Environmental Fate and Transport for Per- and Polyfluoroalkyl Substances

1 Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large group of compounds used in non stick coatings, textiles, paper products, some firefighting foams, and many other products. These compounds have many manufacturing and product applications because they repel oil and water, resist temperature extremes, and reduce friction. PFAS include compounds that vary in molecular weight and can have multiple structures and functional groups. Over the years, manufacturing and use of these compounds has resulted in their presence in the environment. More information about the manufacturing history and use of PFAS, including the two major production processes, electrochemical fluorination (ECF) and telomerization, is included in the *History and Use* fact sheet.

The scientific community is rapidly recognizing the environmental and health effects of PFAS. Some of the perfluoroalkyl acids (PFAAs), such as perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), are mobile, persistent, and bioaccumulative, and are not known to degrade in the environment (USEPA 2003b; ATSDR 2015a; NTP 2016; Concawe 2016). USEPA has compiled an online resource for PFAS information that includes guidance on policy, chemistry and behavior, occurrence, toxicology, site characterization, and remediation technologies (USEPA 2017h). The National Groundwater Association (NGWA) has also published a resource on PFAS that includes information about fate and transport (NGWA 2017).

ITRC has developed a series of fact sheets that summarize the latest science and emerging technologies regarding PFAS. This fact sheet describes:

- four major sources of PFAS (fire training/fire response sites, industrial sites, landfills, and wastewater treatment plants/biosolids)
- processes that influence the fate and transport of PFAS from these sources in the environment (partitioning, transport, and abiotic and biotic transformation)
- processes that affect PFAS concentrations in air, surface water, groundwater, soil and sediment, and biota (plants, invertebrates, fish, and humans)

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.

2 Major Sources of PFAS

There are four major sources of PFAS: fire training/fire response sites, industrial sites, landfills, and wastewater treatment plants/biosolids. Other point and diffuse sources of PFAS exist, and may be significant locally, but generally are expected to be small by comparison to these main four sources. This section provides a general discussion of the fate and transport processes associated with each source. Figures 1 through 3 illustrate conceptual site models (CSMs) for these four sources. Sections 3 and 4 provide specific details on the processes and media identified in the CSMs. See the *History and Use* fact sheet for information on PFAS uses, applications, and releases from each of these sources. Information about risk assessment, and human and ecological receptors is included in the *Site Characterization Considerations, Sampling Precautions and Laboratory Analytical Methods* fact sheet.

2.1 Fire Training/Fire Response Sites

Aqueous film-forming foams (AFFFs) are commercial surfactant solutions used for several decades by the U.S. military, civilian airports, and other facilities to extinguish hydrocarbon fires. In 1969, the U.S. Department of Defense (DOD) issued military specification Mil-F-24385, which dictates the performance of all AFFFs (with performance standards referred to as "Mil-Spec"). Once an AFFF was shown to perform to MIL-F-24385 requirements, the product was listed on the U.S. military's AFFF Qualified Product Listing (QPL). Since July 1, 2006, the Federal Aviation Administration has required Part 139 certified airports purchase only AFFF that is Mil-Spec compliant (FAA 2006, 2016; 14 CFR 139.317).
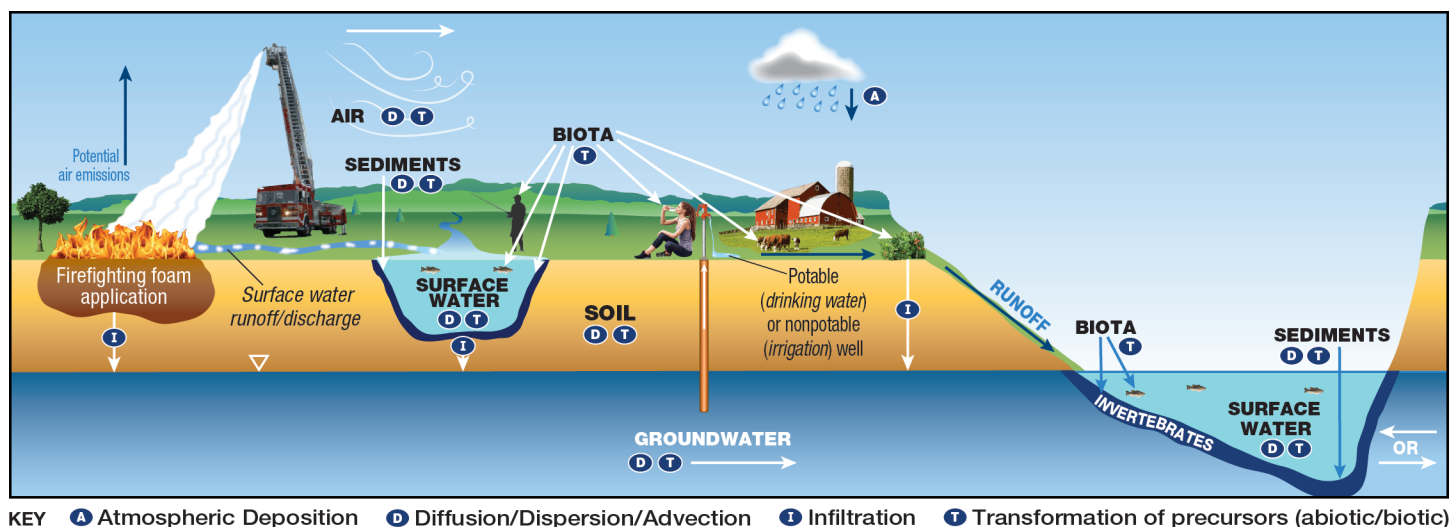
Multiple AFFF formulations have been produced over the years, and the exact composition of any given AFFF used or manufactured in any given year is highly variable (Backe, Day, and Field 2013). The fluorosurfactants in AFFF formulations can either be produced using the electrochemical fluorination (ECF) process or the fluorotelomerization process. Both ECF-derived and telomer-derived AFFF contain highly diverse mixtures of PFAS (Barzen-Hanson et al. 2017). The ECF process results in a PFAS mixture dominated by perfluoroalkyl acids (PFAAs)—both perfluoroalkyl sulfonate (PFSA) and perfluoroalkyl carboxylate (PFCA) homologues, while the fluorotelomerization process produces AFFF formulations dominated by polyfluorinated compounds with lesser amounts of PFAAs (Houtz et al. 2013). ECF-based AFFF formulations were voluntarily phased out of production in the United States in 2002, but DOD reportedly has

over a million gallons of ECF-based AFFF in their inventory as of 2011 (Darwin 2011). Studies to date show ECF-based AFFF is the dominant source of PFAS at AFFF-impacted sites, likely due to the longer period of ECF-based AFFF use and the relative coincidence of implementation of engineering controls for releases and wider use of telomerized AFFF (Pancras et al. 2016; Anderson et al. 2016). Fluorotelomerization-derived AFFFs are still manufactured and used in the United States but have been reformulated to limit, if not eliminate, long-chain PFAS.

2.1.1 AFFF releases

AFFF is released to the environment under various scenarios (see Figure 1). Although fire-training areas (FTAs) have received the most attention, AFFF use at military and civilian facilities is highly varied. In addition to FTAs, many other sites are also likely affected by AFFF due to past emergency response incidents, operational requirements that mandated periodic equipment calibrations on emergency vehicles, and episodic discharge of AFFF-containing fire suppression systems within large aircraft hangars and buildings (Anderson et al. 2016; Thalheimer et al. 2017). Accidental releases of AFFF from storage tanks, railcars, and piping during delivery or transfer have also occurred. Once released to the environment, AFFF can contaminate soil, surface water, and groundwater.

