregate may cause PFAAs to act differently at high concentrations (for example, during release) and could enhance (or in some cases reduce) adsorption on carbon and minerals in the environment (Yu et al. 2009) (Du et al. 2014). For example, adsorption of the hydrophilic portions of PFAS (that is, the “heads”) onto positively charged adsorbent surfaces can contribute to the formation and accumulation of hemimicelles near surfaces, and this has been reported to increase the near-surface aqueous concentration of PFAS relative to that measured in bulk solution (Yu et al. 2009).



**Figure 5-2. Illustration of the formation of PFAS micelles, hemimicelles, and bilayers. Also shown is an example of aggregation at a positively charged surface. Note that the opposite effect (electrostatic repulsion of PFAS) can occur if the surface is negatively charged.**

*Source: D. Adamson, GSI. Used with permission.*

### 5.2.3 Partitioning to Solid Phases

PFAS can partition to a number of different solid-phase materials, including soils and sediments (Higgins and Luthy 2006) and membranes (Fitzgerald et al. 2018). PFAS may also partition to mobile colloids, resulting in facilitated transport (Brusseau et al. 2019). The partitioning of PFAS to solid-phase minerals is the most widely studied and is thought to occur

through two primary processes: 1) sorption to organic carbon via hydrophobic interactions, and 2) electrostatic interactions ([Higgins and Luthy 2006](#)). The relative contribution of each process can vary depending on surface chemistry and other geochemical factors.

In particular, understanding the partitioning behavior of PFCAs and PFSA to soil organic carbon has been the subject of significant research. PFCAs and PFSA are present as organic anions at relevant environmental pH values, and are therefore relatively mobile in groundwater ([Xiao et al. 2015](#)), but will also tend to associate with the organic carbon fraction of soil or sediment ([Higgins and Luthy 2006](#)) ([Guelfo and Higgins 2013](#)) in the saturated zone. Sorption to organic carbon generally increases with increasing perfluoroalkyl tail length ([Higgins and Luthy 2006](#); [Guelfo and Higgins 2013](#); [Sepulvado et al. 2011](#); [Campos Pereira et al. 2018](#)), indicating that the short-chain PFSA (for example, PFBS) and PFCAs (for example, PFHxA) are less retarded than their long-chain counterparts (PFOS and PFOA, respectively). In addition, PFSA tend to sorb more strongly than PFCAs of equal chain length ([Higgins and Luthy 2006](#)), and branched isomers are less sorptive than linear isomers ([Karrman et al. 2011](#)).

PFAS partitioning to solids is variable and uncertain, and depends on site-specific factors.

Table 4-1 presents the range of available organic carbon partitioning coefficients ( $K_{oc}$ ) for environmentally relevant PFAS.  $K_{oc}$  is a soil organic carbon-normalized sorption coefficient and may serve as a useful parameter for evaluating transport potential. However, this parameter does not directly capture any contributions from electrostatic interactions, meaning that estimating retardation in groundwater by measuring the fraction of organic carbon ( $f_{oc}$ ) in soil in combination with a literature-derived  $K_{oc}$  value may underestimate (or in some cases, overestimate) retardation.

[Li, Oliver, and Kookana \(2018\)](#) compiled data from several literature studies to show that the bulk partitioning coefficients ( $K_d$ ) estimated for various PFAS included in these studies were best correlated with organic carbon content and pH. However, a study by [Barzen-Hanson \(2017\)](#) showed a general lack of correlations between soil parameters (such as organic carbon) and partition coefficients derived for some PFAS, such as anionic fluorotelomer sulfonates as well as several cationic and zwitterionic PFAS. [Anderson, Adamson, and Stroo \(2019\)](#) used field data from a large number of sites with AFFF releases to establish that organic carbon significantly influenced PFAS soil-to-groundwater concentration ratios, and they used statistical modeling to derive apparent  $K_{oc}$  values for 18 different PFAS based on these data. Soil type and the nature of the organic carbon also strongly influence sorption of PFAS associated with hydrophobic partitioning. For example, [Zhi and Liu \(2018\)](#) reported that the PFAS sorption potential of pyrogenic carbonaceous material (for example, biochar) was 14–780 times higher than humic-based material with a comparable fraction of organic carbon.

Understanding the effects of sorption associated with hydrophobic partitioning on contaminant transport typically relies on assumptions that 1) there is equilibrium between contaminants in the solid phase and the aqueous phase, and 2) sorption is reversible. In idealized systems, PFAS sorption kinetics vary by constituent, but equilibrium is generally achieved over several days to weeks ([Xiao, Ulrich, et al. 2017](#)). However, in surface water bodies and groundwater, sorption is more likely to be subject to mass transfer effects, and temporal changes in conditions (for example, episodic releases, precipitation events) may also make assumptions about equilibrium challenging. The meta-analysis by [Anderson, Adamson, and Stroo \(2019\)](#) showed that PFAS soil-to-groundwater concentration ratios across multiple sites were strongly influenced by the degree of flushing that had occurred. These results suggest that mass transfer limitations are contributing to increased soil retention at poorly flushed sites (those with low precipitation and deep groundwater), such that equilibrium assumptions for hydrophobic partitioning are not necessarily valid. In addition, there is evidence that desorption occurs more slowly than sorption for certain PFAS ([Higgins and Luthy 2006](#); [Chen, Reinhard, et al. 2016](#); [Zhi and Liu 2018](#)). These findings are particularly relevant for more strongly sorbing compounds like PFOS ([Chen, Jiao, et al. 2016](#)) and have important implications for PFAS fate and transport. For example, any portion of the released PFAS that is strongly retained within sediments or the soil matrix would be more persistent but likely less bioavailable and less subject to migration. Lab-based  $K_d$  values (derived using sorption isotherms) would also likely underestimate the impact of sorption during fate and transport modeling.

The contribution of electrostatic interactions to partitioning is highly dependent on soil type and soil solution chemistry. Most soils contain both fixed-charge and variably charged surfaces, such that the net charge on the soil, as well as charge of functional groups of individual PFAS, can be strongly influenced by pH. For example, the net negative charge on most clay minerals can result in electrostatic interactions with cationic functional groups that are present on some PFAS; however, many PFAS, such as PFOA and PFOS, are anionic at environmentally relevant pH, such that electrostatic repulsion in soils

dominated by negatively charged minerals would enhance the mobility of anionic PFAS relative to cationic and zwitterionic PFAS. Changes in pH potentially impact these electrostatic processes by altering surface charges (or possibly the ionic nature of the PFAS). As a result, decreases in pH have been shown to enhance sorption by anionic PFAS such as PFOS and other PFAAs (Higgins and Luthy 2006), although the buffering capacity of some soils (for example, carbonates) may mitigate these impacts. Furthermore, increased levels of polyvalent cations such as  $\text{Ca}^{2+}$  can lead to increased partitioning to soil (Higgins and Luthy 2006; McKenzie et al. 2015). The effects of these various electrostatic interactions can be complex in an environmental setting and may hinder or facilitate transport of PFAS following a release.

For PFAS such as PFOA and PFOS that are anionic at environmentally relevant pH, measuring the anionic exchange capacity in representative soils may serve as a positive indicator of the importance of electrostatic interactions with minerals. However, because soil pH can range considerably, pH can also serve as a useful measure of potential PFAS mobility. Measurements of cation concentrations or the ionic strength of an aqueous solution may also provide useful information on the potential contribution of electrostatic attraction to enhanced partitioning (through bridging and/or neutralization of negative surface charges). As noted above, additional research is needed to further evaluate if any of these bulk parameters can be used predictively for fate and transport studies (Barzen-Hanson 2017). Regardless, interactions with organic carbon are insufficient to reliably predict PFAS partitioning coefficients, thus field values may be more appropriate for understanding PFAS transport (Knight et al. 2019; Anderson et al. 2016; Li, Oliver, and Kookana 2018).

