



## 4 Physical and Chemical Properties

This section provides information about available physical and chemical properties of PFAS. Understanding of the physical and chemical properties of PFAS is important for the prediction of their fate and transport in the environment. The available information about physical and chemical properties varies between the different PFAS. Tabulated values are included in the Physical and Chemical Properties Table ([Table 4-1](#) provided as a separate Excel file) that is provided as a separate Excel file.

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### 4.1 Challenges and Limitations Related to PFAS Physical and Chemical Properties

Understanding the physical and chemical properties of PFAS is important for the prediction of their fate and transport in the environment. More specifically, reliable values are very important when attempting to explain the environmental behavior of PFAS through mathematical fate and transport modeling, where small variations in values can have large implications on predictions (see [Section 10.4](#) on data analysis and interpretation, which includes a discussion of fate and transport modeling). There is large variation in the depth of published data (a lot is known about some PFAS, but almost nothing about others) on chemical and physical properties of PFAS. Reliable physical and chemical properties of PFAS are scarce (for example, vapor pressure and Henry's Law constants), and some of the available values are estimated using predictive mathematical techniques, which predict properties of compounds from knowledge of their chemical structure. These are collectively referred to as quantitative structure-activity relationship (QSAR) models. Predicted, as opposed to directly measured, values are accompanied by additional uncertainty that may be significant in certain fate and transport modeling scenarios. In addition, many of the available properties are based on the acid form of the PFAA, which is not present in the environment except at low pH. These uncertainties limit confidence in the precision of current fate and transport models. The Physical and Chemical Properties Table ([Table 4-1](#) provided as a separate Excel file) summarizes some of the physical and chemical properties that are available for PFAS.

### 4.2 Physical Properties

This section briefly describes some standard physical properties of PFAS. Additional references for more information are provided. In addition, the Physical and Chemical Properties Table ([Table 4-1](#) provided as a separate Excel file) summarizes some of the physical and chemical properties that have been published for PFAS and are discussed in this section.

#### 4.2.1 Physical State/Appearance

Most PFAS are solids, often crystalline or powdery in form, at room temperature; however, shorter chained compounds (the acid forms of PFCA and PFSA, FTSA and FTOH with a 4- to 6-carbon tail) tend to take liquid form at room temperature (melting point is addressed in [Section 4.2.3](#)).

#### 4.2.2 Density

Density ( $\rho$ ) is the mass per unit volume of a substance. For an individual PFAS compound (or mixture of PFAS) that exists as a liquid at ambient temperatures, density can influence its behavior in the environment.

If the density of the liquid PFAS is greater than that of water, the liquid PFAS has the potential to migrate downward through the water column in groundwater or surface water as a dense nonaqueous phase liquid (DNAPL); see [ITRC \(2003\)](#) for

discussion on density and solubility impacts on DNAPL behavior.. For example, 4:2 FTOH, which is a liquid at 20°C and has a density and aqueous solubility of 1.59 g/cm<sup>3</sup> and 974 mg/L (Table 4-1), respectively, would be predicted to behave similarly to carbon tetrachloride (with a density of 1.59 g/cm<sup>3</sup> and a solubility of 800 mg/L) if released into the environment as a pure product (also referred to as a neat liquid). However, if 4:2 FTOH dissolved in water, the change in density of the solution relative to water is unlikely to result in a separate layer. See Sections [5.2.2](#) and [5.2.4.1](#) for additional information on the behavior of PFAS in aqueous solutions.

### 4.2.3 Melting/Boiling Points

Melting and boiling point information refers to the temperature of phase transitions of pure compounds. These properties determine whether a specific pure PFAS compound will exist as a liquid, solid, or gas under typical environmental temperatures. These data are sparse and can vary among references. Predicted melting and boiling point values are available for most PFAS, but empirically derived values are not available for entire groups of chemicals like FTSAAs and FASAAs. Predicted values are generally useful in understanding the various physical states of PFAS; however, the accuracy of these results is still unknown and warrants further investigation. Like all organic carbon compounds, available data indicate that melting and boiling points of PFAS will tend to increase as the fluorinated chain increases in length. For example, the melting point of PFBA is -17.5°C while the melting point of perfluorotetradecanoic acid (PFTeDA) is 130-135°C. See Table 4-1 for a list of melting and boiling points.