KEY **A** Atmospheric Deposition **D** Diffusion/Dispersion/Advection **I** Infiltration **T** Transformation of precursors (abiotic/biotic)

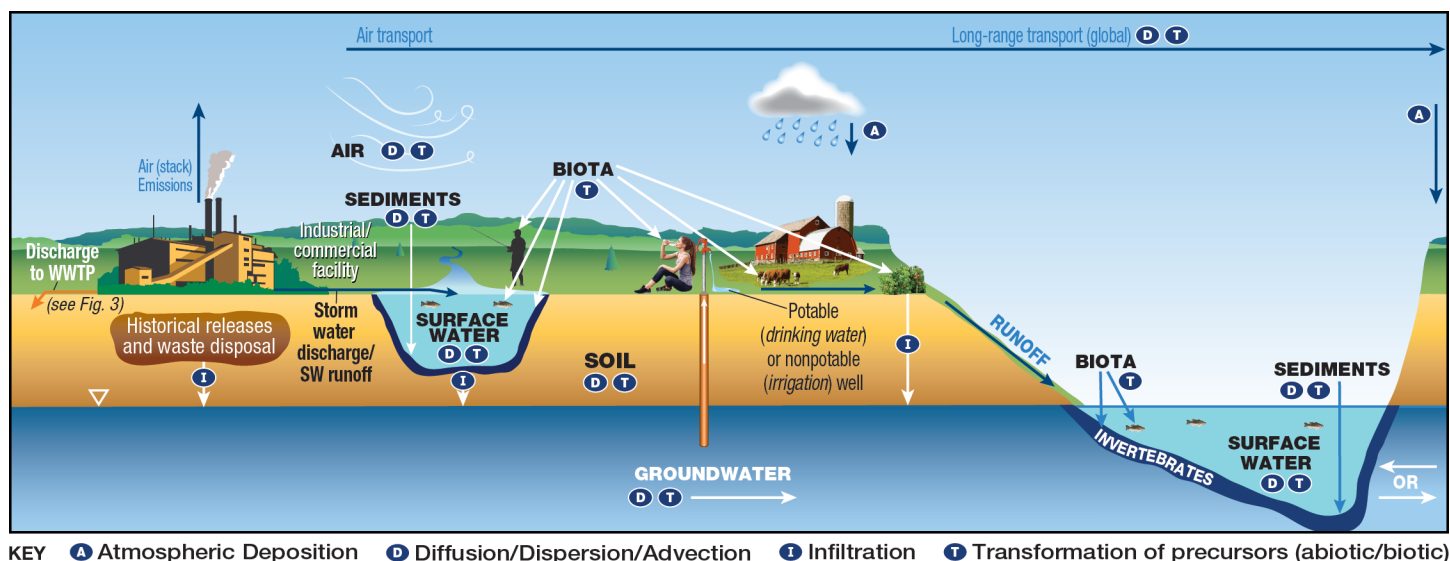**Figure 1. Conceptual site model for fire training areas.**
(Source: Adapted from figure by L. Trozzolo, TRC, used with permission)

AFFF-impacted sites often are also contaminated with petroleum hydrocarbons from unburned fuel. PFAS and hydrocarbon plumes at these sites may follow the same flow paths, though the extent of contamination may be significantly different. These co-contaminants, particularly light nonaqueous phase liquids (LNAPLs), may affect the fate and transport of AFFF-derived PFAS (Guelfo and Higgins 2013; Lipson, Raine, and Webb 2013; McKenzie et al. 2016). Certain air-based or in situ oxidation remedial activities aimed at treating co-contaminants may affect PFAS composition, fate, and transport as well (McKenzie et al. 2015). Additionally, the altered soil and groundwater geochemistry and redox conditions may result in oxidation of some PFAS precursor compounds, degrading them to terminal PFAAs (Harding-Marjanovic et al. 2016; McKenzie et al. 2016; McGuire et al. 2014). In addition to AFFF, firefighting foams may also consist of fluoroprotein and film-forming fluoroprotein foam.

2.2 Industrial Sites

Industrial source sites include primary manufacturing facilities where PFAS-containing products are synthesized and made into products or chemical feedstocks, or where PFAS are used as processing aids in fluoropolymer production (where PFAS are not intended to be in the final product). Secondary manufacturing facilities may use these products or feedstocks as part of industrial processes, such as the coating application to finished products. In some industrial settings, PFAS may be used for worker safety purposes - such as using PFOS-based materials to suppress harmful mists. PFAS composition and release mechanisms will vary for each facility, but general pathways are illlustrated in Figure 2.

KEY   **Ⓐ** Atmospheric Deposition   **Ⓓ** Diffusion/Dispersion/Advection   **Ⓘ** Infiltration   **Ⓣ** Transformation of precursors (abiotic/biotic)

Figure 2. Conceptual site model for industrial sites.
(Source: Adapted from figure by L. Trozzolo, TRC, used with permission)

Manufacturing facilities that may be sources of PFAS releases to the environment include textile and leather processors, paper mills, metal finishers, wire manufacturers, plating facilities, manufacturers, as well as facilities using surfactants, resins, molds, plastics, photolithography, and semiconductors (see the *History and Use* fact sheet for more information).
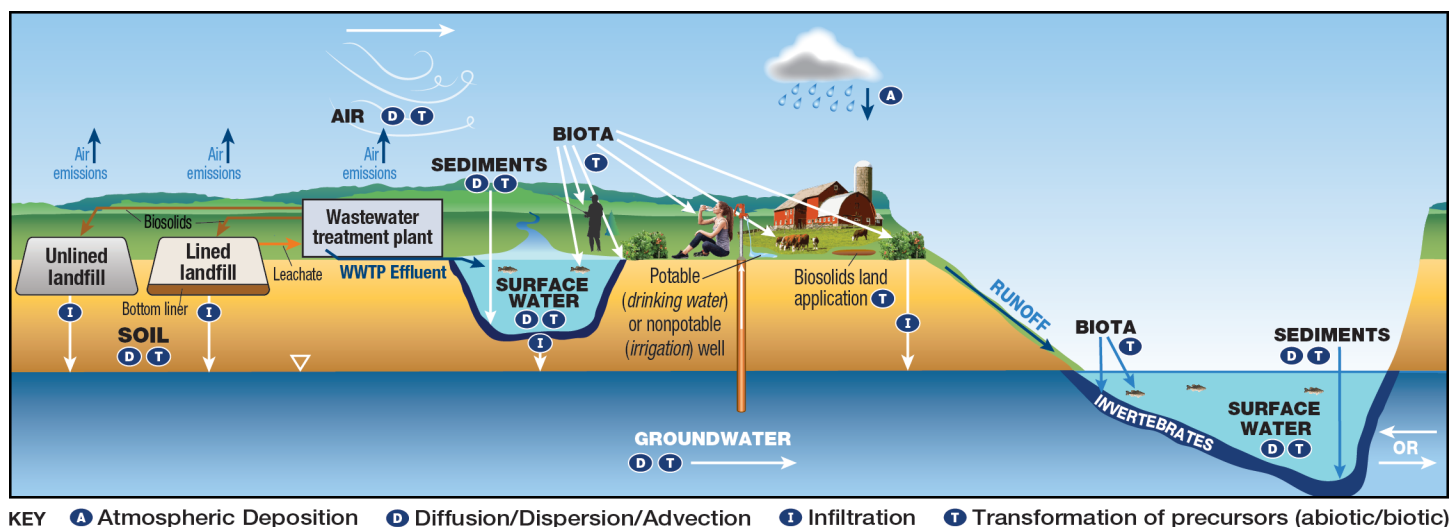
Industrial facilities may release PFAS to the environment via wastewater discharges (see Section 2.4), on- and off-site disposal of wastes, accidental releases such as leaks and spills, and stack emissions. Stack emissions may result in aerial deposition of PFAS to soil and surface water (with subsequent infiltration to groundwater) within the airshed of the facility, as shown in Figure 2 (Davis et al. 2007; Shin et al. 2011). Stack emissions may result in short- and long-range air transport of PFAS. PFAS in aerosols and adsorbed on particles are more likely to be deposited near the source, while long-range transport typically involves PFAS vapors. Industrial facilities may also contain areas where fire training or fire response has occurred, AFFF storage areas, and AFFF fire suppression systems inside buildings.

The composition of PFAS released from industrial facilities depends on the type of PFAS produced or used by the facility. For example, textile coating operations may use water-emulsion or powdered feedstocks that contain greater proportions of PFCAs compared to PFSAs (Lassen et al. 2015; Gremmel, Frömel, and Knepper 2016). In contrast to AFFF release sites, industrial sites may be less likely to co-release contaminants that affect redox or other subsurface fate and transport conditions (unless the site also includes AFFF releases from historical fire training or fire suppression activities).