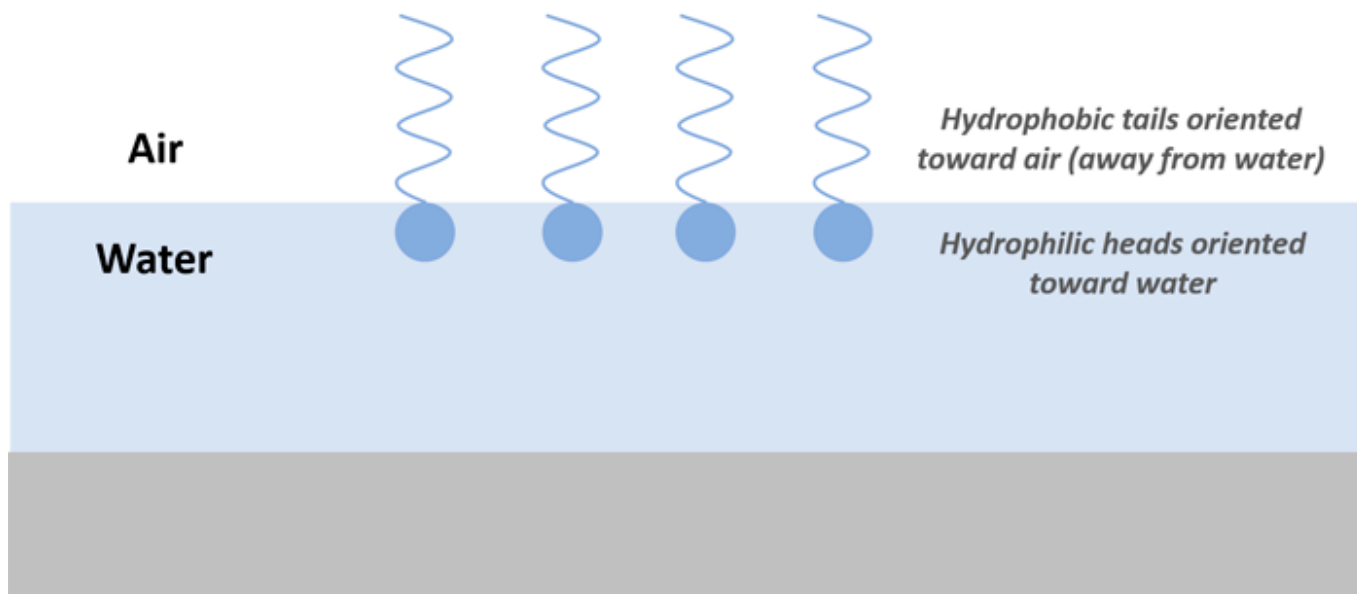
## 5.2.4 Partitioning to Air

PFAAs are, in general, far less volatile than many other groundwater contaminants. Measured vapor pressures for some select PFAAs are available, including the acidic forms of PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUNA), and perfluorododecanoic acid (PFDDA) (Barton, Botelho, and Kaiser 2008; Kaiser et al. 2005), and fluorotelomer alcohols (Krusic et al. 2005). Henry's law constants for several PFAS are reported in Section 4.2.6. Vapor pressures of these compounds are generally low and water solubilities are high, limiting partitioning from water to air (USEPA 2000a). However, under certain conditions, particularly within industrial stack emissions, PFAS can be transported through the atmosphere. In particular, volatiles like FTOHs may be present in the gas phase and anionic PFAS may be sorbed to particulates (Ahrens et al. 2012).

Kaiser et al. (2010) demonstrated the partitioning of PFOA to workplace air from water and dry surfaces. Partitioning to air from these substrates appears to be dependent on conditions within the substrate, with lower pH environments contributing more PFOA mass to air. The protonated acid form of PFOA has an elevated vapor pressure, which may explain these observations (Kaiser et al. 2005). Interestingly, these authors showed that more PFOA partitions from dry surfaces than from water and may contribute significantly to workplace exposures.

### 5.2.4.1 Partitioning to Air/Water Interfaces

As described above, PFAS often exhibit surfactant properties because many contain hydrophobic and hydrophilic portions. The impacts of these properties on transport are complex and have not been extensively investigated. By design, many PFAS will preferentially form films at the air-water interface, with the hydrophobic carbon-fluorine (C-F) tail oriented toward the air and the hydrophilic head group dissolved in the water (Krafft and Riess 2015) (Figure 5-3). This behavior influences aerosol-based transport and deposition, and suggests that accumulation of PFAS at water surfaces will occur (Prevedouros et al. 2006). In addition, this preference for the air-water interface may have important implications for vadose zone transport, where unsaturated conditions provide significant air-water interfacial area (Brusseau 2018; Brusseau et al. 2019). This includes the potential for enhanced retention at the water table and the capillary fringe, which is the subject of significant ongoing research. For example, Brusseau (2018) showed that adsorption of PFOS and PFOA at the air-water interface can increase the retardation factor for aqueous-phase transport; this interfacial process accounted for approximately 50% of the total retention in a model system with 20% air saturation. Using field data, Anderson, Adamson, and Stroo (2019) reported that soils with higher clay contents were associated with lower soil-to-water concentration ratios for multiple PFAS. The authors surmised that the higher water content within these clay-rich zones (relative to zones with more coarse-grained material) decreased the air/water interfacial area available for PFAS partitioning and thus decreased overall soil retention. This pattern was observed despite the potential for negatively charged clay surfaces to reduce anionic PFAS adsorption through electrostatic repulsion.



**Figure 5-3. Example of expected orientation and accumulation of PFAS at air-water interface.**

*Source: D. Adamson, GSI. Used with permission.*

### 5.2.5 Partitioning into NAPL Co-Contaminants

PFAS and petroleum hydrocarbon fuels in the form of NAPLs may commingle at fire training areas, fire response sites, and other locations where fuels were used or disposed concurrently with PFAS-containing materials. In these settings, the released petroleum hydrocarbon fuel forms a NAPL into which the PFAS may partition and accumulate along the NAPL/water interface (Brusseau 2018). These processes may result in increased PFAS mass retained in NAPL source zones, increased PFAS sorption and resulting retardation, and greater persistence of dissolved PFAS (Guelfo and Higgins 2013; McKenzie et al. 2016; Brusseau 2018).

The presence of NAPL may have other effects on PFAS. The presence of biodegradable NAPL, such as petroleum light nonaqueous phase liquids (LNAPLs), may significantly alter the biogeochemistry and oxidation-reduction conditions in the subsurface. For example, subsurface petroleum LNAPLs remaining from a petroleum-based fire tend to locally deplete the concentration of oxygen and other electron acceptors and elevate the concentration of methane. The LNAPL creates a localized zone of anoxic reducing conditions where PFAS aerobic transformation processes are inhibited, and anaerobic transformation processes may occur. These transformation processes are discussed in more detail in Section 5.4.

## 5.3 Media-Specific Migration Processes

The potential impacts of processes such as diffusion into low-permeability matrices, atmospheric transport, and leaching from soil to groundwater are described. Unlike partitioning processes, which involve the exchange of chemicals between media, the following describes processes that occur within specific media that may be important considerations for PFAS migration.

### 5.3.1 Diffusion In and Out of Lower Permeability Materials

Diffusion is the movement of molecules in response to a concentration gradient. Diffusion in groundwater is often ignored because diffusion rates are slow relative to advection. However, contaminant mass in groundwater can diffuse into lower permeability soils or bedrock. Back-diffusion out of these low permeability materials may result in the long-term persistence of PFAS in groundwater even after source removal and remediation. Due to the lack of degradation of PFCAs and PFASs, back-diffusion of these PFAS is also likely to be a more significant process than for conventional contaminants such as chlorinated solvents. PFAS may also diffuse into site materials such as concrete. For example, Baduel (2015) reported that PFAS had penetrated 12 cm into a concrete pad at a fire training area, and diffusion was identified as a contributing process.