### 4.2.4 Solubility

Solubility (S) refers to the ability of a given substance, the solute, to dissolve in a solvent. It is measured in terms of the maximum amount of solute dissolved in a solvent at a specified temperature and pressure. Typical units are milligrams per liter (mg/L) or moles per liter (mol/L). Currently, experimentally measured data for the solubility of PFAS in water are available for just a few of the more studied compounds such as the PFCAs, PFOS, FTSAAs, and fluorotelomer alcohols. This limited availability of experimental data should be considered when relying on PFAS solubility data. Most cited values are based on predicted or modeled values and the input values to these calculations may themselves be estimates. Further, because PFCAs and PFSAAs can form micelles and hemimicelles, as discussed in [Section 4.2.7](#), the reported water solubilities may include microdispersions of micelles in addition to truly solubilized molecules.

Values of solubility for the acid forms of PFAAs and other PFAS are summarized in Table 4-1. Reported values for solubility of individual PFAS analytes may vary depending upon the method used to determine solubility, the form of the analyte (that is, acid or salt), pH, salinity, and whether the value is empirical or obtained through modeling. For example, laboratory studies of water solubilities for PFOS indicate that solubility decreases when the water salt content increases ([3M Company 2000b](#)). Other factors may affect the reported value of solubility as well.

### 4.2.5 Vapor Pressures (V<sub>p</sub>)

Vapor pressure is an indication of the tendency of a substance to partition into the gas phase. Vapor pressure is a measure of volatility in that the higher the vapor pressure of a compound, the more volatile it is. Compounds with higher vapor pressures, because they are in the gaseous phase or sorbed to water vapor in the atmosphere, have a higher potential for long-range transport. Compounds with lower vapor pressures, which are more likely to remain in solid or liquid form, are transported only via soil or surface/groundwater ([Barton, Botelho, and Kaiser 2008](#)), unless they are dissolved into airborne water droplets or sorbed on airborne particulates, as discussed in Sections [5.3.2](#) and [6.1](#).

Values for vapor pressure of PFAS are summarized in Table 4-1. Very little data on measured vapor pressure values for PFAS exist, and much of the data on PFAS is extrapolated or modeled. Caution must be taken when using the vapor pressures for PFAAs listed in the Physical and Chemical Properties Table with respect to the acid or anion form of the compound, which may have very different vapor pressures. Efforts were made to report the values for the acidic form in Table 4-1, but references are not always clear. These values also should not be used for their corresponding salt form for the same reason (for example, the vapor pressure of ammonium perfluorooctanoate has been measured experimentally to be three orders of magnitude lower than the vapor pressure of perfluorooctanoic acid at 25°C ([Barton, Botelho, and Kaiser 2009](#))).

### 4.2.6 Henry's Law Constant (K<sub>h</sub>)

The Henry's law constant (K<sub>h</sub>), as well as the air-water partition coefficient (K<sub>aw</sub>), indicate the relative concentrations of a compound between an aqueous solution and gas phase at equilibrium (air-water distribution ratio) and provide an indication

of the propensity of a chemical to remain dissolved in water versus volatilizing into the gas phase. A chemical with lower solubility and higher volatility will have a higher Henry's law constant than a chemical with higher solubility and lower volatility.

For most organic compounds of moderate to low solubility,  $K_h$  can be approximated by:

$$K_h = (V_p)(M)/S$$

where  $K_h$  is the Henry's law constant,  $V_p$  is vapor pressure,  $M$  is molecular weight, and  $S$  is solubility. This constant can be expressed in a variety of units or as the inverse (water-air distribution ratio); thus, the units of expression should always be confirmed prior to use of this constant.  $K_h$  also displays nonlinear temperature-dependence and is typically reported at 25°C, which is higher than most ambient environmental conditions.

Experimental and modeled Henry's law constants are available for fluorotelomer alcohols (for example, [Wu and Chang \(2011\)](#) and [Xie, Zhao, et al. \(2013\)](#)), PFASs, PFCAs, FTCAs, FTSA, FASEs, and FASAA (for example, [Kwan \(2001\)](#) and [Zhang et al. \(2010\)](#)). For PFAS that can dissociate into anions or cations, as discussed in [Section 4.3.2](#), the Henry's law constant is pH-dependent and reported constants may not be applicable depending on the pH conditions within the solution (for example, [Rayne and Forest \(2009\)](#) and [Johansson et al. \(2017\)](#)). In a study of airborne PFOA release in industrial settings, monitoring above sumps found concentrations 40 times greater when the pH was 1.8 than at neutral pH, and PFOA release from aqueous solution was found to be several times greater at pH 4 than at pH 7 ([Kaiser et al. 2010](#)). Henry's law constant values are not presented in Table 4-1.