2.3 Landfills

Landfills are sources of PFAS because they are the ultimate repositories not only for PFAS-contaminated industrial waste, sewage sludge, and waste from site mitigation, but also for PFAS-bearing consumer goods treated with hydrophobic, stain-resistant coatings (Busch et al. 2010; Eggen, Moeder, and Arukwe 2010). Given the production timeline of PFAS, consumer products landfilled since the 1950s are potential sources to the environment. Industrial waste can be a significant source of PFAS in landfills, particularly those that accept waste from the production or application of PFAS (Oliaei et al. 2013). In addition, many landfills accept sewage sludge from wastewater treatment facilities that may contain PFAS. Figure 3 includes illustrations of landfills and wastewater treatment plants (WWTPs) sources.

KEY   **A** Atmospheric Deposition   **D** Diffusion/Dispersion/Advection   **I** Infiltration   **T** Transformation of precursors (abiotic/biotic)

Figure 3. Conceptual site model for landfills and WWTPs.
(Source: Adapted from figure by L. Trozzolo, TRC, used with permission)

2.3.1 Landfill Construction

Landfills are either lined or unlined (Figure 3). Municipal solid waste, construction and demolition, and industrial landfills constructed since the 1990s are required by federal or state regulations to install a composite liner, a layer of compacted soil, and a leachate collection system (40 CFR 258.40). Leachate collected from landfills is typically treated on site or transported to either a nearby municipal WWTP or evaporation ponds. The processes for managing leachate have implications on the ultimate fate and transport of PFAS. If liners or leachate collection systems fail, PFAS may directly enter the environment. Landfills constructed before the 1990s are not required to have synthetic flexible membrane liners, compacted soil liners, or leachate collection systems, causing waste to be in direct contact with underlying soil or groundwater. Therefore, unlined landfills have a higher potential of contributing PFAS to groundwater (Oliaei et al. 2013). Landfill caps reduce infiltration of water to waste and may reduce the overall mass of PFAS entering the environment from a landfill, but more research on their effectiveness is needed (Hamid, Li, and Grace 2018).

2.3.2 Waste Age

Landfills containing sources of PFAS will continue to release PFAS at slow but relatively steady rates for decades following initial placement. In modeled anaerobic landfill reactors, most of the release is attributed to biological not physical mechanisms, indicating that the low solubility of the compounds is not solely responsible for slow release rates from landfills (Allred et al. 2015; Lang et al. 2016). While landfill leachate PFAS concentrations are relatively high, landfill leachate generally is considered only a minor source to the environment because the volume of leachate generated annually is low compared to the flow volume in most WWTPs (Busch et al. 2010). Legacy industrial waste landfills, however, may constitute a major source to the environment (ATSDR 2008, 2012).

2.3.3 PFAS Composition from Landfills

Relative concentrations of PFAS in leachate and groundwater from landfills are different than those at WWTPs and AFFF-contaminated sites. PFAS with fewer than eight carbons tend to dominate landfill leachate because they are less hydrophobic and therefore more likely to partition to the aqueous phase (Huset et al. 2011; Higgins and Luthy 2007). In particular, 5:3 fluorotelomer carboxylic acid (FTCA) is a common and often dominant constituent of PFAS found in landfills and is released from carpet in model anaerobic landfill reactors. This compound could prove to be an indicator of PFAS in the environment originating from landfills (Lang et al. 2017, 2016). PFAS may also be released to the air from landfills, predominantly as fluorotelomer alcohols (FTOHs) and perfluorobutanoate (PFBA) (Ahrens et al. 2011a). PFAS release rates vary with time for a given waste mass, with climate (for example, rainfall) as the apparent driving factor for the variations (Lang et al. 2017; Benskin et al. 2012).

2.4 Wastewater Treatment Plants

Municipal and industrial WWTPs can provide the following pathways for PFAS to the environment: point source discharges of effluent; leakage or unintended releases from surface impoundments; air emissions; or disposal of biosolids and other byproducts generated during the treatment process (see Figure 3). The composition of PFAS in these

media is a function of the different sources and processes (Chen, Lo, and Lee 2012, Oliaei et al. 2006, Frömel et al. 2016, Schultz et al. 2006) including:

• type and concentration of PFAS received by the WWTP

• biological and chemical transformation of polyfluorinated substances to intermediate and terminal degradation products, such as perfluoroalkyl acids (PFAAs)

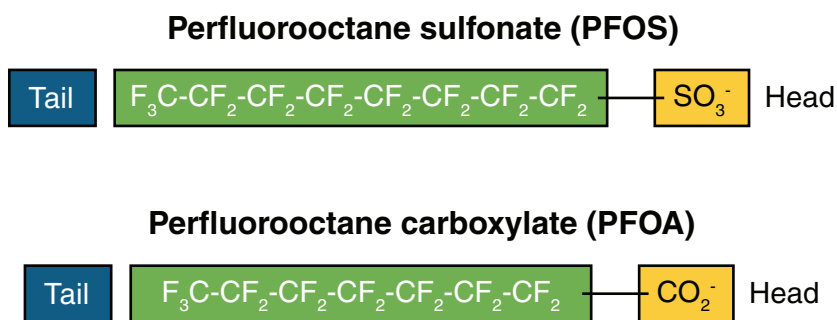• physical or chemical partitioning, or both

At WWTPs, PFAAs may be created from the oxidation of polyfluorinated precursors during the treatment process (Oliaei, Kriens, and Kessler 2006; Frömel et al. 2016). Furthermore, PFAS could be concentrated in solid waste (for example, sewage sludge) throughout the treatment process (Schultz et al. 2006). Depending on waste management and disposal practices, this solid waste could contaminate groundwater, surface water, or both. PFAS may also be introduced to the environment through the land application of biosolids as a beneficial soil amendment, potentially allowing PFAS to enter surface water through runoff or infiltrate to groundwater (Lindstrom et al. 2011). The potential effects on groundwater or surface water depend on the amount and composition of PFAS present in biosolids, soil properties, infiltration rate, and land application practices. While further transformation of polyfluorinated substances in land-applied biosolids to PFAAs has been suggested (Sepulvado et al. 2011), other evidence suggests that some polyfluorinated substances remain in biosolids-amended soils for many years (Rich et al. 2015).

3 Fate and Transport Processes

Partitioning, transport, and transformation of PFAS occurs across multiple media types. While most research literature focuses on PFAAs (especially PFOS and PFOA), processes affecting precursor PFAS that can degrade to PFAAs over time are also important. Figures 1 through 3 illustrate these processes for the four main sources of PFAS. See Section 4 for media-specific discussions of fate and transport.

3.1 Partitioning

PFAS most commonly detected in the environment typically have a carbon-fluorine "tail" and a nonfluorinated "head" consisting of a polar functional group. The tail is hydrophobic and lipophobic, while the head groups are polar and hydrophilic. The competing tendencies of the head and the tail can lead to a wide distribution in the environment. The tail and head structure are illustrated for PFOS and PFOA in the following figure.

Perfluorooctane sulfonate (PFOS)

Tail | F_3C-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2 — SO_3^- Head

Perfluorooctane carboxylate (PFOA)

Tail | F_3C-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2 — CO_2^- Head

Figure 4. The tail and head structure of PFOS and PFOA molecules.

Given heterogeneous subsurface environments, multiple partitioning mechanisms should be considered when characterizing PFAS fate and transport.

Important PFAS partitioning mechanisms include hydrophobic and lipophobic effects, electrostatic interactions, and interfacial behaviors. The hydrophobic and lipophobic effects drive the association with organic carbon in soils, a process PFAS has 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

Partitioning Summary

• Multiple partitioning mechanisms affect PFAS: hydrophobic and lipophobic effects, electrostatic interactions, and interfacial behaviors.

• PFSAs are more strongly sorbed than their PFCA homologues.

• Longer chain PFAAs are more strongly sorbed than shorter chain PFAAs.