The potential impacts of diffusion on PFAS persistence in natural soils are a topic of ongoing research. Determining appropriate diffusion coefficients for the range of PFAS that may be present following a release is a key element in

understanding how this process impacts PFAS persistence.

### 5.3.2 PFAS Transport via Air

Many PFAS have been measured in air ([Section 6.1](#)) and are known to be released to air from a variety of sources ([Section 2.6](#)). Air serves as an important transport media for PFAS, allowing PFAS to disperse in all wind directions, contributing to global dispersion, and leading to localized PFAS deposition to soils and surface water in the vicinity of emission sources (for example, [Shin et al. 2012](#)) which is of potential concern to site investigations.

The role of atmospheric transport depends on PFAS-specific properties such as vapor-particle partitioning, and mechanisms can be complex. Aerosols, representing a suspension of solid particles and liquid droplets in the air, provide a variety of environmental media and surfaces within or upon which a range of PFAS partitioning behavior can be observed. For example, [McMurdo et al. \(2008\)](#) described the release of concentrated PFAS aerosols from a water surface (where PFAS are often located). Airborne transport of PFAS is a potentially relevant migration pathway due to the common types of industrial release (for example, stack emissions). The specific means of PFAS releases from industrial sources have not been extensively studied, but could involve processes such as droplet mobilization from drying and agitation of liquid surfaces. The importance of other sources, such as combustion emissions or windblown foam from fire training and fire response sites, on the fate and transport of PFAS in air may need to be assessed.

Differences between process temperatures (such as those found in drying operations in textile coating operations) and ambient air can plausibly be expected to affect PFAS partitioning. Both water droplets and solid particles can convey PFAS in stack emissions, and some PFAS may exist as vapors at elevated temperatures in stack exhaust. PFAS partitioning can also change as stack effluent cools, for example, as PFAS-containing droplets evaporate and leave solid particulate matter. Technologies such as fabric filters and wet scrubbers are effective at controlling particle emissions, though applications to PFAS have not been formally evaluated.

Once airborne, PFAS can occur in a gaseous state or be incorporated within particulate matter or other aerosols suspended within the air. The composition of the gas phase will be dependent on the industrial process(es) contributing to emissions. Neutral volatile precursor compounds, such as FTOHs, are often the dominant PFAS present in the gas phase ([Table 17-1A](#)) and can account for at least 80% of the total PFAS mass in ambient air in an urban area ([Ahrens et al. 2012](#)).

Over the open oceans and in remote regions, FTOHs also dominate neutral PFAS and almost all are present in the gas phase ([Bossi R. 2016](#); [Lai et al. 2016](#); [Wang, Xie, et al. 2015](#); [Dreyer et al. 2009](#)). In contrast, ionic PFAS, such as PFOA and PFOS, characterized by low vapor pressure and high water solubility, tend to be the dominant species found in airborne particulate matter. PFOA is associated with smaller, ultrafine particles, while PFOS is associated with larger, coarser fractions in both urban and semirural areas ([Ge et al. 2017](#); [Dreyer et al. 2015](#)). Wet and dry deposition are the major mechanisms of removal of PFAS from the atmosphere and can occur from the scavenging of particle-bound PFAS or partitioning of gaseous PFAS to water droplets ([Dreyer et al. 2010](#); [Barton 2007](#); [Hurley et al. 2004](#)). PFAS are commonly found in precipitation (rain and snow), with wet and dry deposition estimated to occur on a time scale of a few days ([Chen, Jiao, et al. 2016](#); [Lin et al. 2014](#); [Taniyasu et al. 2013](#); [Zhao, Zhou, et al. 2013](#); [Dreyer et al. 2010](#); [Kwok et al. 2010](#); [Liu et al. 2009](#); [Barton 2007](#); [Kim and Kannan 2007](#); [Hurley et al. 2004](#)).

Atmospheric deposition can occur as dry or wet deposition, both of which are relevant for PFAS ([Barton 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 via settling, diffusion, or other processes. When precipitation contributes to washout of these PFAS-containing aerosols, the process is known as wet deposition. Wet and dry deposition are the major mechanisms for removal of PFAS from the atmosphere and can occur from the scavenging of particle-bound PFAS or partitioning of gaseous PFAS from water droplets ([Dreyer et al. 2010](#); [Barton 2007](#); [Hurley et al. 2004](#)). Deposition is considered a sink term for the atmosphere because mass is removed and the potential for longer range atmospheric transport is reduced. However, this same process thus represents a potential source of PFAS to terrestrial and aquatic environments. Once settled, PFAS adsorbed onto soils or other surfaces (including indoor surfaces) can be resuspended when particulate matter is disturbed by wind or other physical means. See [Section 6.1](#) for further discussion of atmospheric deposition of PFAS.

Short-range atmospheric transport and deposition can result in PFAS contamination in terrestrial and aquatic systems near points of significant emissions, impacting soil, groundwater, and other media of concern ([Davis et al. 2007](#)). Evidence of releases has been observed in areas where hydrologic transport could not plausibly explain the presence of PFAS in groundwater, with the extent of contamination reaching several miles from sources and in distribution patterns independent



of regional hydrology ([Frisbee et al. 2009](#); [Post 2013](#); [Post, Cohn, and Cooper 2012](#); [NYS DOH 2016b](#); [NH DES 2017](#); [VT DEC 2016b](#)). Releases of ionic PFAS from factories are likely tied to particulate matter ([Barton et al. 2006](#)), which settle to the ground in dry weather and are also wet-scavenged by precipitation ([Slinn 1984](#); [Sehmel 1984](#)).

Predictive models have been applied to estimate PFAS deposition ([Shin et al. 2012](#)). The American Meteorological Society/USEPA regulatory model AERMOD system contains modules to estimate both wet and dry deposition of both aerosols and gases ([USEPA 2016a](#)). It is important to note that validation of these deposition modules has not been completed. Hence, uncertainty exists, and deposition model predictions should be interpreted with caution. Nevertheless, the model may be useful in understanding the pattern of PFAS found in soil and groundwater in the vicinity of PFAS emission sources ([Shin et al. 2012](#)). Key input parameters for emissions from a smokestack or vent include the height of the release point and adjacent structures, source emission rates and particle size distributions, stack effluent properties (temperature and volumetric flow rate), meteorological data, local topography, and land use characteristics. Temporal variability can be important as AERMOD operates on an hourly basis. Several states have recently engaged in or reviewed AERMOD applications to industrial sources, and regulatory agencies including the New Jersey Department of Environmental Protection, New Hampshire Department of Environmental Services, and the Vermont Department of Environmental Conservation can provide valuable information and advice on deposition model application.

Long-range transport processes are responsible for the wide distribution of neutral and ionic PFAS across the earth as evidenced by their occurrence in biota, surface snow, ice cores, seawater, and other environmental media in remote regions as far as the Arctic and Antarctic ([Bossi R. 2016](#); [Kirchgeorg et al. 2016](#); [Rankin et al. 2016](#); [Wang, Xie, et al. 2015](#); [Codling et al. 2014](#); [Wang et al. 2014](#); [Kirchgeorg et al. 2013](#); [Kwok et al. 2013](#); [Benskin, Muir, et al. 2012](#); [Cai, Yang, et al. 2012](#); [Cai, Xie, et al. 2012](#); [Cai, Zhao, et al. 2012](#); [Ahrens, Xie, and Ebinghaus 2010](#); [Dreyer et al. 2009](#); [Young et al. 2007](#)). Distribution of PFAS to remote regions far removed from direct industrial input is believed to occur from both (1) long-range atmospheric transport and subsequent degradation of volatile precursors and (2) transport via ocean currents and release into the air as marine aerosols (sea spray) ([DeSilva, Muir, and Mabury 2009](#); [Armitage et al. 2009](#); [Wania 2007](#); [Ellis et al. 2004](#)).