#### 4.2.7 Critical Micelle Concentration

Given the difference in behavior between the "head" and "tail" of a PFAA molecule, these compounds, when in water, tend to aggregate into micelles (form a sphere with the hydrophobic portion of the molecules on the inside) when present above a certain concentration. Other aggregates, such as hemimicelles or mixed micelles (micelles composed of a mixture of surfactant-type molecules), can form either independently in solution or at boundaries occurring between phases ([Krafft and Riess 2015](#)). Theoretical threshold concentrations for aggregation, generally referred to as critical micelle concentrations (CMCs), are presented in Table 4-1. It is important to note that several studies suggest aggregations may occur at much lower concentrations in groundwater, either due to interactions with particles and/or co-contaminants, or because of spatially variable concentrations within soil matrices ([Brusseau 2018](#)). The formation of these molecular-level assemblies can impact transport properties and the partitioning at air-water interfaces, as discussed in [Section 5.2](#).

#### 4.2.8 Octanol/Water Partition Coefficient ( $K_{ow}$ )

The  $K_{ow}$  is defined as "the ratio of a chemical's concentration in the octanol phase to its concentration in the aqueous phase of a two-phase" ([USEPA 2015f](#)). The  $K_{ow}$  is a useful descriptor of the tendency of a compound to associate with hydrophobic or hydrophilic substances. Direct measurement of the  $K_{ow}$  of alkyl acids has proven difficult because alkyl acids tend to aggregate at the interface between octanol and water ([Kim et al. 2015](#)), although some researchers have employed nontraditional methods with some success ([Jing, Rodgers, and Amemiya 2009](#)). Alternatively,  $K_{ow}$  can be estimated using quantitative tools that predict physical and chemical properties. The  $K_{ow}$  values that are typically tabulated for the PFCAs and PFSA are for the acid form and are therefore not relevant because PFCAs and PFSA are anionic within the typical range of environmental pH.

It should be noted that although  $K_{ow}$  values for some organic contaminants can be used for estimating  $K_{oc}$  and/or uptake in biological systems, they cannot be used for estimating such values for PFAS because they do not behave like a traditional hydrophobic chemicals (see [Section 5.5](#) for further discussion about PFAS uptake into aquatic organisms). For these reasons,  $K_{ow}$  values are not presented in Table 4-1.

#### 4.2.9 Organic Carbon/Water Partition Coefficient ( $K_{oc}$ )

The soil organic carbon/water partition coefficient ( $K_{oc}$ ) is a metric commonly used to quantify the potential of a given dissolved compound to associate with, or sorb to, organic matter occurring in soil. Shorter chained PFAS are more soluble in water, while the longer chain PFAS adsorb and partition more in to sediments ([Dalahmeh et al. 2018](#)). Relative to common PFAS like PFOA and PFOS, studies have suggested  $K_{oc}$  can be appropriately defined as a distribution coefficient ( $K_d$ ) normalized to organic carbon content, thus implying  $K_{oc}$  specifically represents the singular process of hydrophobic

interaction (Milinovic et al. 2015). Broader reviews highlight the complexity and variability of processes that may contribute to the sorption of PFAS and significant differences between laboratory- and field-scale results (Li, Oliver, and Kookana 2018). These reviews suggest simple relationships may be unreliable for predicting organic carbon partitioning for PFAS (see Section 5.2 for more discussion on partitioning). As such, the current state-of-science supports  $K_{oc}$  being reported in relatively broad ranges on a compound-specific basis. The  $K_{oc}$  values included in Table 4-1, while not an exhaustive list, are an indicator of the number of values currently available for PFAS. Discussion of the use of  $K_{oc}$ , including site-specific  $K_{oc}$ , in the prediction of PFAS transport in remedial scenarios is included in Section 10.4.1.

## 4.3 Chemical Properties

This section briefly describes some standard chemical properties of PFAS. Additional references are provided for more information. In addition, the Physical and Chemical Properties Table (Table 4-1 provided as a separate Excel file) summarizes some of the physical and chemical properties that are available for PFAS.

### 4.3.1 Carbon-Fluorine (C-F) Bond Properties

The properties of PFAS are principally due to the unique properties of the carbon-fluorine bond. Some key chemical properties of this bond and the characteristics they impart to PFAS are provided in Table 4-2.