• PFAAs are:
  o relatively mobile in groundwater but tend to associate with the organic carbon fraction of soil and sediment;
  o less volatile than many other groundwater contaminants;
  o sometimes transported on airborne particles; and
  o generated by transformation of volatile precursors.

of PFAAs. Because the head and the tail compete, partitioning to interfaces of environmental media such as soil/water, water/air, and water/NAPL co-contaminants can occur (Guelfo and Higgins 2013; McKenzie et al. 2016; Brusseau 2018).

The partitioning behavior of PFCAs and PFSAs has been studied more in depth than that of other PFAS. At relevant environmental pH values, PFCAs and PFSAs are present as organic anions and are therefore relatively mobile in groundwater (Xiao et al. 2015) but tend to associate with the organic carbon fraction that may be present in soil or sediment (Higgins and Luthy 2006; Guelfo and Higgins 2013). When sufficient organic carbon is present, organic carbon-normalized distribution coefficients (Koc values) can help in evaluating transport potential, though other geochemical factors (for example, pH and presence of polyvalent cations) may also affect PFAS sorption to solid phases. Table 3-1, provided as a separate Excel file, presents the available Koc values for commonly detected PFAAs and a several other PFAS often detected at release sites.

Sorption and retardation generally increase with increasing perfluoroalkyl tail length (Higgins and Luthy 2006; Guelfo and Higgins 2013; Sepulvado et al. 2011), indicating that the short-chain PFSAs (for example, perfluorobutane sulfonic acid [PFBS]) and PFCAs (for example, perfluorohexanoic acid [PFHxA]) are retarded less than their long-chain counterparts (PFOS and PFOA, respectively). In addition, PFSAs tend to sorb more strongly than PFCAs of equal chain length (Higgins and Luthy 2006), and branched isomers have less sorption than linear (Kärrman et al. 2011). Sorption of PFCAs and PFSAs is also affected by soil solution chemistry, with decreased pH and increased levels of polyvalent cations (for example, Ca^{2+}) leading to increased sorption and retardation (Higgins and Luthy 2006; McKenzie et al. 2015).

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 (PFDoA) (Barton, Botelho, and Kaiser 2008; Kaiser et al. 2005). Measured vapor pressures are also available for fluorotelomer alcohols (Krusic et al. 2005). Henry's Law constants are generally unavailable for PFAAs. Vapor pressures of these compounds are generally low and water solubilities are high, limiting partitioning from water to air (USEPA 2000b). However, under certain conditions, particularly within industrial stack emissions, PFAS can be transported through the atmosphere. Volatiles such as FTOHs may be present in the gas phase and anionic PFAS may be sorbed to particulates (Ahrens et al. 2012); see Section 4.1 for a more detailed discussion.

3.2 Transport

The resistance of most PFAS to biotic or abiotic degradation (except for precursor transformation discussed in Section 3.3) means that physical transport processes are critical for PFAS transport and potential for exposure.

3.2.1 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, such as in an expanding groundwater plume. Advection, however, does not reduce concentration along the flow path. While advection is based solely on media properties and is independent of molecular, physical, or chemical properties of the contaminant, modeling the migration of PFAS due to fluid flow requires an understanding of how PFAS interact with the surrounding medium. This modeling should include the effect of sorption (see Section 3.1), which is often expressed in terms of how the contaminant velocity is reduced relative to advective velocity.

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 groundwater, dispersion is limited, meaning that plumes are relatively narrow as they move downgradient from a source (Payne, Quinnan, and Potter 2008). When PFAS plumes are wider than expected based on dispersion alone, the plume width may reflect the contribution of nonpoint sources (for example, air deposition) or comingled plumes (for example, some fire training areas).

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 diffusion; for example, PFAS transport in oceans can be due to eddy diffusion (Lohmann et al. 2013). 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. For instance, at one site PFAS penetrated 12 cm into a concrete pad at a fire training area, and diffusion was a contributing process (Baduel, Paxman, and Mueller 2015).

3.2.2 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; Barton, Zarzecki, and Russell 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. Deposition is generally considered a removal process that reduces longer-range atmospheric transport. See Section 4.1 for further discussion of atmospheric deposition of PFAS.

3.2.3 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 (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 et al. 2012; Yan et al. 2015; Lang et al. 2017). Leaching potential is a function of both media properties (for example, pH, redox conditions, and increased partitioning with organic-rich soil) and PFAS structural properties (for example, ionic charge, and chain length) (Gellrich, Stahl, and Knepper 2012). While some studies have reported PFAS transport by leaching (Lindstrom et al. 2011; Filipovic et al. 2015; Hellsing et al. 2016; Braunig 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). This retention may reduce the potential for PFAS exposure by several pathways (for example, groundwater ingestion), but may increase the long-term persistence of the (soil-bound) source (Baduel, Paxman, and Mueller 2015).

3.2.4 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; this interfacial process accounted for approximately 50% of the total retention in a model system with 20% air saturation (Brusseau 2018). At higher concentrations, PFAAs can form aggregates in which the hydrophilic portions interact with the water phase and the hydrophobic portions interact with each other (for example, micelles or hemimicelles). For PFOS, the critical micelle concentrations (CMC) of 500 to 5,000 mg/L have been reported, 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).

Transport Summary

- 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.

3.3 PFAS Transformation

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

Transformation Summary
• PFAS precursor chemicals 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.

3.3.1 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 PFSAs. For example, PFOS is produced from perfluorooctane sulfonyl fluoride (POSF) (Martin et al. 2010). Other hydrolysis reactions produce PFCAs. The release of PFAAs by abiotic transformation may be slow. For instance, Washington and Jenkins (2015) report a half-life of over 50 years for the hydrolysis of fluorotelomer-derived precursors at neutral pH to form PFOA and other PFCAs. While direct photolysis of PFAS has not been observed, indirect photolysis of some precursors, notably FTOHs, 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, 8:2 FTOH degrades to PFOA in the atmosphere through reactions with hydroxyl radicals and chlorine radicals, with similar reactions for 6:2 and 4:2 FTOHs (Ellis et al. 2004; Wallington et al. 2006).

Perfluoroalkanesulfonamides can also degrade abiotically through oxidation in the atmosphere to form PFCAs in yields that may be 10x greater than FTOHs (Martin et al. 2006). Also, oxidation of precursors by hydroxyl radicals can occur in natural waters, with the fluorotelomer-derived precursors being oxidized more rapidly than ECF-derived precursors (Gauthier and Mabury 2005; Plumlee, McNeill, and Reinhard 2009). Shorter-chain PFSAs 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 (for example, the formation of various polyfluorinated sulfonamido intermediate compounds from ECF-derived precursors), though eventual formation of PFAAs may still be possible (Martin et al. 2010).

3.3.2 Biotic Transformation

While PFOA, PFOS, and all other PFAAs are resistant to microbial degradation, numerous studies have reported biotransformations of various precursors similar to the abiotic transformations discussed in Section 3.3.1. The current literature indicates:

• Numerous aerobic biotransformation pathways exist, with relatively rapid kinetics.

• All polyfluorinated precursors may have the potential to aerobically biotransform to PFAAs.

• Aerobic biotransformation of various fluorotelomer-derived precursors to PFCAs (including PFOA) occurs (for example, Harding-Marjanovic et al. 2015; D'Agostino and Mabury 2017).

• Aerobic biotransformation of various ECF-derived precursors to PFSAs (including PFOS) occurs (Zhang et al. 2017; Mejia-Avendaño and Liu 2015; Mejia-Avendaño et al. 2016).

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 PFSAs (Zhang et al. 2013; Allred et al. 2015).

Note that fluorotelomer-derived precursors do not form PFSAs, while degradation of ECF-derived precursors may form both PFSAs and PFCAs. The extent to which ECF-derived precursors form PFCAs in situ is under study, along with other critical factors such as ambient biotransformation rates. In general, however, biotransformation rates are probably site specific and could be so slow as to be inconsequential at some sites.