### 5.3.3 Leaching

PFAS present in unsaturated soils are subject to downward leaching during precipitation, flooding, or irrigation events that promote dissolution of soil-bound contaminant mass ([Sepulvado et al. 2011](#)) ([Ahrens and Bundshuh 2014](#)). This process can result in PFAS transport from surface soils to groundwater and surface water, because releases often involve surface applications (for example, AFFF and biosolids) 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 media properties (for example, pH, redox conditions, and increased partitioning with organic carbon in soil), PFAS structural properties (for example, ionic charge and chain length), and site conditions that influence the degree of flushing (for example, precipitation rates and depth to groundwater) ([Gellrich, Stahl, and Knepper 2012](#); [Anderson, Adamson, and Stroo 2019](#)).

Although some studies have reported PFAS transport by leaching (Lindstrom et al. 2011 ([Lindstrom et al. 2011](#); [Filipovic et al. 2015](#); [Hellsing et al. 2016](#); [Bräunig et al. 2017](#)), others have observed long-term retention of longer chain PFAS on shallow soils after extended percolation ([Sepulvado et al. 2011](#); [Stahl et al. 2013](#); [Anderson et al. 2016](#)). In a long-term lysimeter study using a silty soil with some clay and natural rainfall, PFOA and shorter chained PFCAs and PFASs traveled more rapidly through the soil column than did PFOS ([Stahl et al. 2013](#)). However, even after 5 years, 96.88% and 99.98% of the mass of PFOA and PFOS, respectively, remained in the soil. This retention of PFOA and PFOS may increase the long-term persistence of the (soil-bound) source ([Baduel 2015](#)).

## 5.4 Transformations

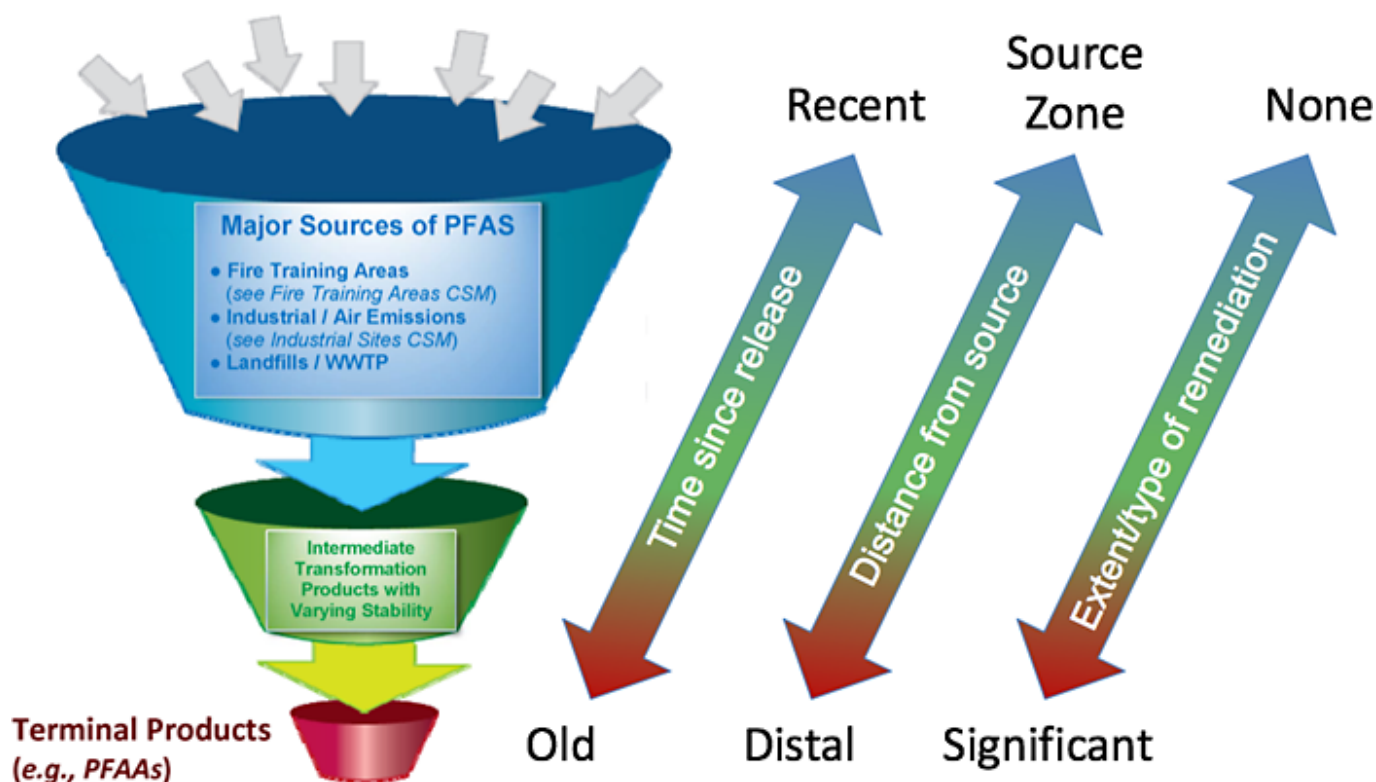
### 5.4.1 Introduction

Numerous studies have reported both biotic and abiotic transformations of some polyfluorinated PFAS. Polyfluorinated PFAS shown to transform are referred to as *precursors* and typically form PFAAs. However, PFAAs have not been shown to degrade or otherwise transform under ambient environmental conditions. The fundamental differences between polyfluorinated precursors and perfluorinated chemicals that affect transformation potential are the presence, location, and number of carbon-hydrogen (C-H) bonds and *potentially* carbon-oxygen (C-O) bonds throughout the alkyl carbon chain. Specifically, PFAS with C-H bonds are subject to a variety of biotic and abiotic reactions that ultimately result in the formation of shorter chain PFAAs. Although available studies on both biotic and abiotic transformation of polyfluorinated PFAS primarily consist of controlled laboratory experiments (discussed below), an increasing number of field studies have also been published

demonstrating the relevance of precursors at a variety of sites with different source scenarios (for example, (Weber et al. 2017) (Dassuncao et al. 2017)).

### 5.4.2 PFAA Precursors

Although PFAAs are limited to a fairly small number of homologous compounds that differ only with respect to carbon chain length and the terminal functional group, the number and diversity of polyfluorinated chemicals is vast. Thousands of PFAS are currently thought to exist (or existed) on the global market, and the vast majority are polyfluorinated (Wang, DeWitt, et al. 2017) (Section 2). However, transformation studies published to date are available for only of a small subsample of these PFAS, and therefore, much uncertainty exists regarding 1) the extent to which precursor transformation occurs on a global scale, 2) which environmental compartments represent the majority of transformation, 3) relevant environmental conditions that affect transformation processes, and 4) transformation rates and pathways. Nevertheless, the fraction of total PFAS that is comprised of PFAAs, that represent the total composition of PFAS both globally and (in particular) at contaminated sites, should be expected to increase due to transformation over time, over distance, and due to remediation, as depicted in Figure 5-4.



**Figure 5-4. Illustration of precursor transformation resulting in the formation of PFAAs.**

Source: L. Trozzolo, TRC, and C. Higgins, Colorado School of Mines. Used with permission and based on [This Photo](#) by Unknown Author is licensed under [CC BY-SA](#).

### 5.4.3 Atmospheric Transformations

Although direct emission of PFCAs has declined globally, atmospheric emission of PFCa precursors has been increasing (Thackray and E Selin 2017) (Wang et al. 2014). Similarly, emission rates for PFSA precursors are increasing globally (Löfstedt Gilljam et al. 2016). Atmospheric transport is an important distribution mechanism for PFAS on both regional and global scales, which has led to documented PFAS occurrence (including PFAAs and PFAA precursors) in remote locations, including arctic regions (Young et al. 2007). Ocean currents also transports PFAS to arctic regions, although the relative contribution of each mechanism is not well understood (Yeung et al. 2017). Regardless of the relative contributions of atmospheric and oceanic transport, atmospheric transport and subsequent transformation of precursors has been documented as an important source of PFAAs in the environment (Young et al. 2007).