**Table 4-2. Fluorine characteristics**

Fluorine Characteristic	Description	Effect	Resulting Property of PFAS
High electronegativity	Tendency to attract shared electrons in a bond	Strong C-F bond	Thermal stability
			Chemical stability (low reactivity)
		Polar bond with partial negative charge toward F	Strong acidity (low pKa) <sup>1</sup>
Low polarizability	Electron cloud density not easily impacted by the electric fields of other molecules	Weak intermolecular interactions	Hydrophobic and lipophobic surfactant properties <sup>2</sup>
		Low surface energy	
Small size <sup>3</sup>	Atomic radius of covalently bonded fluorine is 0.72 Å	Shields carbon	Chemical stability (low reactivity)

<sup>1</sup>When paired with an acid functional group such as a carboxylic or sulfonic acid  
<sup>2</sup>When paired with a functional group that is hydrophilic (for example, a carboxylate)  
<sup>3</sup>Smallest of the halogen atoms  
 Å = angstrom

Properties such as the high electronegativity and small size of fluorine lead to a strong C-F bond, the strongest covalent bond in organic chemistry (Kissa 2001). The low polarizability of fluorine further leads to weak intermolecular interactions, such as Van der Waals interactions and hydrogen bonding (Kissa 2001). These unique properties of fluorine give many PFAS their mutually hydro- and lipophobic (stain-resistant) and surfactant properties and make them thermally and chemically stable. But not all of these characteristics (for example, surface activity) are universal to all PFAS. It is also to be noted that some of the properties, such as disassociation constants or rate constants, which quantify the stability, are not well established for PFAS at this time.

### 4.3.2 Functional Group Properties

PFAS functional groups include carboxylates, sulfonates, sulfates, phosphates, amines, and others, as introduced in Section 2.2.2. These functional groups, including dissociated and undissociated forms, govern many fate and transport properties of PFAS. The ionic state of a compound determines its electrical charge and its physical and chemical properties, which in turn control its fate and transport in the environment. For example, the state (anionic or undissociated acid) of a given PFAS may alter aspects such as volatility and bioaccumulative potential. As further described below, due to their low acid dissociation constants ( $K_a$ ), PFAAs are found in the environment in the anionic (negatively charged) state, except in very rare situations

(for example, pH <3).

Functional groups of some PFAS (ionic PFAS) can dissociate into anions or cations in aqueous solution under appropriate pH conditions. For example, as discussed in [Section 2.2.2](#), PFOA dissociates into the perfluorooctanoate anion and the hydrogen ion when dissolved in water over a wide range of pH conditions. The ion associated with the fluoroalkyl portion of ionic PFAS, other than PFAAs, can be a negatively charged anion, a positively charged cation, or a zwitterion. Therefore, PFAS can be classified into four groups based on functional groups (examples of the structures of many ionic PFAS can be found in [Barzen-Hanson et al. \(2017\)](#)):

- anionic—contains one or more acidic functional groups such as carboxylic acids, sulfonic acids, sulfates, and phosphates, and can release a hydrogen ion, thereby forming an anion (see [Figure 2-6](#) for PFBA dissociation)
- cationic—contains one or more basic functional groups such as amines, which can gain a hydrogen ion and form a cation, or have a permanent charge as in the case of a quaternary ammonium group
- zwitterionic—contains two or more functional groups, at least one of which can form an anion and one of which can form a cation
- nonionic—does not dissociate into ions; for example, alcohols.

Based on the behavior of other cationic and anionic surfactants, cationic PFAS are expected to have different environmental transport characteristics than anionic PFAS ([Place and Field 2012](#)). For example, sorption of organic anions such as PFAA anions is typically suppressed at higher pH due to electrostatic repulsion with the increasingly negative charge from deprotonated oxides and other functional groups present on the soil surface ([Lee and Mabury 2017](#)). Cations can be expected to sorb strongly to soils, which often possess a net negative charge over a range of environmentally relevant pHs. For example, cationic fluorotelomer-based PFAS in an AFFF product have been found to sorb strongly to soils and sediments ([Barzen-Hanson et al. 2017](#)). Zwitterionic PFAS can be expected to sorb to soils and sediment more strongly than anionic PFAS, but less strongly than cationic PFAS, owing to the mixed charges on the functional groups. The transport characteristics of specific PFAS are also highly dependent on matrix interactions, and detailed site-specific information is necessary to accurately predict PFAS transport ([Guelfo and Higgins 2013](#)). See [Section 5.2.3](#) for further discussion of partitioning onto solid matrices.