4 PFAS Occurrence by Medium

PFAS occurrence in various environmental media is an active area of research. The material presented here is not the result of an exhaustive literature review but is included to provide a relative understanding of PFAS concentrations. As discussed in the *Site Characterization Considerations, Sampling Precautions and Laboratory Analytical Methods* fact sheet, analytical methods are still being optimized and standardized; thus, it is difficult to compare results between studies and conclusions may change over time. Media types presented here include air, soil and sediment, groundwater, surface water, and biota. The processes that influence media-specific PFAS concentrations are illustrated in Figures 1 through 3.

4.1 Air

Certain PFAS are found in ambient air, with elevated concentrations observed or expected in urban areas nearest to emission sources, such as manufacturing facilities, WWTPs, fire training facilities, and landfills (Barton et al. 2006; Ahrens et al. 2011a; Liu et al. 2015a). Table 4.1 includes summary information about occurrence of PFAS in outdoor air from selected studies.

Although outdoor air containing PFAS can enter buildings, the presence of indoor sources can cause indoor air concentrations of certain PFAS to be higher than outdoor air concentrations (Fromme et al. 2015; Shoeib et al. 2011). Examples of indoor sources of PFAS include many consumer products such as stain resistant coatings used on carpets and upholstery, water resistant clothing, grease-resistant paper, food packaging, nonstick cookware, cleaning products, personal care products, cosmetics, paints, varnishes, and sealants (ATSDR 2016; Liu et al. 2015; Liu et al. 2014; Gewurtz et al. 2009; Guo et al. 2009).

Once airborne, PFAS can occur in a gaseous state or be associated with particulate matter or other aerosols suspended within the air. Neutral volatile precursor compounds, such as FTOHs, are the dominant PFAS present in the gas phase and accounted for at least 80% of the total PFAS mass in ambient air in one 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, Vorkamp, and Skov 2016; Lai et al. 2016; Wang 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 generally 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, Kaiser, and Russell 2007; Hurley et al. 2004). PFAS are commonly found in rain and snow, with wet and dry deposition estimated to occur on a time scale of a few days (Lin et al. 2014; Taniyasu et al. 2013; Dreyer et al. 2010; Kwok et al. 2010).

Short-range atmospheric transport and deposition may result in PFAS contamination in terrestrial and aquatic systems near points of significant emissions, contaminating soil, groundwater, and other media of concern (Davis et al. 2007), as well as several miles from industrial emission sources (Shin et al. 2011; Post, Cohn, and Cooper 2012; NYS DOH 2016; NH DES 2017; VT DEC 2016). 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). Models indicate that deposition depends on amount of PFAS emissions, local topography, particle size, weather patterns, and release characteristics such as smokestack height, effluent flowrate, and effluent temperature.

In addition to short-range transport and deposition, long-range transport processes are responsible for a wide distribution of PFAS across the earth, as evidenced by their occurrence in biota and environmental media in remote regions as far as the Arctic and Antarctic. Long-range transport processes and effects are similar to atmospheric transport of other recalcitrant compounds (Prevedouros et al. 2006; Benskin et al. 2012).

Table 4.1. Observed PFAS concentrations in outdoor air

Location	Information	Concentrations (pg/m³)
Japan, Hong Kong, and India (Ge et al. 2017)	Sampling and analysis of ambient particles at four sites. Ultrafine particles found to be largest contributor to mass fraction of PFCAs, while most PFOS mass was in the coarse-sized fractions. Seasonal differences in PFAS attributed largely to precipitation.	ΣPFAS (range) was about 5-15.
Shenzhen China (Liu et al. 2015a)	Air samples collected at 13 sites, including industrial areas with many industrial manufacturers, port districts, as well as less industrialized forested and tourist areas. Samples were analyzed for a range of PFCAs and PFSAs.	PFAS concentrations reported as mean ± SD (range): • PFHxS: 0.31 ± 0.39 (ND-1.2) • PFOS: 3.1 ± 1.2 (ND-4.3) • PFBA: 1.9 ± 1.8 (ND-5.0) • PFPeA: 1.9 ± 1.4 (ND-4.0) • PFHxA: 1.5 ± 1.5 (ND-3.6) • PFHpA: 0.042 ± 0.10 (ND-0.30) • PFOA: 5.4 ± 3.8 (1.5–15) • PFNA: 0.49 ± 0.33 (ND-1.0) • PFDA: 0.48 ± 0.38 (ND-1.2) • PFUdA: 0.018 ± 0.064 (ND-0.22) • PFDoA: 0.20 ± 0.19 (ND-0.54) • Overall ΣPFAS: 15 ± 8.8 (3.4–34)
Atlantic Ocean from North Atlantic to Antarctic (Wang et al. 2015a)	Measured neutral PFAS in the atmosphere across the Atlantic from the North Atlantic to the Antarctic, as well as snow from the Antarctic Peninsula.	Total ΣPFAS in air in the gas-phase mean (range): 23.5 (2.8 to 68.8).
Toronto, Canada (Ahrens et al. 2012)	Collected samples from a semi-urban location while investigating an improved technique for measuring the gas-particle partitioning of PFAS using an annular diffusion denuder sampler.	• ΣFTOHs (most abundant PFAS in the gas-phase): 39-153 • ΣFOSAs: 0.02-1.1 • ΣFOSEs: 0.33-0.79 • ΣFTACs: 0.87-5.9 • PFBA (dominant PFCA): 4.0-22.
Parkersburg, West Virginia USA (Barton, Kaiser, and Russell 2007)	Concurrent rain and air samples collected at nine locations at a manufacturing facility during a single precipitation event and analyzed for PFOA.	PFOA predominantly associated with particulates and detected as high as 1,100.
Albany, New York USA (Kim and Kannan 2007)	Measured PFCAs, PFSAs, and FTSAs in air, rain, snow, surface runoff water, and lake water in an urban area.	• ΣPFAS (gas-phase): 5.10-11.6 • ΣPFAS (particle-phase): 2.05-6.04
ND = Nondetect		

4.2 Soil and Sediment

PFAS are found in soil and sediment due to atmospheric deposition, exposure to impacted media (for example, landfill leachate or biosolids), and direct discharge. Soils and sediments may act as secondary sources of PFAS to groundwater and surface water through leaching and percolation processes, respectively. PFAS distribution in soils is complex, reflecting several site-specific factors such as total organic carbon (TOC), particle surface charges, and phase interfaces (see Section 3). Properties of individual PFAS, such as C-F chain length and ionic functional group, are also important factors. PFOS, PFOA, and other long-chain PFCAs are typically the predominant PFAS identified in surface sediments (Rankin et al. 2016; Strynar et al. 2012).

Atmospheric transport and deposition of PFAS occur on regional and global scales (see Table 4.2 and Section 3.3 and Section 4.1). PFAA concentrations have been observed across a wide range of locations, which suggests that detection of a PFAA does not always imply a local source.

Other environmental sources of PFAS to soil include direct application (for example, AFFF and industrial discharge) or soil amended with PFAS-affected media, such as biosolids; see Table 4.2. Individual PFAS concentrations may be above 1,000 ng/g (1 mg/kg) at AFFF sites. In comparison to AFFF sites, published data on soil PFAS concentrations in industrial settings are limited (Table 4.2). PFAS soil concentrations at industrial sites and sites with applied biosolids or sludge may be highly variable, depending on the nature of PFAS release and proximity to the source.

PFAS discharge to surface waters has also affected sediments. Few studies have evaluated PFAS association with field-collected sediments (Table 4.2). Higher concentrations may be present in certain locations associated with direct PFAS discharge.