Widely measured PFCa precursors in the atmosphere include primarily FTOHs (Thackray and E Selin 2017) (Young and Mabury 2010) (Martin et al. 2002). Wang, Xie, et al. (2015) collected marine atmospheric samples during an expedition research cruise that spanned the Southern Ocean, Atlantic Ocean, and Arctic Ocean; samples were analyzed for several precursors, including FTOHs, FTAs, FOSAs, and FOSEs. The researchers found that FTOHs were the predominant species.

Atmospheric transformation of precursors, including FTOHs, may be an important source of PFCAs in the environment, such as those identified in the Arctic ([Schenker et al. 2008](#)). Although direct photolysis of PFAS has not been observed, indirect photolysis of some precursors does occur in the atmosphere and can be a significant contributor to PFCA deposition ([Armitage, MacLeod, and Cousins 2009](#); [Yarwood et al. 2007](#)). For example, hydroxyl and chlorine radicals degrade 8:2 FTOH to PFOA in the atmosphere through reactions with hydroxyl and chlorine radicals, with similar reactions for 6:2 and 4:2 FTOHs ([Ellis et al. 2004](#)) and perfluoroalkylsulfonamides, which may degrade to PFCAs and PFSAs ([Martin et al. 2006](#)). In addition to FTOH, other semivolatile precursors may also undergo atmospheric transformation to PFCAs ([Young and Mabury 2010](#)).

Atmospheric transformation of precursors to PFCAs is a multistep process, and the PFCA product yield is a function of several factors, including ratio of nitros oxides (NO<sub>x</sub>) and peroxy radicals (RO<sub>2</sub>) species. High NO<sub>x</sub> levels result in lower long-chain PFCA yields, thus long-chain PFCA yields are typically higher in remote regions ([Young and Mabury 2010](#)). [Thackray and E Selin \(2017\)](#) calculated theoretical maximum yields for formation of PFOA and PFNA from 8:2 FTOH that were highly variable, ranging from far less than 1% to 40% (PFOA) or 80% (PFNA), depending on local photochemical conditions.

## 5.4.4 In Situ Transformations

### 5.4.4.1 Abiotic Pathways

Abiotic processes shown to cause transformations of precursors in soil and water under ambient environmental conditions include hydrolysis, photolysis, and oxidation. Hydrolysis of some precursors, followed by subsequent biotransformation, can produce PFSAs. An important example is the production of PFOS from perfluorooctane sulfonyl fluoride (POSF) ([Martin et al. 2010](#)). Other hydrolysis reactions produce PFCAs. In particular, [Washington and Jenkins \(2015\)](#) showed that the hydrolysis of fluorotelomer-derived polymeric precursors forms monomeric precursors of PFOA and other PFCAs with half-lives of 50–90 years at neutral pH. Also, oxidation of precursors by hydroxyl radicals can occur in natural waters, with the fluorotelomer-derived precursors being oxidized more rapidly than electrochemical fluorination (ECF)-derived precursors ([Gauthier and Mabury 2005](#); [Plumlee, McNeill, and Reinhard 2009](#)). Shorter chain PFCAs as well as PFSAs such as perfluorobutane sulfonate (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 (for example, the formation of various polyfluorinated sulfonamido intermediate compounds from ECF-derived precursors), though eventual formation of PFAAs may still be possible.

### 5.4.4.2 Aerobic Biological Pathways

Evidence of aerobic biotransformation is provided from studies of PFAS composition throughout the continuum of wastewater treatment (see [Arvaniti \(2015\)](#) for a comprehensive review), field studies at AFFF-impacted sites (for example, [Houtz et al. 2013](#); [McGuire et al. 2014](#)) ([Anderson et al. 2016](#); [Weber et al. 2017](#)), and most authoritatively from microcosm experiments.

The literature on aerobic biotransformation collectively demonstrates, or indirectly supports, conclusions such as the following:

- Numerous aerobic biotransformation pathways exist with relatively rapid kinetics.
- All polyfluorinated precursors studied to date have the potential to aerobically biotransform to PFAAs.
- Aerobic biotransformation of various fluorotelomer-derived precursors *exclusively* results in the formation of PFCAs, including PFOA.
- Aerobic biotransformation of various ECF-derived precursors *primarily* results in the formation of PFSAs, including PFOS.

In detail, most commonly studied in microcosm experiments have been the 6:2 and 8:2 FTOHs in soil, sludge, or aqueous matrices. Although observed degradation rates and intermediates are variable among these studies, ≤ C8 PFCAs have been consistently observed as terminal transformation products ([Dinglasan et al. 2004](#); [Wang, Szostek, Buck, et al. 2005](#); [Wang, Szostek, Folsom, et al. 2005](#); [Liu et al. 2007](#); [Saez, de Voogt, and Parsons 2008](#); [Wang et al. 2009](#)). However, a pure culture experiment with *P. chrysosporium* (a white-rot fungus) reported much lower PFCA yields with alternate pathways ([Tseng et al. 2014](#)). Other telomer-derived polyfluorinated PFAS investigated include the 6:2 fluorotelomer mercapto alkylamido sulfonate ([Weiner et al. 2013](#)), the 6:2 fluorotelomer sulfonate ([Wang et al. 2011](#)), the 4:2, 6:2, and 8:2 fluorotelomer thioether amido sulfonates ([Harding-Marjanovic et al. 2015](#)), the perfluorooctane amido quaternary ammonium salt ([Mejia-Avenidaño et al. 2016](#)), the 6:2 fluorotelomer sulfonamide alkylamine, and the 6:2 fluorotelomer sulfonamide alkylbetaine ([D'Agostino and Mabury 2017](#)). All demonstrate the formation of PFCAs with variable rates and inferred pathways. Aerobic

biotransformation of various ECF-derived polyfluorinated PFAS has also been demonstrated in several studies. Studied PFSA precursors include N-ethyl perfluorooctane sulfonamido ethanol ([Rhoads et al. 2008](#); [Zhao et al. 2016](#); [Zhang et al. 2017](#)), N-ethyl perfluorooctane sulfonamide ([Mejia Avendaño and Liu 2015](#)), and perfluorooctane sulfonamide quaternary ammonium salt ([Mejia-Avendaño et al. 2016](#)). All demonstrate formation of PFASs with variable rates and inferred pathways.

#### 5.4.4.3 Anaerobic Biological Pathways

Only two studies have been published to date conclusively demonstrating biotransformation of polyfluorinated PFAS under anaerobic conditions. In both instances FTOHs were studied. Both studies demonstrated the production of stable polyfluorinated acids under methane-reducing conditions with much slower kinetics relative to aerobic biotransformation ([Zhang, Szostek, et al. 2013](#)) ([Allred et al. 2015](#)). In general, anaerobic biotransformation of polyfluorinated PFAS is not expected to be a significant source of environmental PFAAs.

#### 5.4.5 Polymer Transformation

Polymeric substances in the PFAS family include fluoropolymers, polymeric perfluoropolyethers, and side-chain fluorinated polymers ([Buck et al. 2011](#)). Detailed descriptions of these polymers appear in [Section 2.2.2.1](#). Briefly,

- fluoropolymers are high-molecular weight solid plastics (> 100,000 Daltons, or Da according to [Henry et al. \(2018\)](#)) containing a carbon polymer backbone with fluorine directly attached to backbone carbon atoms.
- polymeric perfluoropolyethers contain an ether polymer backbone with F directly attached to carbon atoms. These polymeric PFAS are complex and mainly used as surfactants and surface protectants.
- side-chain fluorinated polymers contain a nonfluorinated polymeric backbone with fluorinated side chains; these are synthesized from telomer-derived precursors.

Polymer transformation research has indicated the following.