For PFAAs, the acid dissociation constant  $K_a$  is the equilibrium constant for the dissociation of the acid in aqueous solution into the anion and hydrogen ion, and at dilute to moderate concentrations, is defined by the equation:

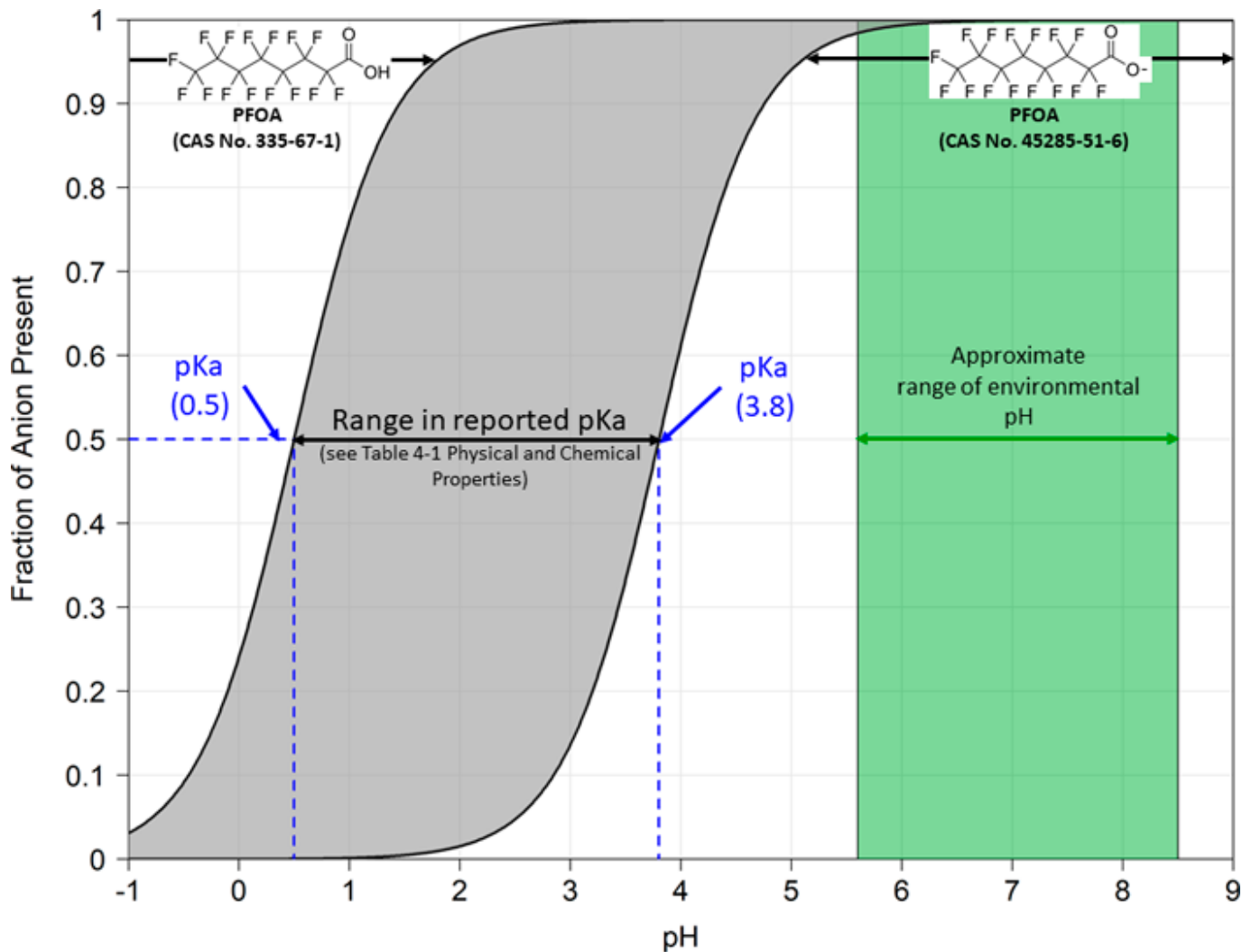
$$K_a = \frac{[\text{anion}^-][\text{H}^+]}{[\text{acid}]}$$

where [acid] is the concentration of the undissociated acid form, [anion<sup>-</sup>] is the concentration of the anion, and [H<sup>+</sup>] is the concentration of the hydrogen ion at equilibrium.