Table 4.2 Observed PFAS concentrations in soil and sediment

Location	Information	Concentrations (µg/kg)
Global Distribution (Rankin et al. 2016)	Worldwide survey of 62 soils samples, PFOA and PFHxA detected in all samples and PFOS detected in all but one sample; PFOS and PFOA the most frequently detected.	• ΣPFCAs: 0.029-14.3 • ΣPFSAs: ND - 3.27 (only one sample was ND Remote area (Lake Bonney, Antarctica): • PFOA = 0.048 • PFOS = 0.007
Global, locations not associated with known PFAS sources (Strynar et al. 2012)	Evaluated 60 soil samples from six countries and reported global median concentrations. PFOS detected in 48% and PFOA detected in 28% of the samples. Note that concentrations <LOQ (~0.5 µg/kg) were assigned a value of LOQ/√2 for the median calculations.	Global median concentrations: • PFOA: 0.124 • PFOS: 0.472
Location near industrial PFAS source (Davis et al. 2007)	Concentrations of ammonium perflurooctanoate (APFO) in two soil borings located within an impacted well-field; concentrations decreased rapidly with depth.	APFO: 110-170
Fire Training/Fire Response (Houtz et al. 2013)	PFOS and PFOA in soils at an unlined fire training area	Median concentrations: • PFOS: 2,400 • PFOA: 21
Fire Training/Fire Response (Anderson et al. 2016)	In a survey of 40 sites impacted by PFAS, the most frequently detected compounds were PFOS (99% of surface samples), PFHxS (77%), and PFOA (79%). PFOS was detected at the highest concentrations.	PFOS: • Median: 53 • Max: 9,700
Industrial Areas (Zareitalabad et al. 2013)	PFOA and PFOS concentrations in soil were compiled.	Max: • PFOA: 48 • PFOS: 10
Municipal Biosolids (Sepulvado et al. 2011)	Six municipal biosolids and biosolid-amended surface soils	Biosolids: • PFOS: 80-219 • MeFOSAA: 63-143 • EtFOSAA: 42-72 • PFOA: 8-68 Biosolid-amended soil: • PFOS: 2-438
Sediments – Lake Ontario, Yangtze & Mississippi Rivers (Qi et al 2016; Yeung et al. 2013; Oliaei et al. 2013; Pan et al. 2014)	Maximum sediment concentrations of PFOA, PFOS, and other PFAAs	10's – 100's
ND = Nondetect LOQ = Limit of Quantitation		

4.3 Groundwater

Groundwater represents a potential PFAS exposure pathway by direct ingestion of contaminated drinking water or indirect ingestion of PFAS in crops irrigated with the contaminated water. Groundwater may also discharge to surface water, which can be another PFAS exposure pathway for human and ecological receptors. Due to the mobility and persistence of PFAA in soil and groundwater, PFAAs are expected to form larger plumes than other contaminants in the same hydrogeological setting. Sorption and partitioning, however, may restrict leaching rates from the vadose zone and reduce the advection-driven transport velocity of PFAS in groundwater, depending on specific properties of the compounds. These processes may help limit plume development and discharge to surface water and may also provide time for transformation of PFAA precursors. Groundwater geochemistry may dictate the extent of transformation since nearly all processes identified to date are aerobic (Liu and Mejia-Avendaño 2013). Groundwater extraction and treatment for containment or remediation of other contaminants can also influence plume development and distribution of PFAS in groundwater. At sites with remediation systems for other contaminants, PFAS-impacted water can be unknowingly reinjected into groundwater, as well as discharged to surface water or wastewater treatment plants and create secondary releases.

USEPA generated the most extensive PFAS groundwater occurrence dataset when it required approximately 4,900 public water systems (all large systems serving more than 10,000 people, plus a subset of smaller systems) to monitor six PFAAs in drinking water at points of entry to the drinking water distribution system. The study was conducted between 2013 and 2015 under the third Unregulated Contaminant Monitoring Rule (UCMR3) and included the results from treated water that largely originated from groundwater wells, but also included surface water and mixed sources. A summary of the UCMR3 occurrence data is included in the *Regulations, Guidance, and Advisories* fact sheet. One or more PFAS were detected in 4% of the reporting public water systems (USEPA 2017b); however, groundwater sources had approximately double the detection rate of surface water sources (Hu et al. 2016). Detections of longer-chain PFAAs were highly associated with groundwater, while shorter-chain PFAAs such as PFBS and perfluoroheptanoic acid (PFHpA) were more associated with surface water. Detections were geographically widespread but showed quantifiable associations with suspected sources including industrial sites, military fire training areas, AFFF-certified airports, and wastewater treatment facilities (Hu et al. 2016).

Groundwater occurrence data collected during several other key studies are summarized Table 4.3.

Table 4.3 Observed PFAS concentrations in groundwater

Location	Information	Concentrations (µg/L)
Various – New Jersey (NJ DEP 2014)	One or more PFAS detected in 19 of 21 untreated groundwater samples from drinking water treatment plants across the state; PFOA was detected in 7 and PFOS was detected in 5 of the 21 samples.	• PFOA: 0.009 – 0.057 • PFOS: 0.005 –0.012
AFFF release sites other than fire training areas (Anderson et al. 2016)	Tested 149 groundwater samples; most commonly detected PFAAs: PFHxS (95%); PFHxA (94%), PFOA (90%), PFPeA (88%), PFBA and PFHpA (85%), PFOS (84%). The frequency of detections for PFSAs in groundwater was generally higher than those of PFCAs which has been attributed to the use of specific AFFF formulations.	Median (Maximum): • PFHxS: 0.87 (290) • PFHxA: 0.82 (120) • PFOS: 4.22 (4,300) • PFOA: 0.405 (250) • PFPeA: 0.53 (66) • PFBA: 0.18 (64) • PFHpA: 0.235 (75)
Fire Training/Fire Response (Moody and Field 1999; Moody et al. 2003; Houtz et al. 2013)	Studies at U.S. military installations and other AFFF release areas have documented relatively high detection frequencies of PFAAs in underlying groundwater.	Maximum: • PFOA: 6,570 • PFOS: 2,300

4.4 Surface Water

Human exposure to PFAS from surface water can occur through direct ingestion or by consuming aquatic biota from contaminated waterbodies. Most PFAAs are acids with low pKa values, which means that in the environment they are most often present in their anionic form (deprotonated, see Section 6.2.2 of the *Naming Conventions and Physical and Chemical Properties* fact sheet). Due to the low volatility and low sorption coefficients of these anions, much of the PFAAs that reach surface water tend to remain in solution, although there is likely to be partitioning to sediment and uptake to biota. Once in surface water, PFAAs can contaminate groundwater through groundwater recharge (Liu et al. 2016; ATSDR 2008) or be transported to the oceans where they are then transported globally by ocean currents (Benskin et al. 2012). Upon reaching saline waters, however, the solubility of anionic PFAAs decreases and sorption increases, which likely results in a salting-out effect that scavenges some PFAAs, especially long-chain PFAAs, to the sediments of estuarine environments (Hong et al. 2013). Despite this, oceans are likely the main sink for PFAS, and have been estimated to contain the majority of PFCAs historically released into the environment (Armitage et al. 2006). In contrast to PFAAs, other PFAS (for example, FTOHs and some perfluoroalkyl sulfonamides) remain neutral at environmentally relevant pHs, have higher volatilities, and tend to partition into air. PFAS composition may also change within surface water because of biotic and abiotic degradation of PFAA precursors, as described in Section 3.3.

Freshwater, marine water, and stormwater PFAS concentrations usually depend on proximity to releases. In addition to releases associated with identified sources, stormwater runoff water from nonpoint sources may contribute significant loads of PFAS to surface water (Wilkinson et al. 2017; Zushi and Masunaga 2009). Table 4.4 shows some typical PFOS and PFOA environmental concentrations, organized by source type. In addition to PFOS and PFOA, many other PFAS have been observed in surface waters, including compounds other than PFAAs. For example, perfluoro-2-propoxypropanoic acid (PFPrOPrA) has been measured in the Cape Fear River in North Carolina at concentrations up to 4560 ng/L (Sun et al. 2016).