- Given the wide range of estimated half-lives, modeling assumptions for estimating the half-lives, different levels of residuals present in the polymer studied, highly variable molecular weights of the polymers studied with different surface area and size and with different extraction protocols, the polymer degradation studies are inconsistent.
- Other environmental conditions that need to be considered are redox, pH, temperature, percent moisture, and microbial activity in the soil microcosms for these long-term studies.
- Additional research is needed primarily on the biotransformation of side-chain fluorinated polymers, which are potential precursors to PFAAs.

Side-chain fluorinated polymers are widely used for many commercial and industrial applications as surfactant and surface-protecting products ([Buck et al. 2011](#)). Therefore, understanding the biotransformation potential of these polyfluorinated polymers is essential. However, few studies have reported on the potential biotransformation of side-chain polymers—for example, the fluorotelomer-based urethane polymer ([Russell et al. 2010](#)). Given the complexity of side-chain fluorinated polymers, there are many discrepancies among these studies. Primarily, the inability to monitor polymer concentrations is problematic. Because analytical methods for direct quantitation of polymers are not available, all the studies except [Rankin et al. \(2014\)](#) monitored suspected FTOH degradation products rather than the disappearance of the polymer ([Wang, Szostek, Buck, et al. 2005](#); [Liu et al. 2007](#); [Wang et al. 2009](#); [Dasu, Liu, and Lee 2012](#); [Dasu and Lee 2016](#)). [Rankin et al. \(2014\)](#) qualitatively monitored the disappearance of the polymer using matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, in addition to monitoring known degradation products. Also, the presence of impurities or nonpolymerized residuals (monomers, oligomers, PFCAs, FTOHs, etc.) complicates data interpretation and potentially confounds conclusions on polymer biodegradation. Finally, the time frame for the biodegradability studies (max = 2 years) is much shorter than the extrapolated half-lives (decades to thousands of years) of these side-chain fluorinated polymers. Hence, modeling assumptions are also critical sources of variability.

[Russell et al. \(2008\)](#); [Russell et al. \(2010\)](#) investigated the biodegradation potential of two types of side-chain fluoropolymers, fluorotelomer-based acrylate polymer and urethane polymer in soils for 2 years. Based on the experimental data for PFOA, the estimated half-life of acrylate polymer was 1,200–1,700 years and urethane polymer was 28–241 years (geometric mean of 102 years). However, the polymer used in this study contained high residuals. Later, [Washington et al. \(2009\)](#) studied the biodegradation potential of fluorotelomer-based polyacrylate, which contained low residuals, and based on the experimental data for PFOA, the acrylate polymer half-life was estimated at 870–1,400 years. Further, based on the assumption that degradation is surface-mediated, the authors also modeled and estimated the half-life for finely grained polymers, which are typical of commercial products. They did this by normalizing to the estimated surface area of the

polymer and derived a half-life of 10-17 years, which suggests fine-grained, side-chain fluoropolymer products may be a potentially significant source of PFCAs to the environment. [Washington et al. \(2015\)](#) studied the biodegradability of commercial acrylate polymer for 376 days in soils using exhaustive extractions ([Washington et al. 2014](#)) and estimated half-lives ranging from 33 to 112 years. In this study, it was also observed that the acrylate polymer can undergo OH-mediated hydrolysis in pH 10 water and it degrades 10-fold faster than in the neutral treatment. This is the only abiotic transformation of side-chain fluorinated polymer reported in the literature, so the mechanism of abiotic degradation needs further investigation. Another research group, [Rankin et al. \(2014\)](#) studied the biodegradation of laboratory-synthesized fluorotelomer-based acrylate polymer in soil, plant, and biosolids for 5.5 months. Degradation rates were faster in plants and biosolids than in soils. Even in this study, a broad range of estimated half-lives of 8-111 years was reported. The modeling assumptions used in different studies lead to variability in reported half-lives ([Russell et al. 2008](#); [Russell et al. 2010](#); [Washington et al. 2009](#); [Washington et al. 2010](#); [Washington et al. 2015](#); [Washington et al. 2018](#)).

#### 5.4.6 Practical Implications

Precursor transformation can complicate CSMs (and risk assessments) and should be considered during comprehensive site investigations. For example, atmospheric emissions of volatile precursors can result in long-range transport where subsequent transformation and deposition can result in detectable levels of PFAAs in environmental media independent of obvious point sources ([Vedagiri et al. 2018](#)). With respect to site-related precursors, transformation of otherwise unmeasured PFAS into detectable PFAAs is obviously relevant to site investigations to the extent transformation occurs after initial site characterization efforts. Additionally, differential transport rates between precursor PFAS and the corresponding terminal PFAA could also confound CSMs if transformation rates are slower than transport rates, as has been suggested ([Weber et al. 2017](#)).

To account for otherwise unmeasurable precursors, several surrogate analytical methods have been developed, including the total oxidizable precursor (TOP) assay ([Houtz and Sedlak 2012](#)), particle-induced gamma-ray emission spectroscopy (PIGE) ([Schaidler et al. 2017](#)), and adsorbable organic fluorine (AOF) followed by combustion ion chromatography ([Wagner et al. 2013](#)). For more information on these surrogate analytical methods to measure precursor concentrations, see [Section 11.2](#).

### 5.5 PFAS Uptake into Aquatic Organisms

Because of their unique chemical properties and persistence in the environment, some PFAS compounds have a propensity to bioaccumulate. With the exception of biota exposed to gross contamination (for example, AFFF spill sites), lower levels are observed in invertebrates and fish and higher levels are observed in animals at the top of the food chain (for example, seagulls, polar bears) ([Furl and Meredith 2010](#)), ([Ahrens and Bundschuh 2014](#)). Tissue levels of PFAS in the rural environment, compared to lipophilic legacy compounds (for example, polychlorinated biphenyls (PCBs), DDT, mercury), remain relatively low ( $\mu\text{g}/\text{kg}$ ).

Ionized PFAS are polar compounds and thus tend to bind to blood proteins instead of distributing into fatty tissues. Several studies ([Jones et al. 2003](#); [Han et al. 2003](#)) reported that PFOS and PFOA are generally bound to serum albumin as well as proteins in the liver and kidney and that the binding does not adversely affect binding of hormones. Thus, traditional methods and models that assume partitioning to lipids to estimate or characterize fate and transport of PFAS in biota (for example,  $\log K_{ow}$ ) cannot be used with this class of compounds.

In fresh or marine waters, partitioning to biota is generally defined using three operational categories.

- Bioconcentration factor (BCF)—the direct uptake of PFAS by an organism from the water column (through the gills), measured as the ratio of the concentration in an organism to the concentration in water (typically measured in the laboratory, units typically in L/kg)
- Bioaccumulation factor (BAF)—the amount of PFAS taken up from bioconcentration plus the contribution of PFAS in the diet of the organism (can be measured in the laboratory or field, typically unitless);
- Biomagnification factor (BMF)—an increase in tissue concentration as one moves up the food chain based on a predator/prey relationship (always measured in the field, typically unitless), often defined as the concentration of chemical in an organism divided by the concentration of chemical in its food.

There are hundreds of publications addressing partitioning of PFAS into biota by all three mechanisms and the subject is too broad to cover in this document. To assist in understanding this process, a sampling of data from some of the more visible review papers, along with references, is provided in [Table 5-1](#) (as a separate Excel file). This table includes values for both

invertebrates and fish. It is also important to add that due to both the historical precedence and domination of most media by PFOA/PFOS, most research evaluating PFAS uptake to aquatic organisms has focused on these two compounds.