The dissociation constant is also commonly expressed as its negative logarithm,  $pK_a$ , where:

$$pK_a = -\log_{10}(K_a)$$

Higher  $pK_a$  values indicate that an acid will dissociate less in water at a given pH than will an acid with a lower  $pK_a$ . When the pH of a solution equals the  $pK_a$ , then one of half of the PFAS molecules will exist as the undissociated acid and one half will exist as the dissociated anion. PFAS with  $pK_a$  values of 4 or less will exist in aqueous solutions at neutral pH (7) almost entirely as the dissociated acid (see [Figure 4-1](#) for a representation of reported  $pK_a$  values for PFOA in relation to environmental pHs from Table 4-1). Because the undissociated acid and anionic forms of PFAAs have very different physical and chemical properties, it is essential to distinguish between the undissociated acid form and the anionic form to select the appropriate physical and chemical parameters for fate and transport evaluations.



**Figure 4-1. Titration curve for PFOA—relation of pKa to environmental pH.**

Source: E. DiFilippo, S.S. Papadopulos & Associates, Inc. Used with permission.

Table 4-1 presents  $pK_a$  values for PFAS. Limited model-predicted and experimental values are available for most PFAAs.

### 4.3.3 Thermal Stability

Thermal stability, the degree to which a chemical remains intact under thermal stress, is an important property to predict how long a chemical will persist in the environment. PFAAs, such as PFOA and PFOS, are extremely stable, thermally and chemically, and resist degradation and oxidation. Thermal stability of PFAAs is primarily attributable to the strength of the C-F bond in the fluoroalkyl tail (Kissa 2001). The stability is determined by the specific functional group that is attached to the fluoroalkyl tail. PFCAs and PFSAs are the most stable fluorinated surfactants. PFAAs decompose at temperatures greater than 400°C, but complete mineralization occurs at temperatures greater than 1,000°C (Lassen et al. 2013). Reports on temperature needed to destroy PFAS vary, but it seems that to destroy PFAS in soil temperatures upwards of 1,000°C may be required (Colgan 2018). It was previously reported that limited PFOS, PFOA, and PFHxA mineralization (less than or equal to 72%) may occur at temperatures of 700°C (Watanabe et al. 2018). In this same study, mineralization reportedly increased to 90% in the presence of granular activated carbon and sodium hydroxide. The thermal stability is lower for the salts of PFAA compounds and depends on which cation is the counterion. For example, the 20% decomposition temperature of sodium perfluorooctanoate is 298°C, but it is 341°C for lithium perfluorooctanoate (Kissa 2001). Additionally, salts of PFSAs are more thermally stable than the corresponding salts of PFCAs (Kissa 2001).

### 4.3.4 Chemical Stability

Like thermal stability, knowledge of the chemical stability of a molecule helps predict its persistence in the environment. PFCAs and PFSA have been shown to be persistent in the environment. PFCAs are resistant to oxidation under environmental conditions; however, transformation has been demonstrated in the presence of oxidants under extreme pressure. In

contrast, transformation of precursors can be associated with substantial changes in the physicochemical properties of those compounds ([CONCAWE 2016](#)).

In the perfluorinated tail of the alkyl acids, the strength of the C-F bond, shielding of carbon by fluorine, and inductive effects (caused by fluorine electronegativity) also lead to chemical stability. For example, electron-rich chemical species called nucleophiles normally would be attracted to the partial positive charge of carbon. If these nucleophiles could get close enough to the carbon to bond, the subsequent reaction could replace a fluorine with the nucleophile and potentially make the molecule vulnerable to degradation. But the relatively large size of the fluorine atoms surrounding the carbon (when compared to hydrogen) prevents this from happening (Schwarzenbach, Gschwend, and Imboden 2003). This is why processes such as hydrolysis, which involve eliminating one or more fluorines, are ineffective at degrading the perfluorinated tails of PFAAs. Similarly, many PFAAs are resistant to degradation by oxidative processes that rely on a loss of electrons (Kissa 2001). PFAAs are also resistant to reductive processes, which involve gaining electrons. Despite having a high affinity for electrons, fluorine does not have vacant orbitals favorable for accepting additional electrons ([Park et al. 2009](#)). In contrast to the stability of perfluorinated tails, polar regions of PFAS (the functional groups), as well as polyfluorinated groups, can be vulnerable to a range of chemical transformations. See [Section 5.4](#) for further discussion of abiotic and biotic transformations.

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