Table 4.4. Observed PFAS concentrations in surface water

Location	Information	Concentrations (ng/L)
Freshwater		
Remote Areas (Filipovic et al. 2015; Eriksson et al. 2013; Stock et al. 2007)	PFOS and PFOA concentrations in the Faroe Islands and remote areas of Sweden have been measured in the 100s of picograms per liter range, while concentrations in the Canadian Arctic have been measured in the single nanogram per liter range.	• 100s of pg/L • Single ng/ L
Industrial Areas, Japan, and Tennessee River, USA (Saito et al. 2004; Hansen et al. 2002)	PFOS concentrations can be as high as 144 ng/L; PFOA concentrations can be as high as 67,000 ng/L.	Maximums: • PFOS: 144 • PFOA: 67,000
Fire Training/Fire Response (Saito et al. 2004; Anderson et al. 2016)	AFFF-impacted surface water can have PFOS concentrations reaching 8970 ng/L and PFOA concentrations reaching 3750 ng/L.	Maximums: • PFOS: 8,970 • PFOA: 3,750
Municipal Wastewater Treatment Facilities (Becker, Gertsmann, and Frank 2008; Boulanger et al. 2005; Wilkinson et al. 2017; MDH 2008)	PFOS and PFOA reported in surface waters near municipal WWTP outfalls, with higher (4x) concentrations reported for surface water near outfalls of WWTP impacted by chrome plating wastewater.	Maximums (near typical WWTPs): • PFOS: 24 • PFOA: 25 Maximum (near WWTP affected by chrome plating waste): • PFOS: 100
Marine Water		
Open Water (Benskin et al. 2012; Cai et al. 2012a; Zhao et al. 2012)	PFAA concentrations in open waters tend to be on the order of picograms per liter.	pg/L
Coastal Areas (Benskin et al. 2012; Cai et al. 2012a; Zhao et al. 2012)	In heavily populated coastal areas, PFAA concentrations can be on the order of a few nanograms per liter.	ng/L

Location	Information	Concentrations (ng/L)
Stormwater		
Residential/Undeveloped (Xiao, Simick, and Gulliver 2012; Wilkinson et al. 2016; Zhao et al. 2013b)	PFAS concentrations measured in residential, campus, and field settings in Minnesota, China, and England, respectively.	Maximums: • PFOS : 15.5 • PFOA : 19.1 • PFHxA : 4 • PFHpA : 22.5 • PFNA : 23
Commercial/heavy traffic – Minneapolis/St. Paul, MN; eastern and central China cities; and England (Xiao, Simick, and Gulliver 2012; Zhao et al. 2013b; Wilkinson et al. 2016)	PFOS and PFOA measured in storm water runoff from streets in areas not related to specific releases, but unidentified local or consumer sources may be responsible for higher concentrations detected.	Range: • PFOS : <LOQ - 590 • PFOA : 3.5 - 1,160 • PFHpA : ND – 6.8 • PFNA : ND – 648 • PFDA : ND – 10.6 • PFUnDA : ND – 2.9
Industrial Areas - Minneapolis and St. Paul, MN (Xiao, Simick, and Gulliver 2012)	PFOS measured in stormwater in an industrial area with suspected PFAS.	Range : • PFOS : 8.7-156
Airport Ditch, likely impacted by AFFF, Korea (Kim et al. 2014)	PFAAs measured, predominately PFHxS and PFOS.	• Total PFAAs: 6.42 - 804

4.5 Biota and Bioaccumulation

PFAS occur widely in biota, specifically in plants, invertebrates, fish, and humans, through bioaccumulation processes. PFAAs, particularly PFOS, are typically the dominant PFAS detected in biota (Houde et al. 2011). PFAA concentrations in biota are influenced by uptake and elimination of both PFAAs and their precursors, as well as biotransformation rates of PFAA precursors; see Section 3.3.2 (Asher et al. 2012; Gebbink, Bignert, and Berger 2016). Therefore, concentrations of PFAAs observed in biota at one location may not reflect concentrations in other environmental media.

4.5.1 Plants

Studies show evidence of uptake and accumulation PFAAs by plants in several settings and applications, including both controlled experiments and field investigations. Concerns about introducing PFAAs into livestock or crops have led to investigations of uptake and accumulation in plants. Uptake mechanisms and the extent to which native plant species remove and accumulate PFAS have not been as well studied.

PFAS may be introduced to plants from soil, water, or air by:

• irrigation water
• the application of biosolids- or sludge-amended soils
• soil and groundwater at PFAS sites or near releases of PFAS
• exposure through contact with rainwater and atmospheric deposition

Studies demonstrating plant uptake of PFAAs have focused on irrigated crops (Stahl et al. 2009; Scher et al. 2018), crops in biosolids-amended soil (Yoo et al. 2011, Blaine et al. 2013, 2014), and aquatic plants in constructed wetlands (Chen, Lo, and Lee 2012). Other investigations have focused on flora exposed to PFAAs in the natural environment (Zhang et al. 2015a) or near known PFAS sources (Shan et al. 2014). Plant uptake and bioaccumulation and partitioning within the plant appear to depend on PFAS chemical structure and the plant species. Most studies report partitioning of PFAAs within plants, with longer-chain PFAAs, especially PFSAs, partitioning to the roots and more soluble, shorter-chain PFAAs, especially PFCAs, partitioning to other parts of the plant (Lechner and Knapp 2011; Stahl et al. 2009; Blaine et al. 2013, 2014; Yoo et al. 2011; Scher et al. 2018; Gobelius, Lewis, and Ahrens 207). The behavior of other PFAS such as PFAA precursors is currently the topic of ongoing research.

4.5.2 Invertebrates

Invertebrates act as the main component of the food web base and play a key role in the dynamics of biomagnification. Aquatic invertebrates can reside in the water column, as well as on (or in) the sediment substrate. In higher trophic level organisms, PFOS has been documented as the dominant PFAS, with concentrations increasing up the food chain, while PFOA has a lower bioaccumulation potential and concentrations are similar among species of different trophic level animals (Houde et al. 2011; Conder et al. 2008). In invertebrates, both PFOS and PFOA have maximum values within similar ranges (Ahrens and Bundschuh 2014). Studies present a PFAS range of approximately 0.1 to 10 µg/kg in invertebrate tissue, although their sources predominantly address marine organisms (Houde et al. 2011). Similar levels of PFOS have been found in freshwater invertebrates (< 2 to 4.3 µg/kg) and with a bioconcentration factor (BCF) (biota/water) estimated at 1,000 L/kg (Kannan et al. 2005). Concentrations of PFOS, PFCAs, and heptadecafluorooctane sulfonamide (PFOSA) have been observed in Lake Ontario invertebrates, ranging from < 0.5 to 280 µg/kg (Martin et al. 2004). The concentrations in invertebrates were higher than in fish from this lake.

In terrestrial systems, current research indicates bioaccumulation potential of PFOS is low, as is biomagnification (increasing concentrations in predators over their prey) from lower to higher trophic level organisms (CEPA 2017). In biosolid amended soils, PFAS bioaccumulation factors (BAFs) in earthworms have ranged from 2.2 to 198 g dw soil/g dw worm (Navarro et al. 2016). Maximum BAFs in earthworms for all PFAS types have been observed at < 45 g dw soil/g dw worm for biosolids amended soils and < 140 g dw soil/g dw worm for soils contaminated with AFFF (Rich et al. 2015).

4.5.3 Fish

Accumulation of PFAS in fish has been documented, particularly for PFOS, longer-chain PFCAs (with eight or more carbons), and perfluorodecane sulfonate (PFDS) (Houde et al. 2011; Martin et al. 2013; Conder et al. 2008). Of the PFAS, PFOS generally has the highest concentrations in fish due to the historically high use of this chemical and its bioaccumulation potential (Houde et al. 2011). PFDS, long-chain PFCAs, and other PFAS have also been measured in fish (Houde et al. 2011; Fakouri Baygi et al. 2016). Shorter-chain PFCAs and PFSAs (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), but as perfluoroalkyl chain length increases, PFSAs are generally more bioaccumulative than PFCAs with the same number of carbons in the chain.

In fish, PFOS tends to partition to the tissue of highest protein density, including the liver, blood serum, and kidney (Falk et al. 2015; Ng and Hungerbühler 2013). This distribution pattern is contrary to other persistent chemicals, which tend to partition to adipose tissue.