### 5.5.1 Bioconcentration

Table 5-1 presents BCFs that are available for aquatic organisms for PFOA, PFDA, PFUnA, PFDoA, PFTA, PFOS, and PFHxS. Information addressing the mechanism of bioconcentration is presented in a study conducted by [Martin et al. \(2003\)](#), who exposed rainbow trout to relatively pure concentrations of each individual compound for 12 days. This study is very informative because it showed that the uptake of PFAS compounds is directly proportional to the length of the carbon chain and inversely proportional to the critical micelle concentration (CMC) (the level at which one half of the molecules are associated as micelles). They also showed that PFAS accumulated to the greatest extent in the blood, followed by the kidney, liver, and gall bladder, with lower levels accumulating in the gonads, followed by adipose tissue and muscle tissue. This tissue-dependent distribution is apparently due to PFAS having a high affinity for serum albumin and fatty acid binding proteins.

Carboxylates and sulfonates with perfluoroalkyl chain lengths shorter than seven and six carbons, respectively, could not be detected in most tissues and were considered to have insignificant BCFs. [Martin et al. \(2003\)](#) also showed that sulfonates had greater BCFs, half-lives, and rates of uptake than the corresponding carboxylate of equal chain length, indicating that hydrophobicity, as predicted by the CMC, is not the only determinant of PFAS bioaccumulation potential and that the functional group must be considered. PFOA had the lowest BCF, which is similar to its behavior in the field, having been reported to be relatively inefficient in accumulating in aquatic organisms. Others have also shown that shorter chain PFCAs and PFSAAs (less than eight and six carbons, respectively) are not readily bioconcentrated or accumulated ([Conder et al. 2008](#); [Martin et al. 2013](#); [Houde et al. 2011](#)).

### 5.5.2 Bioaccumulation

PFAS have accumulated in a variety of wildlife, generally fish-eating species, across the globe. The large amount of literature and inventories of wildlife samples containing PFAS residues attests to the widespread distribution of these compounds due to multiple global sources, with the majority of sampling being conducted to support hypotheses on long-range fate and transport, temporal trends, and industrial sources. Interestingly, most work has been done in the Northern Hemisphere and some authors have opined that levels are lower in the Southern Hemisphere. One study in Australia, however, found among the highest PFOS concentrations reported worldwide in the livers of dolphins in heavily industrialized regions of South Australia ([Gaylard 2017](#)). The study indicates that the population was the highest it has been in the last 30 years, suggesting PFAS is not adversely affecting this population.

Many authors will use the terms “bioconcentration” and “bioaccumulation” interchangeably, which is *incorrect*. Bioaccumulation can be measured in both the laboratory and the field, although the latter is the preferred method, as this has more relevance to the real world, including useful data to apply to the protection of public health (for example, recreational fish consumption). It is also important to state that accumulation should be reported out as a whole-body value, because reporting BCF/BAF according to tissues (blood, liver, kidney) will overestimate the values.

Mechanistically, bioaccumulation in aquatic organisms is not that different from bioconcentration because diet does not play as big a role in uptake of PFAS as uptake from the water column ([Giesy et al. 2010](#)). The classical paradigm for organic pollutants, known as the “target lipid model,” allows for an accurate prediction of toxicants (PAHs, PCBs, chlorinated pesticides) in aquatic organisms by simply knowing the water/octanol coefficient ( $K_{ow}$ ) of the compound. The uniqueness of PFAS colligative properties means this model does not work and there is still a lot of uncertainty surrounding the mechanism of bioaccumulation.

A comparative study by [Conder et al. \(2008\)](#), addressing the differences in bioaccumulation between perfluorocarboxylates, perfluorosulfonates, and legacy compounds, provides key insights into the understanding of the disposition of PFAS in aquatic organisms.

- Bioconcentration and bioaccumulation of perfluorinated acids are directly related to the length of each compound’s fluorinated carbon chain.
- Fluorinated sulfonates are more bioaccumulative than carboxylates of the same carbon chain length.
- Fluorinated carboxylates with seven carbons or fewer (perfluorooctanoate and shorter PFCAs) are not considered bioaccumulative according to promulgated persistent, bioaccumulative, and toxic (PBT) criteria of 1,000–5,000 L/kg.

- PFCAs with seven fluorinated carbons or fewer have low biomagnification potential in food webs.
- More research is necessary to characterize the bioaccumulation potential of carboxylates with longer fluorinated carbon chains (> 7 fluorinated carbons), as carboxylates with longer carbon chains may exhibit partitioning behavior similar to or greater than PFOS.

Table 5-1, which presents some BAFs tabulated from a selection of journal/review articles, validates some of these insights. For example, in comparing BAFs for PFOA with PFOS across all species, it is clear that the BAFs for PFOA are about two orders of magnitude lower than PFOS. Comprehensive reviews ([Ahrens and Bundschuh 2014](#); [Houde et al. 2008](#)) indicate that PFOS (8 carbon chain) is typically the dominant PFAS in animals. They also show that in invertebrates, PFOA and PFOS have similar concentrations (~1-10 ug/kg) and that tissue levels generally increase in concentration with an increase in trophic position of the food chain. Ahrens (2014) [Ahrens and Bundschuh \(2014\)](#) opine that the lower bioaccumulation potential of PFOA may be driven by the shorter (7 carbon) perfluorocarbon chain than seen in PFOS (8 carbon chain). In any event, it is apparent that, like other persistent compounds, bioaccumulation may take the shape of an inverted U-shaped curve; that is, accumulation is limited on one end by shorter chain compounds ( $\leq 7$  carbons) and on the other end of the curve by molecular size (for example,  $\geq 13$  fluorinated carbons).

Finally, it is important to note that PFAS precursors may contribute to the PFAS body burden. Atmospheric measurements have shown the widespread occurrence of PFAS precursors like FTOHs and perfluorinated sulfonamide alcohols. The concept is that, once absorbed by an organism, the precursor(s) would be metabolized to PFOA (for example, from 8:2 fluorotelomer alcohol) or to PFOS (for example, from N-ethyl perfluorooctane sulfonamidoethanol) ([Gebbink, Berger, and Cousins 2015](#); [Galatius et al. 2013](#)). Additional research on how PFAS precursor may contribute to the body burden of fish and wildlife will be needed to determine the overall dynamics involved with the bioaccumulation process.

### 5.5.3 Biomagnification

Studies of PFAS in the Great Lakes and marine/arctic ecosystems have generally shown that there can be trophic level biomagnification within a food web, particularly for PFOS and some long-chain PFCAs ([Martin et al. 2004](#); [Houde et al. 2006](#); [Houde et al. 2011](#); [Butt et al. 2010](#); [Tomy et al. 2004](#); [2009](#)). Because the BMF is the concentration in a predator divided by the concentration in its prey, calculated BMFs are highly variable depending on what types of tissues were analyzed and what assumptions the researcher made in defining biomagnification relative to the animals' prey diet (often determined through analysis of stomach contents). Some authors adjust BMFs according to enrichment based on stable isotopes of carbon and nitrogen, which are termed "trophic magnification factors" (TMFs). TMFs are believed to be a more objective metric in terms of biomagnification between different trophic levels.

[Table 5-1](#) (provided as a separate Excel file) presents BMFs and TMFs calculated for a number of different PFAS compounds. Most of the values in this table are cited from a review by [Franklin \(2016\)](#), who analyzed the results of 24 peer-reviewed studies reporting field-derived BMFs or TMFs for 14 PFAS (with BMF values ranging over several orders of magnitude from  $\ll 1.0$  to  $\gg 1.0$ ). [Franklin \(2016\)](#) made the case that "in practice, the study-to-study (and even within-study) variability of the results is so great that they are of very restricted usefulness for assessing bioaccumulation potential status." He attributes this variability to several factors, including differing ways in which the metrics are expressed (for example, individual tissue analyses versus whole body), nonachievement of the assumed steady-state conditions, uncertainties in feeding ecology, and the metabolism of precursor compounds. Some of the references cited in [Franklin \(2016\)](#) are discussed below.