Due to the difficulty of measuring octanol-water partitioning coefficients (K_{ow}) for PFAS, BAFs rely on calculations from empirical data instead of modeling (Haukås et al. 2007). For PFOS, bioconcentration from water is the predominant route of accumulation in fish (Martin et al. 2003a, b; Giesy et al. 2010), with dietary concentrations playing a reduced role in accumulation. In Michigan, concentrations of PFOS were found to be 10 to 20 times greater in predator fish than in their prey species (Kannan et al. 2005). PFOS appears to be the predominant PFAS concentrated from water, with BAFs in field-based studies ranging from approximately 550 to 26,000 L/kg (Naile et al. 2013; Lanza et al. 2017; Ahrens et al. 2015; Giesy et al. 2010) in whole fish.

Biomagnification and trophic transfer of PFAS in fish have been shown in some food webs (Franklin 2016; Fang et al. 2014). Because PFAS partition into proteins rather than lipids, however, the degree of observed biomagnification and trophic transfer in the field may be related to the quantity and composition of protein in the tissue measured, as well as the capability of the fish for metabolic biotransformation of PFAA precursors (Butt et al. 2010; Asher et al. 2012; Gebbink, Bignert, and Berger 2016).

Fish occurrence data collected during several other key studies are summarized in Table 4.5.

Table 4.5 Observed PFAS concentrations in fish

Location	Information	Concentrations (µg/kg)
Industrial (Oliaei et al. 2013; Delinsky et al. 2010)	Near PFAS production plants, individual fish tissues such as liver, blood, and muscle have been reported to have elevated PFOS.	Maximum PFOS: • Liver: 6,350 • Blood: 29,600 • Muscle: 2,000
AFFF spill (Moody et al. 2002; Gewurtz et al. 2014; Lanza et al. 2017)	PFOS in fish liver, muscle, and whole fish samples were detected following an AFFF spill.	Maximum PFOS: • Liver: 72,900 • Muscle: 6,160 • Whole fish: 9,350
Wastewater treatment plant (Becker, Gerstmann, and Frank 2010; Li et al. 2008; Schuetze et al. 2010)	PFOS concentrations have been detected in fish collected near the outfall of wastewater treatment plants.	Maximum PFOS: Liver: 400 Serum: 84 Muscle tissue: 225

4.5.4 Humans

The accepted method for determining PFAS levels in humans is measurement in blood serum, because blood serum levels reflect cumulative exposure over several years (ATSDR 2015, 2015a; CDC 2017b). Biomonitoring studies indicate that some long-chain PFAAs are globally distributed in human sera (ATSDR 2015; Kato, Ye and Calafat 2015). The Center for Disease Control's National Health and Nutrition Examination Survey (NHANES) currently includes blood serum monitoring for twelve PFAAs. NHANES data indicate that monitored PFAAs concentrations have generally decreased since first collected from the U.S. population between 1999 and 2000. Serum PFOS and PFOA levels are generally higher in males, serum PFOS levels are generally higher than PFOA, and serum PFOS levels are higher in those 20 years and older than in those 12-19 years of age (CDC 2017a). Representative blood levels are provided in Table 4.6. Local exposures can lead to elevated PFAS concentrations in some populations, including (Olsen et al. 2017):

• proximity to industrial facilities using PFAS
• proximity to airports using AFFFs
• accidental industrial releases
• groundwater contamination-associated landfill leachates or biosolids application

Elevated PFAS serum concentrations may also result from ingestion of contaminated drinking water from surface water intakes at locations long distances (for example, hundreds of miles) downstream from an industrial source (Herrick et al. 2017). Long-term ingestion of low levels of PFAS (including those below health values) in drinking water may result in exposures substantially higher than in the general population not consuming contaminated drinking water (Post, Gleason and Cooper 2017; Bartell 2017).

The predominant route of exposure to most PFAS for the general public (as opposed to those living near a PFAS source or occupationally exposed) is typically the ingestion of PFAS in food (Gebbink, Berger, and Cousins 2015). Exposures are associated with contaminated foodstuffs, as well as the use of food-related consumer products such as grease-resistant paper or pizza boxes and nonstick cookware (ATSDR 2016). Hand-to-mouth transfer from treated textiles (for example, carpets and furniture) and indoor dust are also identified as significant sources of ingestion, particularly for children.

Proximity to atmospheric emission sources may also constitute a major source for the public through inhalation or depositional uptake routes (ATSDR 2015, 2016; USEPA 2016e, f). PFAS may be transferred from mother to fetus, and to breastfeeding infants. Both breastfed infants and infants ingesting formula prepared with PFAS-contaminated water may have higher exposure levels (Fromme et al. 2010; Mogensen et al. 2015). Occupational exposure to PFAS may be higher than the general exposures described above.

PFAS are not well adsorbed through the skin (ATSDR 2015a; USEPA 2016e, f), so dermal contact is not expected to be an important exposure route for the general public compared to other exposure pathways. However, dermal contact may pose a risk for people with high-level occupational exposures.

PFAAs are not metabolized, and long-chain PFAAs are excreted very slowly in humans, with half-lives of several years. Therefore, these compounds accumulate over time with continued exposure and remain in the body for many years after exposure ends (ATSDR 2015). Studies have reported both biotic and abiotic transformations of some polyfluorinated

substances (precursors), which may form PFAAs (Buck et al. 2011), see also Section 3.3. Ingested precursors can be transformed in the body to PFAAs (USEPA 2016e, f). PFAS bioaccumulation potential generally increases with increasing chain-length. As with other organisms, PFAS in humans generally bind to proteins and accumulate in protein-rich tissues, including the blood, liver, and kidneys (ATSDR 2015). Because some PFAS biomagnify in food webs, the ingestion of contaminated biota, especially fish and apex predators, may be a major exposure route (ATSDR 2015; USEPA 2016e, f).

Table 4.6 Observed PFAS concentrations in humans[1]

| Location	Information	Concentrations (µg/L)
General U.S. population levels 1999-2000 (CDC 2017b)	1562 NHANES participants' serum collected in 1999-2000	Geometric mean in serum: • PFOA: 5.21 • PFNA: 0.551 • PFOS: 30.4 • PFHxS: 2.13
General U.S. population levels 1999-2000 (CDC 2017b)	2165 NHANES participants' serum collected in 2013-14	Geometric mean in serum: • PFOA: 1.94 • PFNA: 0.675 • PFDA: 0.185 • PFOS: 4.99 • PFHxS: 1.35
General U.S. population levels, 2000-2001 (Olsen et al. 2017)	645 blood donors' serum collected in 2000-2001	Geometric mean in serum: • PFOA: 4.7 • PFNA: 0.6 • PFDeA: 0.2 • PFOS: 35.1 • PFHxS: 2.3
General U.S. population levels, 2015 (Olsen et al. 2017)	616 blood donors' plasma collected in 2015	Geometric mean in plasma: • PFOA: 1.1 • PFNA: 0.4 • PFDA: 0.1 • PFOS: 4.3 • PFHxS: 0.9
General U.S. population levels, California (CA OEHHA 2013)	856 California teachers, serum collected in 2011-13	Geometric mean in serum: • PFOA: 2.5 • PFNA: 0.9 • PFDeA: 0.2 • PFUnA: 0.1 • PFOS: 6.9 • PFHxS: 1.6
Occupationally exposed U.S. population, California (Dobraca et al. 2015; CA OEHHA 2012)	101 firefighters, serum collected in 2010-11	Geometric mean in serum: • PFOA: 3.8 • PFNA: 1.1 • PFDeA: 0.9 • PFUnA: 0.2 • PFOS: 12.5 • PFHxS: 2.3
Residents near a PFOA production facility, U.S. (Emmett et al. 2006)	Serum collected 2004-2005	Mean in serum: • PFOA: 423

Note 1: Detection levels vary among studies. Data shown for select PFAS found in all or virtually all subjects. Other PFAS were analyzed and/or detected at some frequency in these studies.

5 References and Acronyms

The references cited in this fact sheet, and the other ITRC PFAS fact sheets, are included in one combined list that is available on the ITRC web site. The combined acronyms list is also available on the ITRC web site.
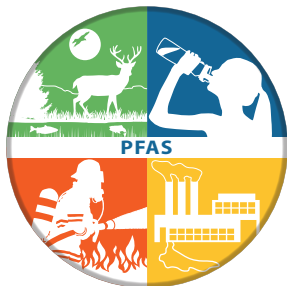
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