[Martin et al. \(2010\)](#) estimated BMFs for a pelagic food web in Lake Ontario, with the lake trout as the top predator. They were able to show, after adjusting for benthic versus pelagic organisms, that some PFAS compounds biomagnify, with TMFs ranging from 0.51 for FOSA to 5.88 for PFOS. Contrary to other freshwater studies, [Lescord et al. \(2015\)](#) showed that trophic position did not correlate with the degree of biomagnification. These authors observed negative relationships between PFAS and stable nitrogen isotope ratios ( $\delta^{15}\text{N}$ ) in three out of six lakes, suggesting no biomagnification of PFAS through freshwater arctic food webs. Overall, their results suggested that a taxon's horizontal but not vertical position in the food web affects its PFAS concentrations.

A study by [Houde et al. \(2006\)](#) looked at PFOS and C8-C14 perfluorinated carboxylates in the bottlenose dolphin at two marine sites (Sarasota Bay, FL, and Charleston, SC). Based on estimated TMFs, those authors concluded that PFOS and C8-C11 PFCAs biomagnified in this marine food web (Table 5-1, also cited by [Franklin 2016](#)). Interestingly, for PFCAs, PFOA had the highest TMF, with values progressively decreasing as chain length increased. [Conder et al. \(2008\)](#) reported similar results for perfluorinated acids, with BMF values ranging from 0.1 to 20 (geometric mean of 2). They concluded and [Lescord et al. \(2015\)](#) affirmed that PFCAs with less than seven carbons, and PFSAs with less than six carbons, do not biomagnify and

that the bioaccumulation of PFCAs can be directly related to fluorinated carbon chain length (just as the bioaccumulation of persistent lipophilic compounds can be related to hydrophobicity). [Conder et al. \(2008\)](#) also noted that the biomagnification of PFCAs in aquatic food webs is lower than that of most persistent lipophilic compounds, with PFOS being the only perfluorinated acid consistently exhibiting the potential for biomagnification. Finally, [Butt et al. \(2008\)](#) observed biomagnification factors for PFAS in “ringed seal–polar bear” food webs of the Canadian Arctic. Biomagnification factors were greater than one for C8–C14 PFCAs, as well as for PFOS and PFOSA. Like [Houde et al. \(2006\)](#), they observed a decrease in BMF as the carbon chain number increased.

## 5.6 PFAS Uptake into Plants

Because PFAS have both hydrophilic and hydrophobic properties, plants can be expected to take these compounds up through their root systems, after which they would be translocated to stems, shoots, leaves, and fruiting bodies. It is logical to assume that plants growing closer to contaminated sources or irrigated with PFAS-containing water would have higher levels of PFAS compounds compared to plants more distant from the PFAS source, subject to site-specific conditions such as soil properties. It has already been documented that the land application of biosolids may contaminate soil with PFAS compounds and that animals fed silage from land-applied fields will have elevated levels in their tissues ([Lindstrom et al. 2011](#); [Skutlarek, Exner, and Farber 2006](#)). This also raises concerns about contamination of wildlife consuming plants from agricultural areas. Airborne PFAS emissions from industrial sites in China were found to impact the concentration of PFAS in bark and tree leaves, with the theory that the bioconcentration in the latter may occur through uptake through the stomata ([Shan et al. 2014](#)).

### 5.6.1 Bioconcentration/Bioaccumulation

[Table 5-2](#) (provided as a separate Excel file) contains BCF and BAF values for 14 different PFAS for a variety of plant species. In the cited plant uptake studies, BCF and BAF are defined as PFAS concentration in plant(mass/mass) divided by PFAS concentration in soil (mass/mass) and are used interchangeably. This differs from the definition of BCF and BAF for animals in [Section 5.5](#). A number of BAF values were obtained from studies in which PFAS was introduced to crops through irrigation water or biosolids-amended soils ([Blaine et al. 2013](#); [Blaine, Rich, Sedlacko, Hundal, et al. 2014](#); [Blaine, Rich, Sedlacko, Hyland, et al. 2014](#)). The materials harvested for analysis included both inedible (for example, plant leaves) and edible portions of crops (fruit, lettuce leaves, and roots). Other BCFs and BAFs were obtained from investigations of plants exposed to PFAS from soil, groundwater, surface water, or air in close proximity to PFAS release sites ([Mudumbi et al. 2014](#); [Zhang et al. 2015](#); [Gobelius, Lewis, and Ahrens 2017](#)). In general, it can be observed that 1) the shorter chain (more water soluble) PFAS are taken up more readily than the longer chain homologues, and 2) the majority of the plant BCFs and BAFs fall between a range of 0.1 and 10. A BCF or BAF of 1.0 indicates no net accumulation of PFAS from soil to plant. Such a BCF or BAF indicates that the soils and the plant of interest have the same concentration of PFAS per unit weight. This, however, does not indicate that an equilibrium condition exists between soils and plants. Some plants, like lettuce, contain a large percentage of water, which may help to explain the relatively high BAF of 56.8 observed by [Blaine et al. \(2013\)](#). In the controlled studies of edible crops, short-chain PFCAs and PFSAs exhibited greater BAFs compared to long-chain compounds.

[Blaine et al. \(2013\)](#) studied the uptake of PFAAs by greenhouse lettuce and tomato grown in soils prepared to mimic an industrially impacted biosolids-amended soil, a municipal biosolids-amended soil, and a control soil (but incorporated contaminated biosolids equivalent to 10 times higher than the agronomic rates allowed for Class B biosolids), a municipal biosolids-amended soil, and a control soil. BCFs for many PFAAs were well above unity, with PFBA having the highest BCF in lettuce (56.8) and PFPeA the highest in tomato (17.1) in the industrially impacted biosolids-amended soil. BAFs for PFCAs and PFSAs were, in general, slightly higher in the industrially impacted soil than in the municipal soil (~0.3–0.8 log units). The BCFs for PFAAs in greenhouse lettuce decreased approximately 0.3 log units per -CF<sub>2</sub> group (one carbon, two fluorine groups in a molecule). They also conducted a limited field study, in which they measured PFAA levels in lettuce and tomato grown in field soil amended with only a single application of biosolids (at the agronomic rate for nitrogen). The PFAA levels were predominantly below the limit of quantitation (LOQ). In addition, corn stover, corn grains, and soil were collected from several full-scale biosolids-amended farm fields. At these fields, all PFAAs were below the LOQ in the corn grains and only trace amounts of PFBA and PFPeA were detected in the corn stover. The [Blaine et al. \(2013\)](#) study confirms that the bioconcentration of PFAAs from biosolids-amended soils depends strongly on PFAA concentrations, soil properties, type of crop, and analyte. BCFs developed in [Blaine et al. \(2013\)](#) [Blaine et al. \(2013\)](#) can be seen in [Table 5-2](#).

[Gobelius, Lewis, and Ahrens \(2017\)](#) studied the uptake of 26 PFAS in plants (trees) at an AFFF (fire training) site with contaminated soil and groundwater. Samples from groundwater and different plant species (birch, spruce, cherry, ash, elder, beechfern, and wild strawberry) and tissues (that is, roots, trunk/cores, twigs, leaves/needles) were collected. Foliage had



the highest BCFs of all tissues, ranging from 0 to 14,000 and accumulated the highest number of PFAS (8 out of 26), with birch sap showing BCF values up to 41 for 6:2 FTSA. The highest mean BCFs were found for 6:2 FTSA (472; n = 52), PFOS (28; n = 36), PFHxS (10; n = 42), and PFOA (5; n = 24), which might correspond to the AFFF composition used at the site. For PFOA, the mean BCFs ( $\pm$ s.d.) were  $18 \pm 15$  for spruce, followed by birch ( $1.2 \pm 1.5$ ) and cherry ( $0.25 \pm 0.043$ ). The authors concluded that PFAS were detected in all plant species, and the distribution followed the order of “shoots to roots”—that is, leaves > twigs/stems > trunk > roots. They cited other authors who have shown that “this order has proven applicable to all samples and species.” Hence, PFAS tend to accumulate in the vegetative portions rather than in the plant storage tissues.

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